

David Mecerreyes *Editor*

Applications of Ionic Liquids in Polymer Science and Technology

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Editor

David Mecerreyes
Institute for Polymer Materials, POLYMAT
University of the Basque Country UPV/EHU
Donostia-San Sebastian, Spain

IKERBASQUE
Basque Foundation for Science
Bilbao, Spain

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About the Editor

David Mecerreyes Institute for Polymer Materials, POLYMAT, University of the Basque Country UPV/EHU, Donostia-San Sebastian, Spain

IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

Professor David Mecerreyes was born in San Sebastian, Spain, in 1971. After his undergraduate studies in San Sebastian, he presented his Ph.D. in 1998 CERM-University of Liege (Belgium) under the supervision of Prof. R. Jérôme in the macromolecular engineering of biodegradable aliphatic polyester. Then he moved to IBM Almaden Research Center in San Jose, California, to work in the development of polymer brushes and nanoporous materials for microelectronics until 2000. Back in Spain, he worked for 10 years in the Technology Center CIDETEC-IK4 specialized in electrochemistry. In 2011 he moved to POLYMAT (www.polyumat.eu), at the University of the Basque Country. At present, he is the principal investigator of the Innovative Polymers Group at POLYMAT. He is one of the pioneers of the use of ionic liquids in polymer chemistry and the development of functional ionic polymers. In his career he has published more than 180 scientific articles, 3 book chapters, and 5 international patents.

His actual expertises include organic, polymer chemistry, materials science, electrochemistry, and nanotechnology. The actual goal of the Innovative Polymers Group is the synthesis of innovative polymers or energy and environmental applications. His research activities are oriented towards a sustainable polymer chemistry which involves less hazardous and more efficient polymer catalysts, safer solvents and chemicals, polymers that biodegrade or can be easily recycled, and the use of renewable feedstocks in polymer science. The group has a highly collaborative spirit and devotion to work together with researchers interested in the applications of our polymers. The group is currently developing polymers for *emerging technologies* such as bioelectronic devices, gas membranes, electrochemical energy storage, drug delivery, or water purification systems.

Contributors

Michael H. Allen Macromolecules and Interfaces Institute, Department of Chemistry, Virginia Tech, Blacksburg, VA, USA

Jared L. Anderson Department of Chemistry and School of Green Chemistry and Engineering, The University of Toledo, Toledo, OH, USA

Markus Antonietti Max-Planck-Institute of Colloids and Interfaces, Research Campus Golm, Potsdam, Germany

Pierre-Henri Aubert Laboratoire de Physicochimie des Polymères et des Interfaces (EA 2528), Fédération “Institut des Matériaux”, Université de Cergy-Pontoise, Cergy-Pontoise, France

Itxaso Azcune Materials Division, IK4-CIDETEC Research Centre, Donostia-San Sebastián, Spain

Daniel Carriazo Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain

Claude Chevrot Laboratoire de Physicochimie des Polymères et des Interfaces (EA 2528), Fédération “Institut des Matériaux”, Université de Cergy-Pontoise, Cergy-Pontoise, France

Paul Coupillaud Laboratoire de Chimie des Polymères Organiques, Université de Bordeaux & Centre National de la Recherche Scientifique, Pessac, France

Jannick Duchet-Rumeau CNRS UMR 5223, Ingénierie des Matériaux Polymères

M. Luisa Ferrer Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain

Aratz Genua Materials Division, IK4-CIDETEC Research Centre, Donostia-San Sebastián, Spain

Jean-François Gérard INSA Lyon, Villeurbanne, France

María C. Gutiérrez Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain

Sean T. Hemp Macromolecules and Interfaces Institute, Department of Chemistry, Virginia Tech, Blacksburg, VA, USA

Mehmet Işık POLYMAT, University of the Basque Country UPV/EHU, San Sebastian, Spain

Sebastien Livi Université de Lyon, Lyon, France

Timothy E. Long Macromolecules and Interfaces Institute, Department of Chemistry, Virginia Tech, Blacksburg, VA, USA

Kasina Manojkumar Organic Chemistry Division, School of Advanced Sciences, VIT University, Vellore, India

Rebeca Marcilla IMDEA Energy Institute, Móstoles, Madrid, Spain

Isabel M. Marrucho Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Oeiras, Portugal

David Mecerreyes Institute for Polymer Materials, POLYMAT, University of the Basque Country UPV/EHU, Donostia-San Sebastian, Spain

Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Francisco del Monte Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain

Ibon Odriozola Materials Division, IK4-CIDETEC Research Centre, Donostia-San Sebastián, Spain

Cédric Plesse Laboratoire de Physicochimie des Polymères et des Interfaces (EA 2528), Fédération “Institut des Matériaux”, Université de Cergy-Pontoise, Cergy-Pontoise, France

Alaitz Ruiz de Luzuriaga Materials Division, IK4-CIDETEC Research Centre, Donostia-San Sebastián, Spain

Haritz Sardon POLYMAT, University of the Basque Country UPV/EHU, San Sebastian, Spain

María C. Serrano Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain

Akella Sivaramakrishna Organic Chemistry Division, School of Advanced Sciences, VIT University, Vellore, India

Daniel Taton Laboratoire de Chimie des Polymères Organiques, Université de Bordeaux & Centre National de la Recherche Scientifique, Pessac, France

John Texter School of Engineering Technology, Eastern Michigan University, Ypsilanti, MI, USA

Dominique Teyssié Laboratoire de Physicochimie des Polymères et des Interfaces (EA 2528), Fédération “Institut des Matériaux”, Université de Cergy-Pontoise, Cergy-Pontoise, France

Girum Ayalneh Tiruye IMDEA Energy Institute, Móstoles, Madrid, Spain

Liliana C. Tomé Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Oeiras, Portugal

Frédéric Vidal Laboratoire de Physicochimie des Polymères et des Interfaces (EA 2528), Fédération “Institut des Matériaux”, Université de Cergy-Pontoise, Cergy-Pontoise, France

Kari Vijayakrishna Organic Chemistry Division, School of Advanced Sciences, VIT University, Vellore, India

Honglian Yu Department of Chemistry and School of Green Chemistry and Engineering, The University of Toledo, Toledo, OH, USA

Jiayin Yuan Max-Planck-Institute of Colloids and Interfaces, Research Campus Golm, Potsdam, Germany

Cheng Zhang Department of Chemistry and School of Green Chemistry and Engineering, The University of Toledo, Toledo, OH, USA

Sebastien Livi, Jean-François Gérard, and Jannick Duchet-Rumeau

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Abstract

This chapter discusses the state of the art in the use of ionic liquids as polymer additives. Examples include ionic liquids as functional additives into polymer electrolytes or as lubricants, plasticizers, and building blocks in a polymer matrix or as surfactants of layered silicates in nanocomposites. The discussion will include the influence of the cation/anion combination of the ionic liquids on the physical properties of the resulting materials.

S. Livi (✉)
Université de Lyon, Lyon, France
e-mail: sebastien.livi@iusa-lyon.fr

J.-F. Gérard
INSA Lyon, Villeurbanne, France

J. Duchet-Rumeau
CNRS UMR 5223, Ingénierie des Matériaux Polymères
e-mail: jannick.duchet@iusa-lyon.fr

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Introduction

In recent years, the major challenge of industrial and academic research was to develop new polymer-based materials with unique and tunable properties. One of the innovative pathways is the use of ionic liquids (ILs) as additives within polymer matrices. In fact, due to their unique properties such as their excellent chemical and thermal stabilities, their low vapor pressure, their important ionic conductivity, their flame resistance, and their ability to dissolve many polymers, these organic salts having a melting temperature below 100 °C are original compounds to replace toxic and volatile conventional solvents as well as for processing aids. Moreover, ILs have been widely promoted these last 20 years as “green solvents” due to their recyclability, i.e., their ability to be reused several times. Finally, the main advantage of ILs is the endless number of cation/anion combinations, necessary to synthesize task-specific ionic liquids for polymers.

Despite their many excellent properties, the use of ILs in the chemical industry is still limited due to their rather expensive price and their relatively reduced commercial availability. Nevertheless, the use of ILs is increasingly used for polymers which could lead to large consumptions of ILs. If ILs are investigated as new media for synthesis and modification of polymers [1, 2] or as efficient solvent for polysaccharide-, lignin-, or cellulose-based polymers [3–6], few studies in the literature still report the use of ionic liquids as multifunctional additives in polymer matrices for processing advanced materials. For example, ILs can be considered as templates for designing porous polymers [7, 8] or as novel electrolyte for electrochemical applications [9, 10]. Some works mention the use of ILs as lubricants to improve the wear resistance of polymers [11, 12]. In other studies, ILs are regarded as processing aids for polymer processing since they behave as plasticizers leading to a decrease of glass transition temperature of polymer in which ILs are introduced [13, 14]. More recently, ionic liquids are used as new catalyst and hardener for preparing epoxy networks from bisphenol-A-based epoxy prepolymer [15, 16]. In the field of nanocomposites, ILs based on ammonium cations have been conventionally used as surfactant agents of lamellar silicates such as montmorillonite (MMT) or layered double hydroxide (LDH) during the last 20 years since the early works on nanocomposites from Toyota [17]. Such a surface treatment (cation exchange) leads to organoclays characterized by an improved compatibility with most of the polymers. Imposed interfacial interactions are formation of polymer–clay nanocomposites including a control over the distribution in size and dispersion of the nanofillers. New applications of ILs include the design of new classes of nanoscale-structured materials for which ILs are used as new building blocks. Due to their high charge density, ILs are excellent candidates to generate a possible structuration into a polymer matrix from a nanoscale self-assembling process [18].

This chapter aims to provide a unique place to discuss state-of-the-art approaches both in the field of ionic liquids and polymers combined with ionic liquids to the exceptional and diverse properties and applications of such advanced materials. We will focus and describe the use of the thermostable ionic liquids mainly based on pyridinium, imidazolium, and phosphonium cations as functional additives into polymer electrolytes or as lubricants, plasticizers, and building blocks in a polymer matrix or as surfactants of layered silicates in nanocomposites. The discussion will include the influence of the cation/anion combination of the ionic liquids on the physical properties of the resulting materials.

Polymer Electrolytes

There are several types of polymer gel electrolytes that are used in various fields of applications such as in secondary batteries, sensors, and various ionic devices [19–21]. Typically, the preparation of polymer electrolytes from solutions requires polar organic solvents and electrolyte salts in a polymer matrix. The term “gel electrolyte” is used to describe these soft materials. In this case, the properties of solvents used such as viscosity and dielectric constant as well as concentration of salts play a key role on the conductivity of the electrolyte [22]. However, the use of organic solvents which are volatile generates flammability problems when used at high temperatures.

These drawbacks have prompted the research to find a new alternative to conventional organic solvents. For replacing these solvents, ionic liquids have recently been selected and are of great interest in research on the electrochemical applications. These ILs have been chosen for their unique characteristics, including excellent thermal stability, nonflammability, nonvolatility, low melting temperature, and very high ionic conductivity [23, 24]. Moreover, ILs have been proven to be effective biocompatible media [25–27]. Effective adhesion of ILs on electrode surfaces has been found to be useful to perform direct electrochemistry of redox proteins [28–38].

Ionic liquids have also been used as supporting salts to analyze the redox signal of the biomolecules [39–45]. The ILs exhibiting the highest conductivities can serve the same purpose for preparative-scale electrochemistry [46–49] in selective fluorination [50, 51], in oxidation of alcohols [52, 53], in carbon–carbon bond formation [54–57], in electrocatalyzed dehalogenation reactions [58–61], or in sono(electro)chemistry [62, 63]. In addition, their inherent conductivity suppresses the need to use for additional supporting salts. As a consequence, ILs allow to perform electrolysis in an easier way and simplify the product recovery.

The most widely studied cations are the imidazolium and pyridinium ionic liquids combined with anions such as PF_6^- , BF_4^- , CF_3SO_3^- , and $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ [64–66]. In the literature, different polymer electrolytes containing ionic liquids obtained by various methods were described, i.e., polymerization of ionic liquids [67, 68], inclusion of room-temperature ionic liquids in different polymers [66, 69], and preparation of polymer gel with hydrophilic and hydrophobic ionic

liquids [70]. All research reported previously have demonstrated that ILs display a high conductivity which is suitable for these applications.

Usually, most of the polymers used in polymer electrolyte systems are based on high-molecular weight poly(ethylene oxide), PEO [66]. Recently, various polymers such as poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN), poly(vinylidene fluoride) (PVDF), and poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) have been studied [71, 72]. For example, Susan et al. [73] have synthesized polymer gel by polymerization of methyl methacrylate (MMA) in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid with a small amount of cross-linker to stabilize the resulting membrane. They have obtained ionic gels that exhibit ionic conductivities at room temperature, high mechanical strength, transparency, and flexibility which are required for polymer electrolytes. For the preparation of electrolyte membranes with improved mechanical properties and higher ionic conductivity in the temperature range from 20 °C to 140 °C, Sing et al. [74] have used 2,3-dimethyl-1-octylimidazolium, with triflate anions into a PVDF-HFP matrix.

In the field of polymer electrolytes, ionic liquids have shown their importance. All these promising results about the plasticizers, lubricants, or polymer electrolyte allow for expecting new insights in the field of advanced materials.

Lubricants

In the field of lubricants, imidazolium ionic liquids are commonly used in different assemblies of steel combined with steel [75–77], aluminum [78, 79], polymer [80], or in coatings based on nickel and chromium [81, 82]. In addition to their lubricant nature [83], the advantage of ionic liquids is their ability to be used on a wide range of temperature according to their excellent thermal stability. In addition, the dipole character and the ability to formation of boundary films and protective tribo-layers of ILs contribute to their excellent performance [84]. Yao et al. [85] have synthesized a series of 1,3-dialkylimidazolium with long alkyl chains in order to be used as lubricants for steel–steel joints in a temperature range between 25 °C and 150 °C. They concluded that the addition of the ionic liquids functionalized with long alkyl chains generated a reduction of friction and anti-wear properties, mainly at high temperatures. Jimenez et al. [86] studied the influence of the chemical nature of cation or anion. Three ionic liquids were compared to improve the wear behavior of steel–steel contacts, i.e., imidazolium ionic liquids denoted 1-methyl-3-octylimidazolium tetrafluoroborate (BF_4^-) and 3-hexyl-1-methylimidazolium hexafluorophosphate (PF_6^-) versus a quaternary ammonium containing halide anion (Cl^-). Then, the ionic liquids have been compared to a conventional oil at room temperature. They showed that the use of mineral oil or ammonium ionic liquids as lubricant on steel gives high friction coefficients and wear rates. On the other side, ILs based on imidazolium cation associated to hexafluorophosphate and tetrafluoroborate anions display better lubricating performances than the ammonium salt from 25 °C to 200 °C, which is due to higher thermal stability of imidazolium salts.

Recently, ionic liquids have been introduced as an internal or external lubricant in polymer–metal assemblies. Sanes et al. [81] studied the influence of the 1-hexyl-3-methylimidazolium hexafluorophosphate ionic liquid on the tribological properties of polyamide PA-6. The addition of ionic liquid (3 wt%) in the polyamide matrix does not affect the storage and loss modulus, whereas the presence of imidazolium ILs plays a decisive role on the tribological properties of the polymer. Indeed, in $-35\text{ }^{\circ}\text{C}/+67\text{ }^{\circ}\text{C}$ temperature range, neat PA-6 matrix already displays a reduced friction, whereas the PA-6 combined with 3 wt% of IL leads to lower friction constant values. The authors explain these performances by the formation of stable adsorbed layers of the highly polar ionic liquid molecules on the steel surface.

More recently, numerous studies were dedicated to the use of ionic liquids [87, 88]. In fact, new ionic liquids based on phosphonium and pyrrolidinium cations have recently been used [89, 90]. For example, Yu et al. have used new series of tetraalkylphosphonium cation combined with phosphate and phosphinate anions [89]. They have demonstrated that the use of a small amount of phosphonium-based ILs (5 wt%) led to significant friction and wear reductions (2–3 orders of magnitude). Pejakovic et al. have also investigated the influence of pyrrolidinium ILs as lubricant additives for steel–steel contact lubrication [90].

New kinds of ionic liquids such as dicationic and crown-type ILs appear in the literature [91]. Jiang et al. showed that the design of these new structures of ionic liquids led to excellent tribological performance either by reducing friction or by improving anti-wear properties. In addition, these synthesized ILs are noncorrosion lubricants [91].

As the lubricant market represents several million tons annually [92], there is a large interest in assessing the ecotoxicity and biodegradability of ionic liquids [93, 94]. Thus, Stolte et al. have highlighted that the ILs based on ammonium and pyrrolidinium cations coupled with sulfate and sulfonate counterions displayed minor toxic effects in the biological test systems performed [94].

In conclusion, the use of ionic liquids as lubricants in assemblies of metal–metal (majority) or metal–polymer type is promising. However, the high price of ionic liquids and the low commercial availability of original structures severely limit their use.

Plasticizers

In recent years, ionic liquids have been considered as new alternatives of conventional plasticizers for polymers such as starch, poly(vinyl chloride) (PVC), and poly(methyl methacrylate) (PMMA). In fact, conventional plasticizers consider combinations of phthalate compounds which are now strongly concerned by REACH regulation. However, very few studies have investigated ILs as new plasticizers for economic reasons. In fact, the cost of ionic liquids is currently too high for a large diffusion of these products in industrial applications. Sankri et al. [95] have prepared thermoplastic starch by melt processing using 1-butyl-3-methylimidazolium chloride as plasticizer instead of glycerol which is commonly used for starch processing. The authors have compared the effect of imidazolium ionic liquid to glycerol plasticizer one on the mechanical properties of

thermoplastic starch. The results are significant in the case of imidazolium since an increase of the strain at break from 100 % to 400 % combined to a sharp drop in Young's modulus is observed. They have attributed this modulus decrease to a reduction of intermolecular hydrogen bonds between starch chains. Scott et al. [14] have used room-temperature ionic liquids (RTILs) based on imidazolium cations as plasticizers for poly(methyl methacrylate). For such a polymer, dioctyl phthalate (DOP) is the usual plasticizer. Butylmethylimidazolium and hexylmethylimidazolium associated to hexafluorophosphate have been considered as excellent plasticizers for PMMA due to the fact that these ILs reduce the glass transition temperature while improving the thermal stability. Rahmann et al. [96] have used different ionic liquids varying by the cation chemical nature, i.e., imidazolium, phosphonium, or ammonium, as novel plasticizers for poly(vinyl chloride) (PVC) matrix. A higher decrease in the glass transition temperature of PVC compared to conventional plasticizers was obtained with an improved flexibility of material. A better leaching and migration resistance with ILs than with the conventional plasticizers was proven as well. Nevertheless, the behaviors of ionic liquids and conventional plasticizers remain identical when subjected under far-range UV exposure. More recently, due to the high cost of ILs, other authors have decided to introduce different ionic liquids within engineering polymer like the biomedical grades [97, 98]. In fact, Dias et al. have studied the use of phosphonium-based ionic liquids as plasticizers into a medical grade of poly(vinyl chloride) [97]. The thermomechanical properties, gas permeabilities, as well as the biocompatibility have been investigated. Indeed, the authors have highlighted the improvement of the viscoelastic properties of the polymer materials as well as one significant increase (+50 °C) of the thermal stability of PVC film. In addition, the phosphonium ionic liquid with Tf_2N anion displayed excellent hemolytic compatibility. Biodegradable polymers and in particular aliphatic polyesters of the poly(hydroxy acid) type such as polylactic acid (PLA) have been investigated [99]. Other matrices were also studied in the literature such as poly(vinylidene fluoride) (PVDF) and polyether-block-amide copolymer (Pebax[®]) [19, 100]. For example, Guo et al. who studied the Cr (VI) transport through a polymer membrane have combined the use of an imidazolium ionic liquid as a plasticizer and a phosphonium ionic liquid as a carrier which led to an increase of the diffusion coefficient (four times faster) compared to the PVDF matrix without ionic liquid. In the field of membrane separation technique, the huge advantage of this new membrane is a longer reusability and at larger flux [19]. In the elastomeric co-polyamide membranes, a compromise between two opposing effects is observed as a function of IL amount: the complete dissolution of the crystalline polyether phase with further plasticization of the polymer matrix by the IL, enhancing the ductility but also a progressive weakening of the membrane due to a reduction of crystal fraction responsible for the mechanical strength [100].

In conclusion, we have demonstrated that the use of ionic liquids as plasticizer agent is emerging in the field of engineering polymers such as PVC or Pebax[®]. Thus, the use of high-performance polymers can justify the high cost of ionic liquids as these ones could bring additional functionalities.

Porous Polymers and Foams

The use of ionic liquids in the preparation of porous polymer is a route which was also considered. Indeed, the elimination of ILs from a mixture of polymers is a simple process. Zhu et al. [7] have prepared polyurea with pore sizes of 100–500 nm by interfacial polymerization between hexane and a series of imidazolium combined with hexafluorophosphate and tetrafluoroborate anions. Other authors have prepared by in situ polymerization a series of porous composites containing polymers and ionic liquids [101]. Another method used to achieve porous polymers is the polymerization of microemulsions, previously stabilized by ionic liquids as surfactants. This procedure of preparation can lead to different polymer gels and finally to porous polymers after anionic exchange [8]. Ionic liquids can also play a significant role as additive for the preparation of microcellular foams coupled with the supercritical carbon dioxide (scCO₂) as foaming agent [102]. More recently, our laboratory developed a simple and scalable process to prepare microcellular polystyrene-ionic liquid foams. The influence of the chemical nature of ionic liquids (1 wt%) on the microcellular morphology of PS matrix is shown in Fig. 1.1.

In this work, we have demonstrated that the presence of fluorinated chains generated a lower polarizability of IL and led to lower solubility parameters. Thus, the presence of CO₂-philic perfluorinated chains on the imidazolium cation reduces the cell size from 100 (neat polystyrene pore size) to 45 μm .

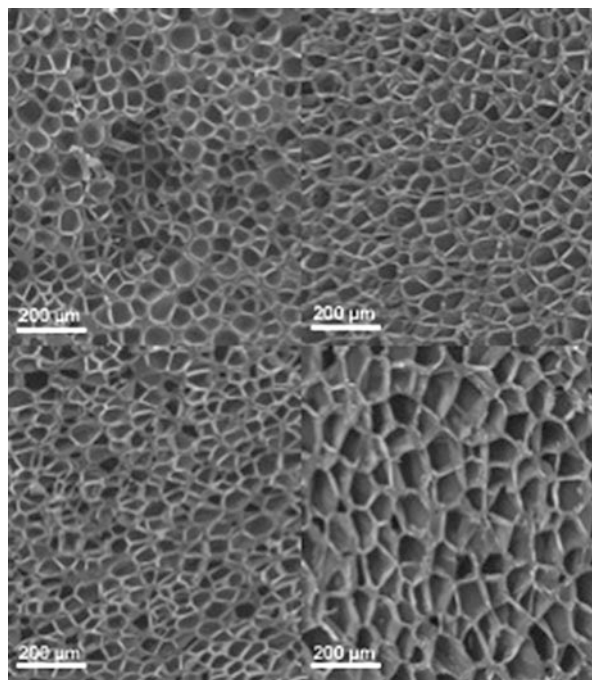


Fig. 1.1 TEM micrographs of (a) neat polystyrene (PS) and PS combined with ILs; (b) polystyrene/fluorinated pyridinium ionic liquid (PS/ C₁₂FPy I[−]); (c) polystyrene/fluorinated imidazolium ionic liquid (PS/ C₁₈C₁₂Flm I[−]); (d) polystyrene/fluorinated phosphonium ionic liquid (PS/C₁₂FP I[−])

In summary, ionic liquids are an excellent alternative to inorganic particles usually used to generate nucleation, necessary for the foaming process from their high specific surface and high aspect ratio such as layered silicates. Moreover, ILs limit the use of large amount of inorganic fillers which allows for circumventing the problem of distribution/dispersion of nanofillers in the polymer matrix. However, many studies are needed to provide an understanding of foaming process.

Organic Polymers Supporting ILs

The use of ionic liquids supported on hybrid materials is a new area of application of ILs. Indeed, the idea to use recoverable and reusable catalysts is very judicious from a point of economical and environmental view. In the literature, the hybrid organic–inorganic materials containing imidazolium immobilized on silica particles are most often encountered [103]. However, some recent works mention the use of polystyrene to support ILs (PSILs) [104]. Chi et al. [104] have investigated the catalytic properties of this material for nucleophilic fluorination and different substitutions. They have demonstrated that the longest linker (dodecyl) associated with tetrafluoroborate counteranion (BF_4^-) leads to the best catalytic activity unlike to PSILs associated with other anions [105]. Despite a slight development in catalytic reactions [106], the synthesis of poly(ethylene glycol) (PEG)-supported ionic liquids showed interesting physical and chemical properties [107].

Supramolecular Polymers

The supramolecular structures could be prepared from self-assembling processes involving hydrogen bonds [108], host–guest interactions [109], metal–ligand coordination [110], as well as ionic interactions [111]. The latter ones, encountered in the field of electrolytes [112], have been widely used to create chemical/physical cross-linked structures in polymer matrix such as alginates [113], halatopolymers [114], and a wide variety of ionomers [115].

Wathier and Grinstaff [116] suggested that ionic liquids could lead the in situ formation of ionic networks based on coordinating ion pairs. Indeed, the authors have synthesized an ionic liquid composed of a dication (tetraalkylphosphonium) and a tetraanion (ethylenediaminetetraacetate). They have demonstrated that Coulomb interactions are governed by pairwise interactions between cation and anion, and the extended structure of the ionic liquid may lead to a supramolecular ionic network as shown in Fig. 1.2.

The authors have also suggested that the ramification of multivalent ions could lead to networks while the presence of large ions would lead to a loose coordination which would enhance the toughness of the resulting materials. In fact, the combination of the improved mechanical properties linked to the homogeneity and high charge densities of ionic liquids could lead to a new range of optimized materials matching the ionomers' properties. However, these ionic materials can often undergo

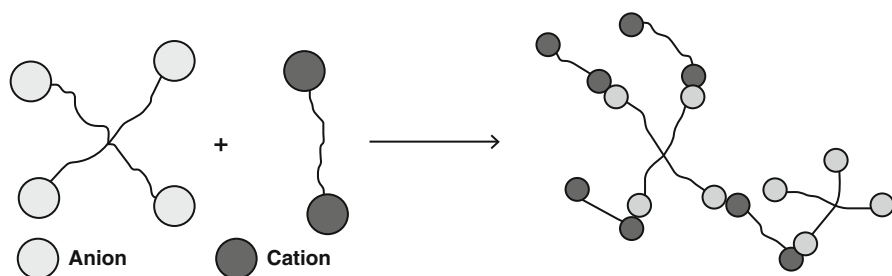


Fig. 1.2 Schematic diagram of a supramolecular ionic network

phase separation phenomena involving long-range interactions which lead to difficulties for establishing structure–property relationships. Ionic liquids have also been used in the preparation of the self-assembly of dendrons into supramolecular columns and sphere [117]. These supramolecular structures contain the ionic liquid part segregated as a core. As a consequence, the ILs could be used as nanoreactors allowing reactions in confined ionic liquid geometries. Recently, ionic liquids based on pyridinium, imidazolium, and phosphonium have been used as functional building blocks in a fluorinated matrix to achieve materials with excellent mechanical properties coupled at a nanoscale structuration [118]. These authors have demonstrated that the chemical nature of the organic cations as well as anions plays a significant role in the distribution and the structuration of ionic domains in the polymer matrix. Thus, co-continuous or “spider-web” morphologies have been generated. The influence of the chemical nature of ILs on the structuration of ionic clusters in a fluorinated matrix is given in Fig. 1.3.

In addition, the authors have also highlighted significant increases in Young’s modulus and strain at break, especially for the phosphonium ionic liquid combined with iodide counterion (+160 % and +190 %, respectively).

In summary, the versatility of ionic liquids opens a new path in the field of supramolecular organizations, and it is possible to consider ionic domains as structuring agents in order to design materials with enhanced properties as it is the case for the ionomers compared to the neat corresponding polymers. Then, to achieve significantly optimized polymer/IL blends, a lot of works are needed to find the suitable association between the task-specific IL and the matrix.

Surfactant Agents

Ionic Liquids: Surfactant Agents of Layered Silicates

For many years, the low cost of phyllosilicates, like montmorillonite (MMT), was their main advantage to their use in the field of polymer nanocomposites. Nevertheless, this type of nanoparticle is only compatible with hydrophilic polymers such as poly(vinyl alcohol) (PVA) or poly(ethylene oxide) [119, 120].

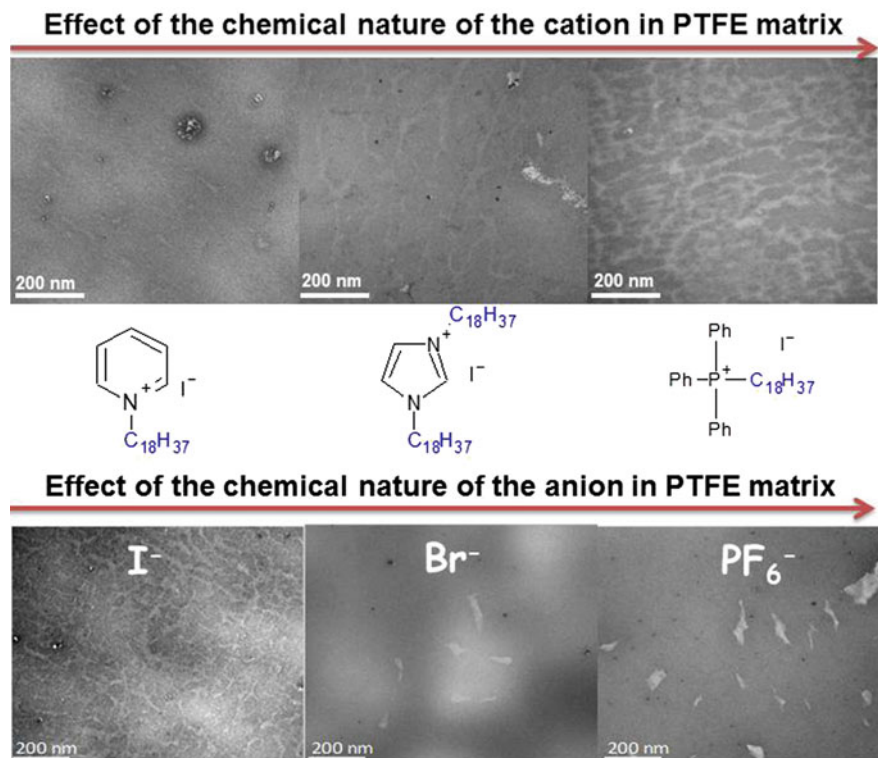


Fig. 1.3 TEM micrographs showing the influence of the chemical nature of the cation and anion on the morphologies of PTFE/IL blends

In fact, regarding hydrophobic polymers, a nonmiscibility is observed which generates poor interfacial interactions between the layered silicates and the polymer matrix and microcomposite-like morphologies. Thus, this lack of compatibility leads to poor thermal, mechanical, and barrier properties. In conclusion, it is therefore necessary to modify the surface of clays. The most commonly used surface treatments involve cationic exchange.

Gieseking and Hendricks revealed for the first time the intercalation of inorganic exchangeable cations (Ca^{2+} , Mg^{2+} , K^{+}) by organic cations in an aqueous medium [121, 122]. As the processing of polymer requires in many cases high temperatures, thermostable ionic liquids have been widely used in the literature [123–127]. In fact, different organic cations containing nitrogen or phosphorus compounds such as pyridinium, imidazolium, quinolinium, and phosphonium were investigated due to their excellent thermal behavior compared to conventional quaternary ammonium [128–131]. For example, Awad et al. have highlighted that the chemical structure of the imidazole ring enhances the thermal stability of the imidazolium cation compared to the ammonium salt one [131]. Then, the use of phosphonium ionic liquids was justified by the well-known properties of

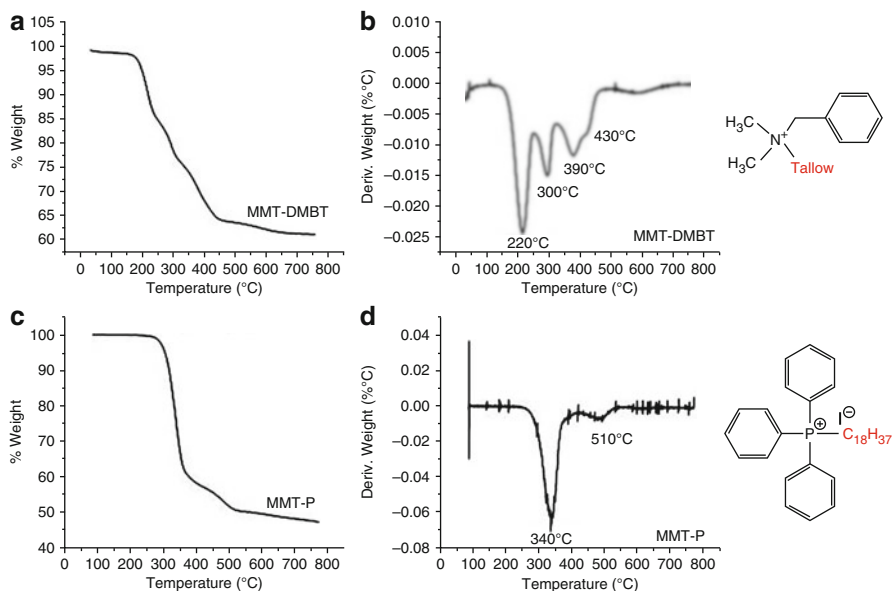


Fig. 1.4 TGA curves of organically modified montmorillonite: (a, b) MMT-A, (c) MMT-I, (d) MMT-P

phosphorus compounds, such as flame retardancy and heat stabilization [132, 133]. Thus, Livi et al. have shown the better thermal behavior of phosphonium and imidazolium ionic liquids compared to ammonium salts [129]. Indeed, the degradation temperature is delayed of +50 and +120 °C for imidazolium- and phosphonium-modified montmorillonite, respectively, compared to ammonium-modified montmorillonite. The TGA curves of the montmorillonite modified with ammonium, phosphonium, and imidazolium salts are presented in Fig. 1.4.

Other authors have revealed the influence of the chemical nature of the anion on the thermal stability of ionic liquids [126, 131]. For example, Awad et al. have highlighted that the fluorinated anions such as hexafluorophosphate PF_6^- or tetrafluoroborate BF_4^- are more thermally stable compared to use of halide anions (bromide, iodide, or chloride).

IL-Treated Layered Silicates for Polymer Nanocomposites

Nevertheless, despite these numerous studies on the thermal stability of ionic liquids that modified layered silicates, very few studies have reported the influence of these organophilic montmorillonites on the morphologies as well as on the final properties of polymer materials [134, 135]. For this reason, this section will be devoted to the use of thermostable ionic liquids into different polymer matrices such as poly(styrene) [123], poly(ethylene) [134], poly(propylene) [135], and poly(vinylidene fluoride) [136].

Polyolefin/MMT-IL Nanocomposites

In the literature, some authors have studied the influence of a low amount of ionic liquid-treated montmorillonites (<5 % wt) on the final properties of polyethylene or polypropylene matrices [126, 129, 135]. In fact, Mittal et al. using melt-compounding method have highlighted the good affinity between imidazolium-treated clays and PP matrix by characterizing by transmission electronic microscopy a mixed intercalated/exfoliated morphology with few tactoids and a few single clay layers. Thus, the good distribution of clay layers in polymer matrix allows an increase of the Young's modulus of 35 % and an improvement of +90 °C of the thermal stability as well as a significant increase of the relative oxygen permeation. Nevertheless, a decrease of the elongation at break was also observed [135]. Others studies on PP nanocomposites based on imidazolium-treated MMT have been also reported [137–140]. Ding et al. have observed a significant increase of 170 °C of the degradation temperature on PP/MMT-IL nanocomposites prepared from solution intercalation method compared to neat PP matrix. They have attributed this result to the exfoliation of MMT layers in the PP matrix [137]. On the high-density polyethylene, a comparative study on the influence of the chemical nature of the cation on the thermal and mechanical properties has been performed [126, 129]. Thus, Livi et al. have shown that the physically adsorbed surfactants act as a compatibilizing agent in situ at the clay layer/polymer matrix interface which induces a very good stiffness–toughness compromise combined with a very high nanofiller distribution level. Indeed, the authors have demonstrated that the addition of only 2 % wt of imidazolium and phosphonium montmorillonites leads to an increase of 40 % and 50 % of Young's modulus, respectively, without reducing its fracture behavior [127].

PVDF/MMT-IL Nanocomposites

Poly(vinylidene fluoride) (PVDF) nanocomposites based on ionic liquid-modified montmorillonites have been prepared mainly by melt compounding [128, 136]. Then, the effect of the ILs based on ammonium, pyridinium, and phosphonium cations has been investigated on the morphology, the crystalline phase, and the mechanical properties. Patro et al. have highlighted that the pyridinium and ammonium salts generate exfoliated morphologies compared to phosphonium ILs which leads to an intercalated nanocomposite structure [137]. Thus, significant increases in the strain at break were obtained by using 5 wt% of organophilic montmorillonites (175 and 200 % for pyridinium- and phosphonium-modified MMT) [136]. Moreover, IL-modified MMT, especially phosphonium-treated MMT, can be efficient nucleating agents and generate the formation of β -phase which is the phase relevant for dielectrical applications. Recently, different authors have shown that the use of 1 wt% of montmorillonite modified by an ionic liquid functionalized with a perfluorinated chain leads to a dramatic improvement of elongation at break of 630 % without reducing the rigidity of polymer matrix [127]. In addition, the authors also compared the influence of the chemical nature of the imidazolium salt functionalized either with short or long alkyl chains or with fluorinated chains on the morphology. Figure 1.5 summarizes the different morphologies observed.

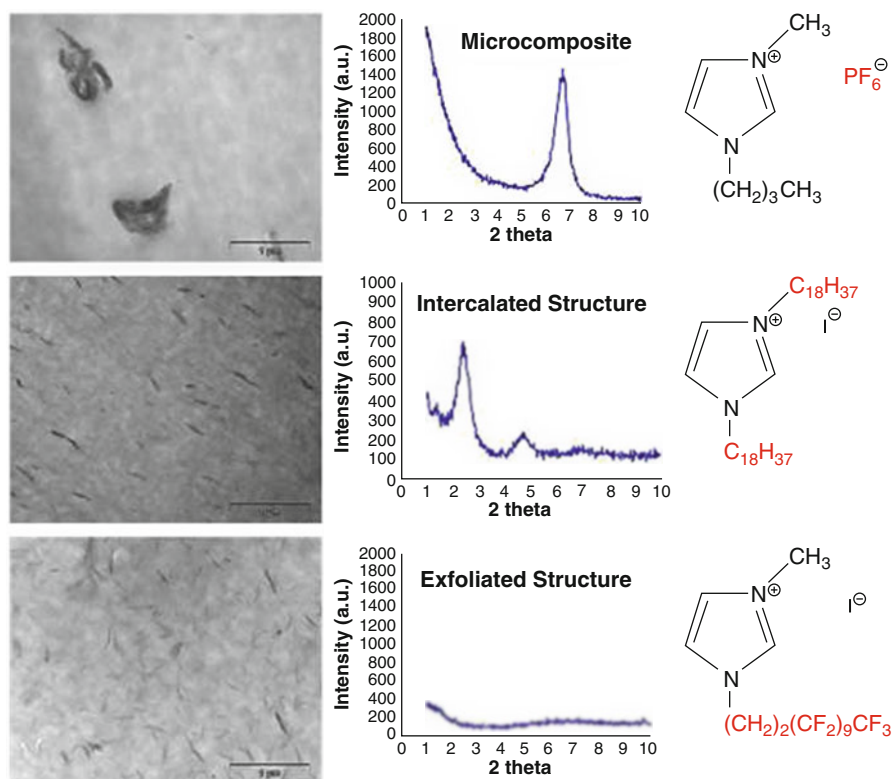


Fig. 1.5 WAXD patterns and TEM images of three different types of nanocomposites based on imidazolium montmorillonite/PVDF

Polystyrene/MMT-IL Nanocomposites

Different routes of processing of the nanocomposites based on PS have been used as well as various surfactant agents based on pyridinium, phosphonium, and quinolinium ionic liquids [141–145] in order to study their effects on the final properties of the polymer nanocomposites. Bottino et al. have investigated the influence of the ammonium and imidazolium salts as well as the effects of their alkyl chain length on the morphology combined to the photooxidation properties [146]. In both cases, the use of ionic liquids leads to a decrease of photooxidation properties of the nanocomposites in comparison to the neat PS matrix. Modesti et al. who have processed by melt compounding poly(styrene-co-acrylonitrile) (SAN)/modified clay nanocomposites containing ammonium-, imidazolium-, or phosphonium-modified montmorillonites have highlighted the key role of the functionalization of the surfactant agent [142]. In fact, a better dispersion of clay layers into the matrix has been demonstrated for imidazolium and phosphonium bearing aromatic functions. Recently, different authors have demonstrated that ionic liquids are excellent candidates for fire resistance of PS matrix [147–149].

Indeed, Pucci et al. who have prepared different montmorillonites treated with polymerizable alkyl vinylbenzyl imidazolium chlorides have obtained an increase of the degradation temperature of +60 °C [147].

In conclusion, pyridinium, imidazolium, or phosphonium ionic liquids are emerging as excellent candidates for the preparation of polymer/layered silicate nanocomposites. The key point is that a small amount of IL-modified montmorillonites is enough to achieve good thermal, mechanical, and barrier properties. Nevertheless, to get significantly optimized polymer nanocomposites, a lot of works are needed to find the most suitable functionalization of IL to polymer matrix.

Conclusions

The primary objective of this chapter has been to enhance and highlight the benefits as well as the opportunities proposed by ionic liquids in the field of polymers either as plasticizer, lubricant building blocks, and reinforcing agents or as interfacial agents for layered silicates. Thus, the use of a small amount of ionic liquids in various polymer matrices can lead to significant increases in their final properties such as barrier, thermal, mechanical, corrosion resistance, and conductive properties.

However, the cost and the accessibility to the original structure of ionic liquids significantly limit their use in the field of polymers. For these reasons, it is necessary to intensify research on ionic liquids in order to bring understanding and to demonstrate the benefits of ionic liquids compared to their disadvantages. In conclusion, this chapter is an overview of the true potential of ionic liquids in polymer science. In fact, the different cation/anion combinations as well as the numerous possible functionalization suggest to us that it is conceivable to synthesize from an infinite set of ionic liquids bringing specific functionalities depending on the selected polymer.

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Deep Eutectic Solvents Playing Multiple Roles in the Synthesis of Porous Carbon Materials

2

Daniel Carriazo, María C. Serrano, María C. Gutiérrez,
M. Luisa Ferrer, and Francisco del Monte

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Abstract

This chapter discusses the use of deep eutectic solvent-assisted syntheses which allow the preparation of both chemically and structurally modified carbon monoliths suitable as electrodes in supercapacitor cells. Either carbons or carbon-carbon nanocomposites exhibiting a hierarchical structure and a tailored composition (either nitrogen or phosphorus doped) could be attained by the use of different mixtures of deep eutectic solvents (DESs). Carbons prepared from DESs are also suitable for CO₂ adsorption and CO₂-N₂ and/or CO₂-CH₄ separation processes. These features, besides the low-cost character of our carbons, open interesting perspectives for their application as sorbents in separation technologies for CO₂ low-pressure post-combustion processes and natural gas upgrading.

Keywords

Deep eutectic solvents • Carbons • Ionic liquids • Supercapacitors • CO₂ sorbents

D. Carriazo • M.C. Serrano • M.C. Gutiérrez • M.L. Ferrer • F. del Monte (✉)
Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain
e-mail: delmonte@icmm.csic.es

Introduction

It is generally assumed that solvents played a capital role in any synthetic process [1, 2]. Homogenization of reagents and products within the reaction media is obviously the main function of solvents, but they can also influence the activation energies and the reaction thermodynamics. Aqueous, nonaqueous, or mixed solvents have been the solvent of choice depending on the peculiarities of the synthesis. Moreover, in materials science and from a green chemistry point of view, the progress for the preparation of advanced materials with controlled structure and/or unprecedented functionality depends largely on the core competence of materials chemists to design and develop novel synthetic strategies that, at any stage of the synthesis, limit the use of chemical reagents, solvents, and surfactants. As mentioned above, solvent reduction is of paramount importance. It is worth noting that they typically represent over 85 % of mass utilization in a typical chemical manufacturing process, and considering that recovery efficiency is far from satisfactory, they are major contributors to environmental pollution. The development of solvent-free alternative processes would be the ideal situation. Otherwise (i.e., if none of the reagents is a liquid that can be used as the reaction medium), replacement of volatile organic solvents by nonflammable, nonvolatile, nontoxic, and inexpensive “green solvents” would be desired. Within this context, research on deep eutectic solvents (DESs, a related class of ionic liquids – ILs) as an alternative reaction medium is gaining increased interest.

DESs are molecular complexes typically formed between quaternary ammonium or phosphonium salts and hydrogen-bond donors. The charge delocalization occurring through hydrogen bonding between the halide anion and the hydrogen-donor moiety is responsible for the decrease of the freezing point of the mixture relative to the melting points of the individual components. DESs share many characteristics of conventional ILs (e.g., nonreactive with water, nonvolatile, and biodegradable) while offering certain advantages. For instance, the preparation of eutectic mixtures in a pure state can be accomplished more easily than that of ILs with no need of post-synthesis purification because the purity of the resulting DES will simply depend on the purity of its individual components. Moreover, the low cost of those eutectic mixtures based on readily available components makes them particularly desirable (more so than conventional ILs) for large-scale synthetic applications. Examples of low-cost eutectic mixtures include DESs based on choline chloride (ChCl) first described by Abbott and coworkers [3–6]; low-melting eutectic mixtures of sugar, urea, and salts first described by König and coworkers [7–9]; “natural deep eutectic solvents” (NADES) first described by Choi et al. [10, 11]; and low-transition-temperature mixtures (LTTMs) described by Kroon and coworkers [12]. Interestingly, the use of ChCl, natural carboxylic acids, amino acids, different sugars, and even water provides certain biodegradable and renewable features to the resulting eutectic mixtures.

Organic synthesis [13–19], separation processes [20–23], biomass processing [24–29], and carbon dioxide adsorption [30, 31] constitute the principal fields where DESs have been applied. Moreover, the eco-friendly and low-toxic character

of some DESs has allowed their use as solvents for both natural and synthetic membrane-like structures [32] and proteins [33–36] and even for whole microorganisms [37] with preservation of their intrinsic activity. Examples of materials prepared from “all-in-one” DESs include metal phosphates [38], oxalatophosphates [39], aluminophosphates [40, 41], carboxymethylphosphonates [42], oxalatophosphonates [43], polyoxometalate-based hybrids [44], zeolites [45], or metal–organic frameworks (MOFs) [46]. Readers are referred to the review published by Morris and coworkers for further information on ionothermal syntheses of zeolites, MOFs, and inorganic–organic hybrids [47]. Moreover, there is another excellent and recent review published by Jérôme and coworkers highlighting the most interesting works using DESs not only in this latter field but also in electrochemistry [53]. While recognizing the tremendous relevance in this topic, this book chapter will not continue describing them. We consider that there are already excellent reviews covering most of the recent advances in this area so that readers are referred to them for detailed information [48–53]. Recently, we have also reviewed the use of DESs in the synthesis of polymers and related materials [54, 55]. In this book chapter, we will focus on how the use of DESs allows the synthesis of different porous carbon materials (section “[Introduction](#)”). We will also describe the fields where these porous carbons can be more successfully applied (section “[Use of DESs in the Synthesis of Porous Carbon Materials](#)”).

Use of DESs in the Synthesis of Porous Carbon Materials

The most common synthetic processes for carbon preparation is the carbonization of polymers obtained by polycondensation between resorcinol and formaldehyde [56–58]. This process typically needs the presence of certain additives (e.g., block copolymers) if one desires controlling the porous structure of the resulting carbon [59, 60]. This is by no means a trivial issue given that hierarchical structures – comprising both small (e.g., micro- and meso-) and large (e.g., macro-) pores – proved more effective than non-hierarchical ones in most of the applications where carbons (e.g., as adsorbents, filters, or electrodes, among others) have been used (see section “[Use of DESs in the Synthesis of Porous Carbon Materials](#)” below) [61–63].

The preparation of resorcinol-based DESs opened interesting perspectives in this field. For instance, Carriazo et al. reported on the preparation of DESs from mixtures of resorcinol and CHCl_3 or urea, resorcinol, and CHCl_3 (Fig. 2.1) that, upon polycondensation with formaldehyde, resulted in the formation of monolithic carbons with a bimodal porosity that comprises both micropores and large mesopores of ca. 10 and 23 nm, respectively [64]. The morphology of the resulting carbons consisted of a bicontinuous porous network built of highly cross-linked clusters that aggregated and assembled into a stiff, interconnected structure. This sort of morphology is typical of carbons obtained via spinodal decomposition processes where the formation of a polymer-rich phase by polycondensation is accompanied by the segregation of the non-condensed matter (creating first

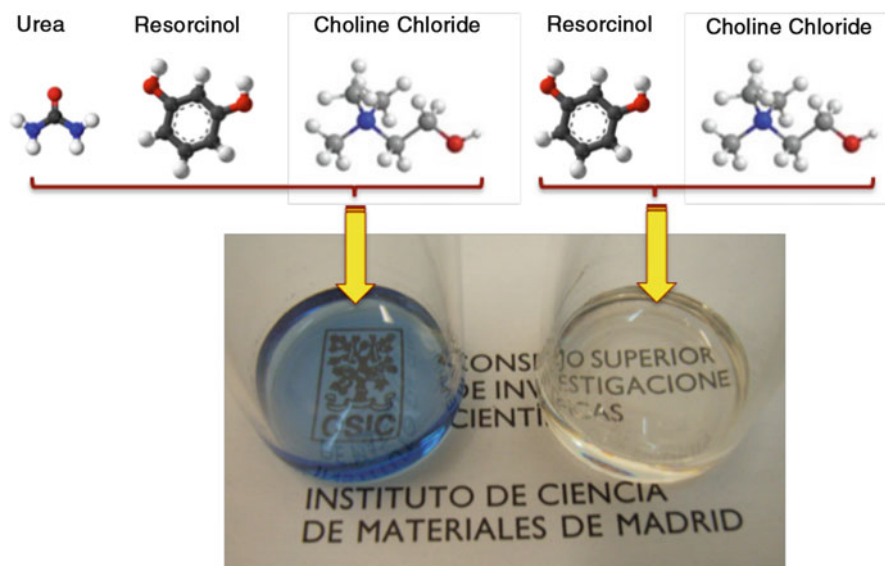


Fig. 2.1 Picture shows the liquid aspect of the eutectic mixtures based on urea, resorcinol, and ChCl (*left*) and resorcinol and ChCl (*right*) (Adapted with permission from Ref. [64])

a polymer-poor phase that, ultimately, becomes a polymer-depleted phase), the elimination of which (either before carbonization by washing or during carbonization by thermal decomposition) results in the formation of the above-mentioned bicontinuous porous structure. In our case, Carriazo et al. hypothesized that one of the components forming the DES (e.g., resorcinol) is acting as precursor of the polymer phase, while the second one (e.g., ChCl) is segregated into the polymer-depleted phase (Fig. 2.2). This mechanism actually resembles that mentioned above for the synthesis of zeolites [45] except that DES rupture results from resorcinol–formaldehyde polycondensation rather than from thermal decomposition (i.e., via ionothermal synthesis). Interestingly, simple washing with water of the polymer resulting after polycondensation allowed fully recovering of ChCl – as demonstrated by gravimetric analysis and NMR spectroscopy – as the only by-product of the reaction, which opens the path to ChCl reutilization in subsequent reaction processes.

The wide range of DES that can be prepared provides a remarkable versatility – in both structural and compositional terms – to the carbons that can be obtained through this synthetic approach. For instance, one can control the dimensions of both the macro- and the micropores of the resulting carbon. The former was achieved by using ternary DESs composed of resorcinol, urea, and ChCl [64] while the latter upon the use of DESs composed of not only resorcinol but also an alkyl-modified resorcinol (e.g., hexylresorcinol) as precursors for the polycondensation reaction (Fig. 2.3) [65]. Moreover, the preparation of carbon–carbon–carbon nanotube (CNT) composites with intriguing structures can also be done upon the use of low-viscosity DESs that allow the homogeneous dispersion of high loadings of CNTs before

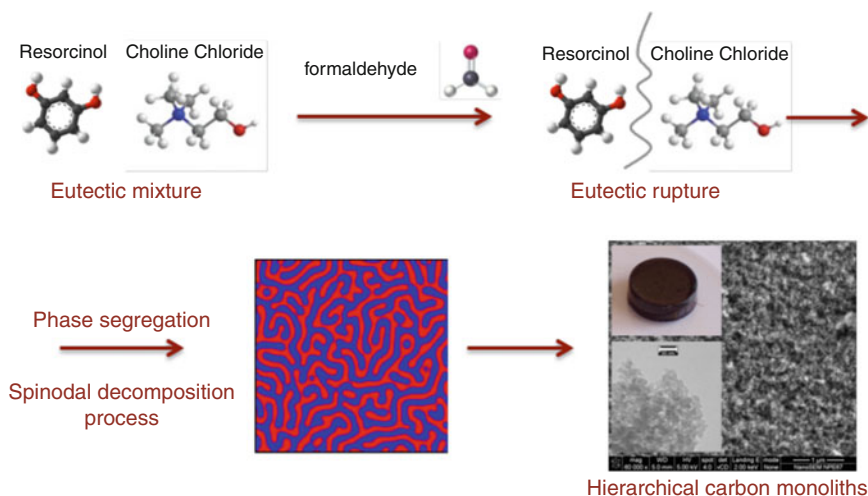


Fig. 2.2 Scheme representing the formation of hierarchical carbon monoliths upon addition of formaldehyde to the eutectic mixture of resorcinol and ChCl, followed by eutectic rupture, phase segregation in a spinodal-decomposition-like process, and scale bars: TEM micrograph: 50 nm; SEM image: 1 μ m (Adapted with permission from Ref. [55])

polycondensation starts (Fig. 2.4) [66]. Finally, either N-doped or P-doped hierarchical carbons can also be obtained upon the use of DESs containing nitrogen-rich precursors (e.g., hydroxypyridine) or phosphorus-based catalysts (e.g., phosphoric acid), respectively (Figs. 2.5 and 2.6) [67, 68]. All this range of structures and compositions open the path to the use of these porous carbons in applications with a tremendous environmental interest like energy storage and CO₂ capture and separation.

Application of Porous Carbon Materials

As Electrodes in Supercapacitors

Electric double-layer capacitors (EDLC, also called supercapacitors) are energy storage devices based on the electrical adsorption of ions at the electrode/electrolyte interface (non-faradaic process) [69]. Porous carbons are being widely used as electrode materials for supercapacitors because of their high specific surface area and relatively good electrical conductivity [70]. The EDL formation is especially efficient in carbon pores of size below 1 nm that ideally matches the ion's size [71]. However, for good dynamic charge propagation, the presence of meso- and macropores should aid the electrolyte transportation throughout the bulk material [56]. It should be noted that numerous porous carbons are known to suffer from electrolyte kinetic problems that are related to inner-pore ion transport [56, 69]. Thus, carbon monoliths with three-dimensional (3D) hierarchical porous structures (micro-, meso- and, macroporous)

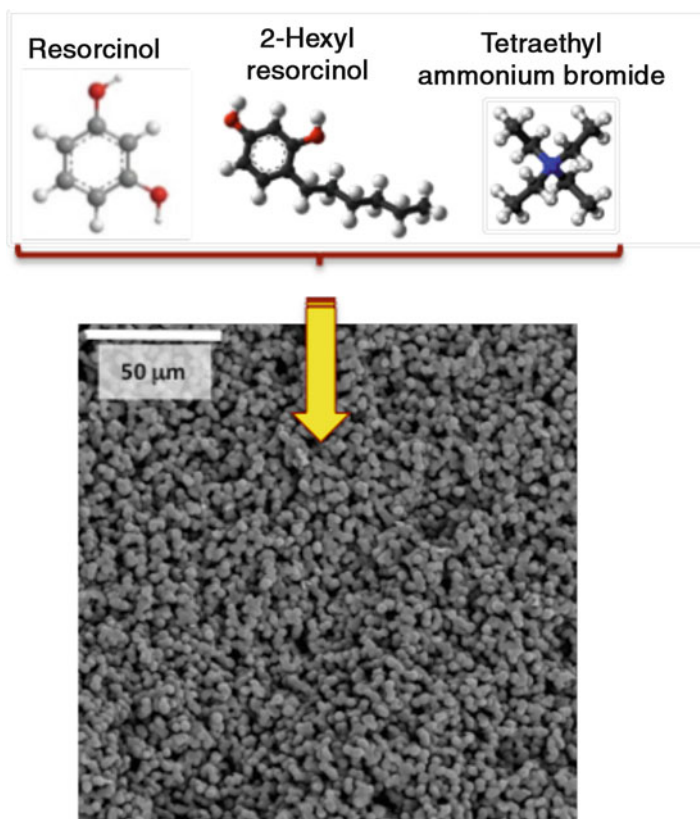


Fig. 2.3 Scheme representing the condensation of the eutectic mixture composed of resorcinol, hexylresorcinol, and tetraethylammonium bromide and SEM micrograph of the resulting carbon (Adapted with permission from Ref. [55])

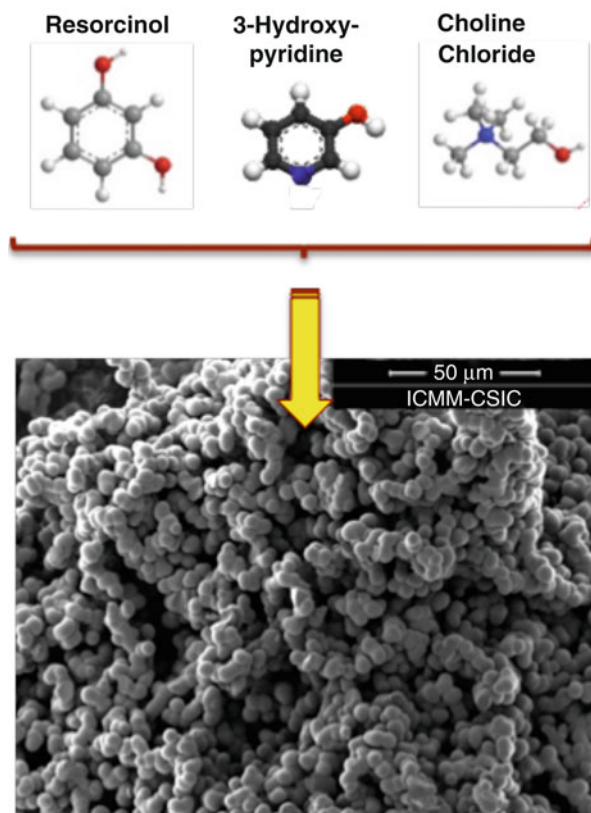
have recently been proposed as promising electrode materials for EDLC given that they facilitate ion transport by providing a smaller resistance and shorter diffusion pathways. Moreover, ion-buffering reservoirs can be formed in the macropores to minimize the diffusion distances to the inner surfaces. Actually, the physicochemical properties of the electrolyte in the macropores are similar to those of the bulk electrolyte with the lowest resistance [72]. Besides, the use of 3D monolithic architectures can enable its direct assembly into the supercapacitor cell [73] and, ultimately, the miniaturization of energy storage devices [74].

Numerous hierarchically structured carbon monoliths (for EDLC as well as for other applications) have been produced via condensation of resorcinol and formaldehyde and subsequent carbonization [57, 58]. The hierarchical structure has typically been obtained by the application of either supercritical or freeze-drying processes prior to carbonization or impregnation of preformed macroporous structures with the



Fig. 2.4 Scheme representing the catalytic condensation of furfuryl alcohol by the eutectic mixture of *p*-toluene sulfonic acid and ChCl for the formation, after carbonization, of carbon-carbon nanotube composites. SEM (**a**, **c** and **d**; scale bars: 5, 1 and 1 μm , respectively) and TEM (**b**, scale bar: 50 nm) micrographs show the hierarchical structure of the resulting monoliths (Adapted with permission from Ref. [55])

Fig. 2.5 Scheme representing the condensation of the eutectic mixture composed of resorcinol, 3-hydroxypyridine and ChCl, and SEM micrograph of the resulting carbon. Adapted with permission from [67].



resorcinol–formaldehyde sol (e.g., silica aerogels which, after carbonization, are eliminated by fluorhydric acid treatments). The direct carbonization of natural organic structures has recently gained increased interest for the formation of hierarchically structured carbon monoliths that are rich in oxygen and favor the occurrence of pseudocapacitive processes [75]. The use of surfactant-templated approaches for the preparation of carbon spheres has also been described for cationic and nonionic surfactants [76]. Such a surfactant approach has recently been extended to mixtures of long-chain PEO–PPO–PEO triblock copolymers (e.g., PEO₁₀₁–PPO₅₆–PEO₁₀₁ and PEO₂₀–PPO₇₀–PEO₂₀) [59] which, under hydrothermal conditions, result in the formation of hierarchically structured CA with well-ordered mesopores of ca. 3 nm and macropores of ca. 3 mm. More recently, our group used a short-chain PPO–PEO–PPO triblock copolymer that produced hierarchically structured carbon monoliths with macro- and micropores, the latter providing to these monoliths an interesting performance as electrodes in supercapacitor cells. However, the preparation of carbonaceous adsorbents with tailor-made hierarchical structures and surface functionalities without the aid of this type of structure-directing agents (SDAs) is yet challenging. Within the context of template-free syntheses capable to fulfill these demanding specifications, the use of DESs is especially interesting in sustainable

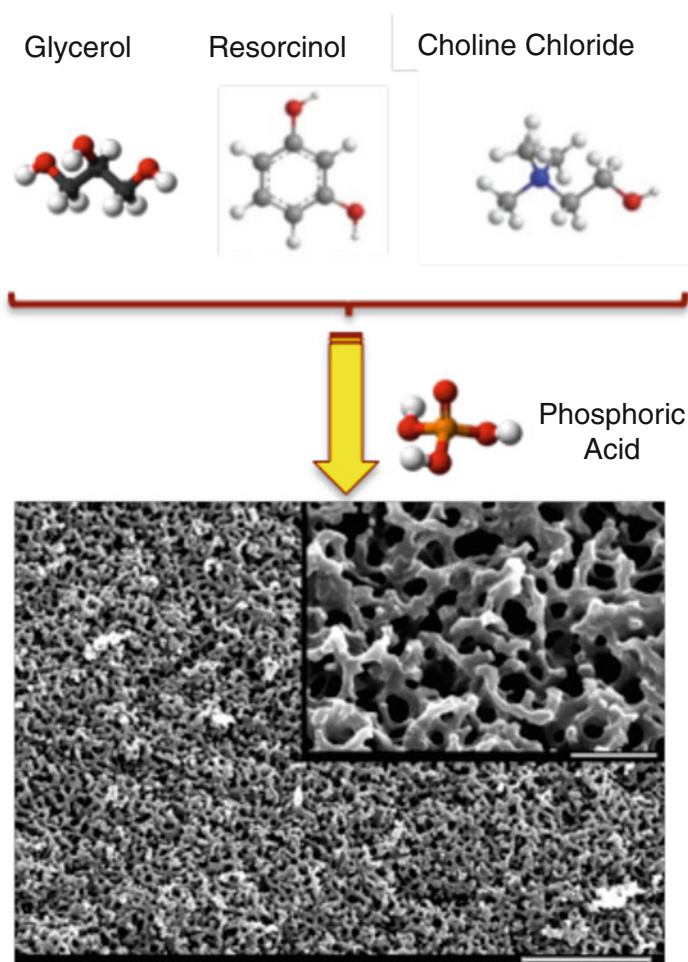


Fig. 2.6 Scheme representing the catalytic (e.g., with phosphoric acid) condensation of the eutectic mixture composed of resorcinol, glycerol and ChCl, and SEM (bars were in main micrograph and of the resulting carbon) (Adapted with permission from Ref. [55])

terms because DESs are capable to play multiple roles (e.g., from reaction medium to carbonaceous precursors up to SDAs) in the synthetic process, hence promoting a significant economy of reagents. A full description of the capabilities of DES-assisted syntheses was provided above.

Nonetheless, with regard to the use of the resulting monolithic carbons as electrodes in supercapacitors, the use of DES-assisted syntheses has allowed exploring two different approaches with the aim of improving the performance of the supercapacitor cell in terms of either energy or power density. For instance, the preparation of monolithic carbons functionalized with phosphate moieties opens interesting perspectives [68]. The synthesis started from a ternary DES composed of resorcinol, ChCl,

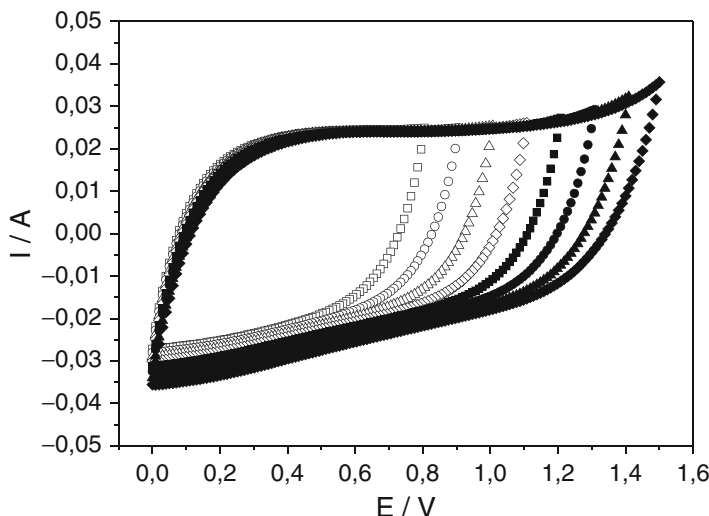


Fig. 2.7 Voltammograms of a phosphorous-doped carbon monolith – with cylindrical shape and 1.4 mm in height – recorded at 5 mV/s for voltages ranging up to 1.5 V (Adapted with permission from Ref. [68])

and glycerol in a molar ratio of 1:1:1. Polycondensation was carried out by the addition of formaldehyde and using phosphoric acid as catalyst. Phosphate-functionalized carbon monoliths were obtained upon the carbonization of the resulting phenolic resin, while non-doped carbon monoliths were obtained when phosphoric acid was washed out from the phenolic resin before carbonization.

The voltammograms of the phosphate-functionalized carbon monoliths exhibited a rectangular shape that was maintained for voltages of up to 1.4 V (Fig. 2.7). In earlier work describing the performance of phosphate-functionalized carbons [77], the widening of the operational voltage window to potentials well above the theoretical decomposition potential of water (1.23 V) has been ascribed to the blockage of non-stable but electrochemically active oxidation sites (e.g., quinone groups) by phosphate groups so that capacitance deterioration processes associated with free oxygen atoms were minimized. Actually, non-functionalized carbons exhibited a clear deformation of the rectangular shape of the voltammogram at much lower voltages (e.g., 1 V) than the phosphate-functionalized ones.

The specific capacitances (C_{esp} , normalized by the mass of the carbon monolith) for monoliths with 3.3 and 1.4 mm in height were ca. 195 and 197 F/g, respectively (Fig. 2.8). Meanwhile, non-doped carbons exhibited a slightly superior specific capacitance (210 F/g) because of its larger surface area. Actually, the capacitance normalized per surface area was similar for both non-doped and doped samples. In any case, the best retention of the capacitance at high current densities was found for the phosphorus-doped carbon monoliths of 1.4 mm in height. Nonetheless, the most remarkable result was the enhancement of the energy density of the phosphorus-doped carbon monoliths versus the non-doped ones as consequence of operational voltage window widening.

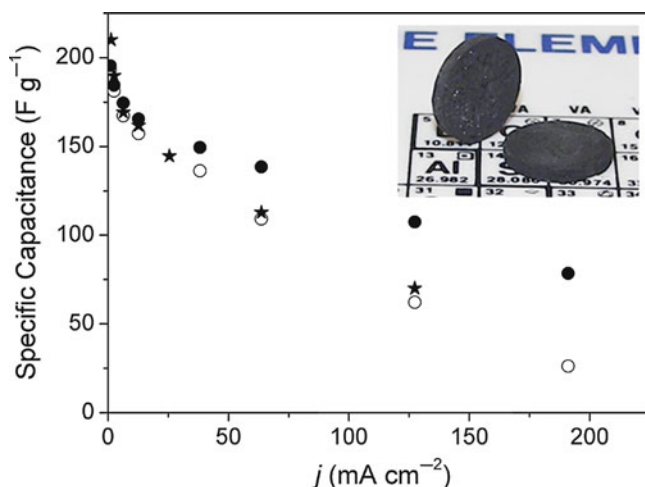


Fig. 2.8 Specific capacitance versus current density for phosphorous-doped monoliths of 1.4 mm (open circles) and 3.3 mm in height (solid circles). The response of a non-doped monolith is also represented for comparison (solid stars). The inset shows a picture of the two monoliths of 1.4 mm in height assembled into the supercapacitor cell (Adapted with permission from Ref. [68])

In a different approach, our efforts focused on the preparation of porous carbon composites containing CNTs. It has been observed that the presence of graphitic carbon entities (e.g., CNTs [78] and nanohorns [79] or even graphene oxide [80]) may provide an interesting performance – in terms of both mechanical properties and electrical conductivity – to the composites. From a synthetic point of view, the challenge resides in the achievement of (1) a homogenous dispersion of these entities throughout the monolith structure and (2) composites with surface areas in range to or above those of carbon aerogels. Particularly interesting in terms of conductivity and surface area were those composites based on double-walled CNTs (DWCNTs), although the authors expressed the convenience of substituting the surfactants used for CNTs dispersion [81]. As an alternative to the use of surfactants, we described the preparation of multiwalled CNT (MWCNT) composites by furfuryl alcohol condensation and using a protic DES – based on complexes of para-toluene sulfonic acid (pTsOH) and CHCl_3 – as both the reaction medium and the protic catalyst promoting the polycondensation [66]. There were certain features of the pTsOH-based DES that were particularly interesting for this reaction. For instance, its low viscosity favored the dispersion of a significant amount of MWCNTs (e.g., at the percolation threshold) into the starting reaction medium.

The resulting gels were washed twice with abundant water (ca. 35 mL) for DES clearance. Carbonization of washed gels was accomplished at 800 °C in N_2 atmosphere. Nitrogen adsorption–desorption measurements provided surface areas of ca. 500 m²/g. While carbons without MWCNTs exhibited a bicontinuous porous network built of colloidal clusters, the bicontinuous porous network of MWCNT–carbon composites resembled a fiber-like structure. This morphology

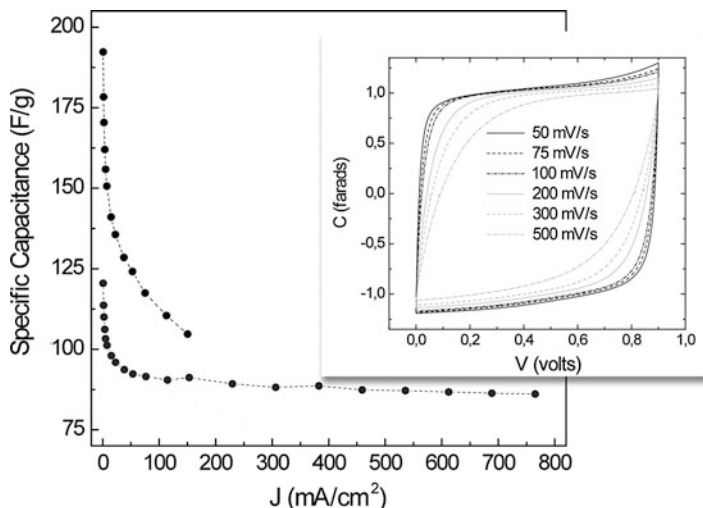


Fig. 2.9 Specific capacitance versus current density for the monolithic composite (*solid circles* reaching current densities of ca. 750 mA/cm²). For comparison, the same plot is represented for a monolith without MWCNT (*solid circles* reaching current densities of ca. 150 mA/cm²). *Insets* show a set of voltammograms recorded in 2 M H₂SO₄ for the monolithic composite at voltage scan rates ranging from 50 to 500 mV/s (Reprinted with permission from Ref. [66])

revealed the occurrence of furfuryl alcohol condensation on the MWCNT surface because of the acidity gained during MWCNT functionalization. The intimate interaction between the carbon network coming from furfuryl alcohol polycondensation and the MWCNT surface was observed at both TEM and SEM (Fig. 2.4). The continuous MWCNT network glued by a carbon shell that coats every MWCNT and forms strong junctions between them provided some remarkable properties – in terms of both the electrical conductivity (up to 4.8 S/cm, as measured by the four-probe method) and the elastic character (Young modulus, 11 MPa) – to the monolithic composites.

The specific capacitance of the resulting monolithic composites was below that we have recently measured in H₂SO₄ for other monolithic carbons of similar dimensions (1.2 cm diameter, 1 mm height) and textures (ca. 120 F/g versus 220 F/g) because of the poor contribution of the CNTs to the overall capacitance (ca. 30 F/g for MWCNTs). Nonetheless, the high electrical conductivity and elastic character of the monolithic composite – that favored the intimate contact between the monolith and the current collector when assembled into the capacitor cell – contributed to retain 75 % of the initial capacitance at high current densities of 765 mA/cm² (ca. 29 A/g), well above the 55 % at only 150 mA/cm² found for bare porous carbon monoliths of similar dimensions (Fig. 2.9). The rapid electrical response of the monolithic composites was also reflected in the power performance of the supercapacitor cell, with power densities of ca. 7.2 kW/kg at energy densities of 2.2 Wh/kg.

As CO₂ Adsorbents

CO₂ emissions have dramatically increased over the last few decades because of the continuous use of fossil fuels as the main energy source. Mitigation of global climate change needs an urgent and drastic reduction of carbon dioxide emission from combustion of fossil fuels. Among other technologies, a number of solid sorbents including zeolites, functionalized porous silica, MOFs, and carbonaceous materials have proved effective for carbon capture and storage [82]. There is not an ideal adsorbent, and each one shows its particular advantages and drawbacks. Nonetheless, our opinion is that the use of carbon-based materials is especially promising because of their relatively low cost and easy regeneration. For instance, carbons obtained by direct carbonization of either petroleum pitch [83] or biomass [84] have exhibited CO₂-adsorption capabilities close to the best ones ever reported for non-carbonaceous adsorbents. The yet advantage of the latter ones resides in their synthetic origin so that one can prepare them with tailor-made high surface areas and surface functionalities. It is worth noting that these features provide not only high CO₂-adsorption capability but also extraordinary selectivity for gas separation purposes.

Within this context, it is generally assumed that adsorbents having high isosteric heats are very selective for CO₂ adsorption in the presence of other gases, but they need a relatively high energy for regeneration, whereas those having low isosteric heats are easily regenerated, but their selectivity is poor. Carbon-based materials have been typically included in this latter group, and concerns have arisen with regard to the insufficient selectivity and adsorption capacity – the latter eventually compromising the energy for regeneration as compared to that of the industry benchmark (e.g., aqueous monoethanolamine, MEA) – to work under realistic flue gas conditions [85]. This drawback can be partially compensated by the low cost of carbon-based adsorbents so that the ultimate cost of recovered CO₂ in flue gas conditions for activated carbon or charcoal can be as low as \$20–37 per ton (which is up to ca. 60 % lower than the figures of \$40–50 per ton for the benchmark cost for an optimized MEA process) [86]. Nonetheless, it is obvious that these serious drawbacks should be better overcome by the design of novel synthetic procedures that, while keeping the use of cheap precursors, do not compromise the purity and/or the reproducibility of the composition from batch to batch and offer the possibility to tailor certain properties of the resulting carbons (e.g., porosity and/or nitrogen content) and, hence, their performance. In structural terms, hierarchical porous carbons are also attracting much attention because of the combination of high surface area and pore volume, provided by micro- and small mesopores, and accessibility to these active sites, provided by macro- and medium/large mesopores. Unfortunately, the use of certain additives (e.g., block copolymers) as SDAs in conventional polycondensations raise concerns about the low cost of the resulting materials. Block copolymer recovering (e.g., washing out) after polycondensation and reuse could be an option, but this is by no means trivial because of the impeded diffusion of pseudo-high-molecular-weight substances through small pores. Actually, recent reports demonstrate that the design of sustainable synthetic routes that

allow the preparation of carbonaceous adsorbents with tailor-made hierarchical structures and surface functionalities is yet challenging.

As mentioned above, the wide range of DES that can be prepared, from not only resorcinol but also other synthetic precursors, provides a remarkable versatility – in both structural and compositional terms – to the carbons that can be obtained through this synthetic approach. For instance, we have recently used DESs composed of resorcinol, 3-hydroxypyridine, and CHCl_3 for the synthesis of nitrogen-doped carbon monoliths exhibiting a hierarchical porous structure [67]. Carbons were obtained upon carbonization at 600 and 800 °C in N_2 atmosphere with remarkable carbon conversions, e.g., 83 and 71 %, respectively. The presence of structural nitrogen was studied by X-ray photoelectron spectroscopy (XPS). Five types of nitrogen (pyridinic-N at 398.7 ± 0.3 eV, pyrrolic-N or pyridone-N at 400.3 ± 0.3 eV, quaternary-N at 401.4 ± 0.5 eV, and oxidized-N at 402–405 eV) can be distinguished in carbonaceous materials by deconvolution analysis of the $\text{N}1s$ electron binding energy distribution [87]. It is worth noting that, in organic xerogels, the peak at 401.4 ± 0.5 eV is assigned to pyridinium (by protonation of pyridinic-N) rather than to quaternary-N because the latter is not yet formed [88]. Pyridinic-N and quaternary-N (the latter coming from the pyridinium groups found in organic xerogels) were the two main nitrogen types found in every sample no matter the thermal treatment. The intensity ratio of pyridinic-N versus quaternary-N decreased along with the temperature (within the 600–800 °C range) as consequence of the concomitant rearrangement of the carbon network [89]. XPS also revealed some minor amounts of oxidized-N impurities in the samples thermally treated at 800 °C.

The CO_2 -capture performance of nitrogen-doped carbons – at 25 °C and at ambient pressure – was ca. 2.5–2.6 mmol/g for samples thermally treated at 600 °C and reached up to ca. 3.3 mmol/g for samples thermally treated at 800 °C (Fig. 2.10). The data found for our synthesized carbons were below the best data

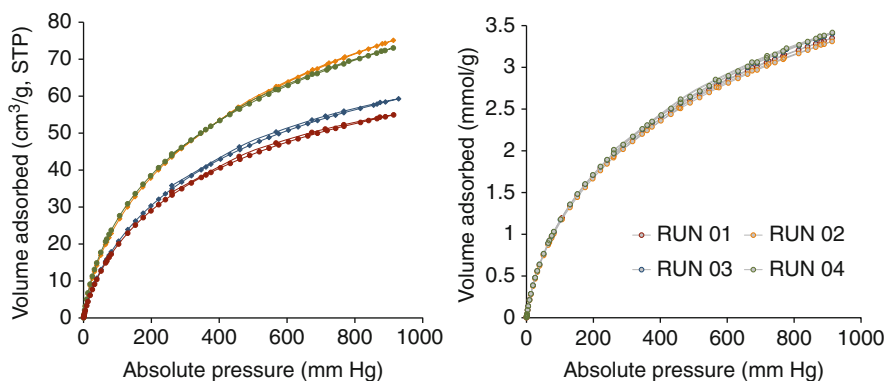
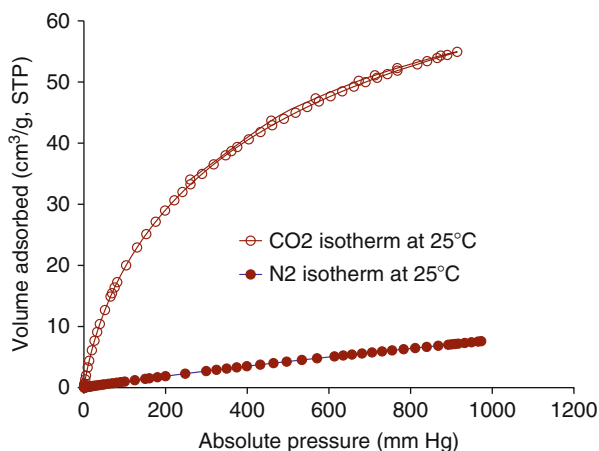


Fig. 2.10 *Left:* CO_2 -sorption isotherms of nitrogen-doped monoliths obtained from polycondensation of two different DESs compositions and after thermal treatments at 600 (red circles and blue diamonds, respectively) and 800 °C (green circles and orange diamonds, respectively). *Right:* CO_2 -multicycle-sorption isotherms of one of the nitrogen-doped monoliths obtained after thermal treatment at 800 °C (Reprinted with permission from Ref. [67])

Fig. 2.11 CO₂ (red open circles) and N₂ (red solid circles) isotherms measured at 25 °C for nitrogen-doped monoliths obtained after thermal treatment at 600 °C. Reprinted with permission from [67]

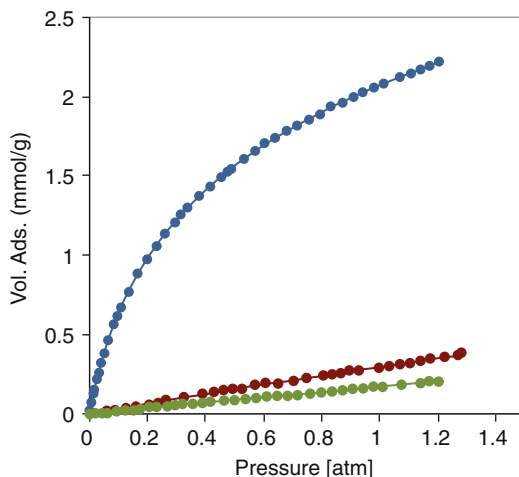


reported for carbonaceous materials obtained from either petroleum pitch or by hydrothermal carbonization of polysaccharides and biomass (up to 4.8 mmol/g) [83, 84] but slightly above those recently found for synthesized nitrogen-doped porous carbons (ca. 3.1 mmol/g) [90]. Nitrogen-doped carbons benefit from a certain basic character that favors CO₂ adsorption. However, the achievement of high CO₂-capture performances not only relies on the surface chemistry provided by basic nitrogen groups but also on the micropore surface area. The especially remarkable CO₂-adsorption capacity found in samples thermally treated at 800 °C revealed that, while preserving a certain nitrogen content (ca. 5 wt%), the increase in the micropore surface area contributes favorably to the overall enhancement of the CO₂-capture performance.

Besides the CO₂ adsorption capacity, we also explored the selectivity of CO₂ versus N₂ adsorption. The CO₂–N₂ selectivity measured under equilibrium conditions at 25 °C and 1 atm was always above 5.7 (Fig. 2.11). As a general trend, the selectivity was higher for the samples obtained at 600 than at 800 °C, which confirms the benefits of having nitrogen functionalizations to anchor CO₂ molecules. Moreover, the adsorptive performance of the samples was also evaluated for a synthetic flue gas containing 15 % CO₂ at 25 °C and 1 atm (typical conditions of flue gas in post-combustion processes). For this purpose, the adsorption equilibrium of the binary gas mixture was calculated from the pure component adsorption data using the Ideal Adsorbed Solution Theory (IAST) equation [91] and the Jensen formulation for the pure gas isotherms [92]. Interestingly, the CO₂–N₂ selectivity calculated at low CO₂ partial pressures (characteristic of post-combustion processes) was just slightly below that obtained from the single-component gas data.

We have also described the synthesis of DESs composed of resorcinol and 4-hexylresorcinol (as hydrogen donors) and tetraethylammonium bromide (as hydrogen acceptor) that played an important role in the preparation of hierarchical porous (bimodal, with micro- and macropores) carbon monoliths [65]. In this case, DESs provided a suitable liquid medium for 4-hexylresorcinol dissolution that was

Fig. 2.12 CO₂ (blue), N₂ (red), and CH₄ (green) adsorption isotherms at 298 K of carbon monoliths prepared from resorcinol, 4-hexylresorcinol, and tetraethylammonium bromide (Adapted with permission from Ref. [65])



not possible otherwise (e.g., using aqueous solutions). The use of 4-hexylresorcinol was by no means a trivial issue because it played a capital role in the formation of the particularly narrow microporosity that, ultimately, characterized the resulting carbons. This feature was actually confirmed upon the analysis of the textural properties by nitrogen adsorption–desorption isotherms at 77 K. Under these conditions, the N₂ uptake was negligible for every carbon. Meanwhile, the CO₂ adsorption isotherms at 273 K revealed a remarkable adsorption capacity at 760 mmHg with uptakes of up to 3.0 mmol of CO₂ per gram of carbon. The application of the Dubinin–Radushkevich and Stoeckli–Ballerini equations to the CO₂ adsorption isotherms revealed that the average micropore diameter of every sample was never above 0.6 nm. The restricted diffusion of N₂ at 77 K through micropores of such small dimensions explains the negligible N₂ uptake described above.

In this work, we have also investigated the performance of these carbons for gas separation purposes. Thus, we studied the adsorption capacity of strategic gases (e.g., N₂, CO₂, and CH₄) at 900 mmHg and at temperatures near ambient conditions. The adsorption capacity of CO₂ was 2.2 mmol/g and decreased to 0.39 mmol/g for N₂ and to 0.20–0.55 mmol/g (depending on the sample) for CH₄ (Fig. 2.12). It is generally assumed that the CO₂-uptake capacity is dictated by many factors such as surface area, pore functionality, and pore size, among the principal ones. Considering the non-doped nature of our carbons, the selective adsorption of CO₂ was ascribed to the molecular sieve character of these carbons so that gases having small kinetic diameters (e.g., 0.33 nm for CO₂) are preferentially adsorbed over those having large ones (e.g., 0.36 nm for N₂ or 0.38 nm for CH₄). This poor N₂ and CH₄ uptake indicated that the porous morphology of our carbons was bottleneck type (i.e., typical of molecular sieves) combining wide pore bodies (of around 0.6 nm according to the Stoeckli–Ballerini equation) and narrow pore entrances that prevented N₂ or CH₄ diffusion into the wide pore bodies.

Given that high CO₂-uptake capacity at 1 bar does not necessarily lead to a large selectivity for CO₂ over other components of a gas mixture – particularly for

low-pressure post-combustion applications where the flue gas usually contains less than 15 % of CO_2 – we also evaluated the adsorption selectivity at low pressures (e.g., the Henry's law regime) that are representative of flue gas streams characteristic of post-combustion and natural gas fields. The $\text{CO}_2\text{--N}_2$ selectivity calculated from the Henry's law constant was in the range of or slightly above those previously reported for typical adsorbents (non-doped carbons and carbon monoliths, zeolites, or MOFs, among others) [93–98]. More remarkable was the $\text{CO}_2\text{--CH}_4$ selectivity that, in certain cases, reached unprecedented values as compared to most of the sorbents reported to date [95, 98–100]. This occurrence revealed the particularly suitable performance of these molecular sieve carbons for $\text{CO}_2\text{--CH}_4$ separation processes carried out at low pressures.

As for nitrogen-doped carbons, we investigated the selectivity of these carbons by the application of the IAST to the experimental adsorption isotherms of CO_2 , CH_4 , and N_2 obtained for the single components. Besides the $\text{CO}_2\text{--N}_2$ mixture evaluated before for nitrogen-doped carbons (e.g., with a v/v gas composition of 15/85), we also evaluated $\text{CO}_2\text{--CH}_4$ mixtures characteristic of natural gas upgrading processes (e.g., with v/v gas compositions of 15/85 and 30/70). In terms of IAST predictions, our carbons were in range to the best carbons recently described [101, 102] and only some organic frameworks have been capable of providing further efficiency [103–105].

Conclusions

This chapter showed either carbons or carbon–carbon nanocomposites exhibiting a hierarchical structure, and a tailored composition (either nitrogen or phosphorus doped) could be attained by the use of different mixtures of DESs (not only binary but also ternary, quaternary, etc.) that are capable of providing (1) the solvent with the viscosity desired for reagent homogenization, (2) the precursor with the molecular composition required for doping, and (3) the SDA that ultimately governs the structural organization of the precursors. While the number of examples described above is yet limited, the virtually unlimited flexibility of combinations of mixtures that can be used for DES preparation allows envisaging the suitable application of DES-based synthetic processes for tailoring novel properties and thus obtaining new families of carbon materials.

At this stage, we have demonstrated that DES-assisted syntheses allow the preparation of both chemically and structurally modified carbon monoliths suitable as electrodes in supercapacitor cells. In the former case, the presence of phosphate moieties allowed the widening of the working electrochemical window and, hence, a significant improvement of the energy density provided by these electrodes based on phosphorus-doped carbon monoliths as compared to those based on non-doped ones. In the latter case, the excellent capability of DESs as solvents for MWCNT suspension allowed homogeneous MWCNT distribution throughout the entire monolithic structure, the interconnection of which was responsible of the high electrical conductivity and the elastic character found in the MWCNT–carbon

composites. These features were by no means trivial and determined the capability of the monolithic composites to exhibit a superior performance in terms of power density thanks to improved retention of the initial capacitance at high current densities. It is obvious that future work should focus on the preparation of carbons exhibiting a simultaneous enhancement of the energy and the power performance.

Carbons prepared from DESs are also suitable for CO₂ adsorption and CO₂-N₂ and/or CO₂-CH₄ separation processes. In terms of adsorption capacity, we obtained figures comparable to – or even better than – those recently reported for some of the most successful sorbents, either carbonaceous or non-carbonaceous type. Particularly interesting was the selectivity calculated by the IAST equation. These features, besides the low-cost character of our carbons, open interesting perspectives for their application as sorbents in separation technologies for CO₂ low-pressure post-combustion processes and natural gas upgrading.

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Poly(Ionic Liquid)s as Ionic Liquid-Based Innovative Polyelectrolytes

3

Jiayin Yuan and Markus Antonietti

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Abstract

Poly(ionic liquid) or polymerized ionic liquids (PILs) have been recently recognized as innovative polyelectrolytes attracting rapidly increasing interest in a multitude of fields of polymer and materials science. The chemical structures, the synthetic strategies, and the versatile applications of PILs will be discussed here to provide an overview of this newly emerging topic.

Keywords

Poly(ionic liquid) • Polymerized ionic liquids • Polyelectrolyte • Ionic liquid

J. Yuan • M. Antonietti (✉)

Max-Planck-Institute of Colloids and Interfaces, Research Campus Golm, Potsdam, Germany

e-mail: Jiayin.yuan@mpikg.mpg.de; markus.antonietti@mpikg.mpg.de

Introduction

Poly(ionic liquid)s or polymerized ionic liquids (PILs) refer to a unique class of polyelectrolytes, which are commonly the polymerization products of ionic liquid (IL) monomers (Fig. 3.1) [1–5]. In such a synthetic approach, individual IL species are covalently connected through a polymeric backbone to present a dynamic macromolecular architecture. This structure configuration combines some IL characters with the general profile of macromolecules and creates new properties and functions. The physical features of PILs and ILs are sometimes closely but not necessarily related to each other. Compared to ILs, PILs possess enhanced mechanical stability, improved processability, dynamic chains, durability, and spatial controllability of the IL moieties. In the bulk state, ILs turn liquid below 100 °C or even at room temperature, while most PILs reported to date are solids, albeit with a relatively lower glass transition temperature. In contrast to conventional polyelectrolyte solids, which are usually glassy until thermal decomposition, such as poly(sodium acrylate) or poly(sodium styrene sulfonate), PILs are more similar to ordinary polymers in terms of glass transition temperature.

Originally the concept of PILs was proposed in the 1990s in pursuit of solid electrolytes that could potentially substitute ILs in electrochemical devices [6–9]. In the past 5 years, the research scope of PILs has been vastly broadened. Previously unknown chemical structures, unusual properties, and freshly established functions of PILs have been spotted, which go far beyond the normal property and application window of ILs and traditional polyelectrolytes. The rapid progress in PIL chemistry has delivered many novel and versatile polyelectrolytes that are of fundamental research importance and meanwhile provide qualified materials to solve problems in many devices and systems. Nowadays, PILs can

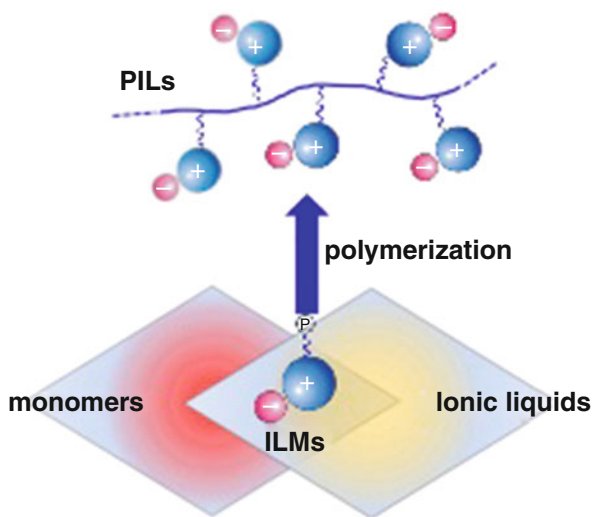


Fig. 3.1 Illustration of the relationship between ILs and PILs. ILMs: ionic liquid monomers. “P”: polymerizable group

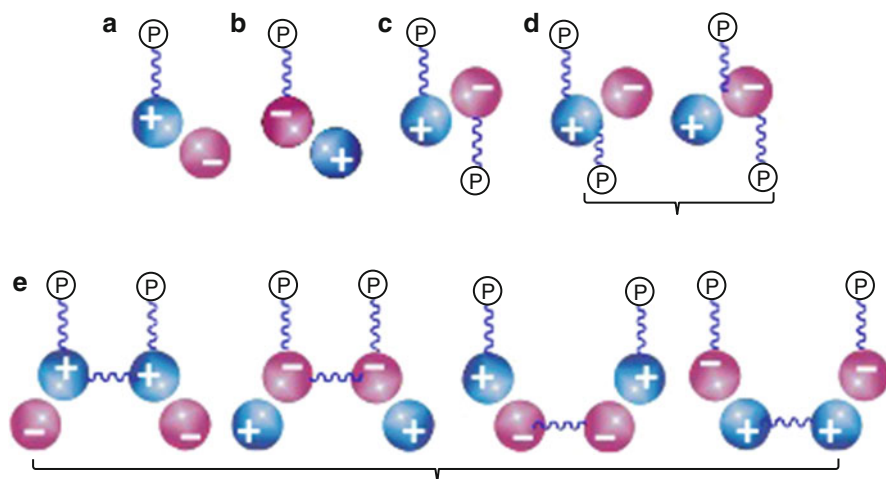


Fig. 3.2 Five basic forms of IL monomer structures. “p” is a polymerizable unit

“revolutionize” polyelectrolyte research and have become a truly interdisciplinary topic among polymer chemistry and physics, materials science, catalysis, separation, analytical chemistry, and electrochemistry.

Chemistry of Poly(Ionic Liquid)s

Chemical Structure of Ionic Liquid Monomers

An IL monomer is defined as an IL compound that bears a polymerizable functionality in its chemical structure. This structural configuration allows polymer scientists to treat IL molecules via polymerization concept. From a function point of view, IL monomer acts as an interface bridging the IL community and the polymer science. The five most common forms of IL monomers are illustrated in Fig. 3.2. The classification criteria of these forms are according to the relative position of the polymerizable unit in the IL chemical structure. This unit can be selected from (meth)acrylate, styrenic, vinylimidazolium, norbornyl, and other units. It can locate either on the cation (Fig. 3.2a) or anion (Fig. 3.2b), depending on the desired polymer architecture. An IL monomer may possess two polymerizable units either shared individually by the cation and anion (Fig. 3.2c) or exclusively by the cation/anion (Fig. 3.2d). The polymerization of monomers with two polymerization units (Form C and Form D) will end up with a cross-linked PIL network rather than a linear polymer conformation. Though rarely reported, two IL monomer structures might be covalently coupled by an alkyl chain spacer to form a new type of IL monomer, as shown in Fig. 3.2e. Currently, the IL monomer with a single polymerizable unit on the cation (Fig. 3.2a) dominates the PIL research in many groups [10]. Furthermore, an IL monomer may copolymerize with other common

comonomers to modulate the charge distribution along the polymer chain and consequently modify the physical properties of PILs, for instance, their solubility and aggregation behavior in different solvents.

Polymerizations of IL Monomers

Two strategies are majorly involved in the synthesis of PILs: straightforward polymerization of IL monomers and chemical modification of extant polymers. These two strategies are individually coupled with several polymerization techniques, such as conventional and controlled radical polymerization, ring-opening metathesis polymerization, step-growth polymerization, and some more. The structure characteristics of PILs, such as the molecular weight, molecular weight distribution, macromolecular architecture, topological structure, etc., can be finely controlled by the combination of the synthetic strategies and the polymerization techniques.

Straightforward Polymerization of IL Monomers

Conventional Free Radical Polymerization

Conventional free radical polymerization is the most frequently applied polymerization method for the synthesis of PILs due to its easy implement and superior tolerance toward many functional organic groups and impurities in the reaction mixture. Because of the ionic character, IL monomers contain usually a small fraction of moisture; therefore, anion polymerizations of IL monomers are practically inapplicable. Figure 3.3 displays the synthesis of methacrylate-, vinylimidazolium-, and styrene-based cationic IL monomers (structure form in Fig. 3.2a) by quaternization reaction, which are in turn thermally polymerized into the corresponding PILs. For example, the synthesis of (meth)acryloyl-functionalized PILs can be accomplished in a three-step synthetic protocol: (1) (meth)acryloyl chloride reacts with a hydroxyl-containing halo-alkane to build up the corresponding ester compound with halide terminus; (2) the ester compound bearing a distal halide reacts with a *N*-alkyl imidazole molecule via quaternization reaction to yield a (meth)acryloyl-based dialkylimidazolium IL monomer; and (3) the formed (meth)acryloyl-based IL monomer is polymerized similar to common (meth)acrylate monomer in the presence of thermal initiators, such as 2,2'-azo-bis-isobutyronitrile (AIBN) [11, 12]. In literature, there are many kinds of (meth)acryloyl-based PILs, which differ from each other in terms of (1) the spacer between the (meth)acrylate and imidazolium groups, (2) the alkyl chain on the cation, (3) the cation type, and (4) the anion type that can be effectively exchanged via metathesis reaction involving silver salts [13, 14].

Apart from the quaternization reaction, neutralization is another important reaction for the synthesis of IL monomers. For example, an IL monomer with tetrafluoroborate anion was prepared by reacting *N*-vinyl imidazole with tetrafluoroboric acid in a mixture of water and ethanol [7]. The preparation process

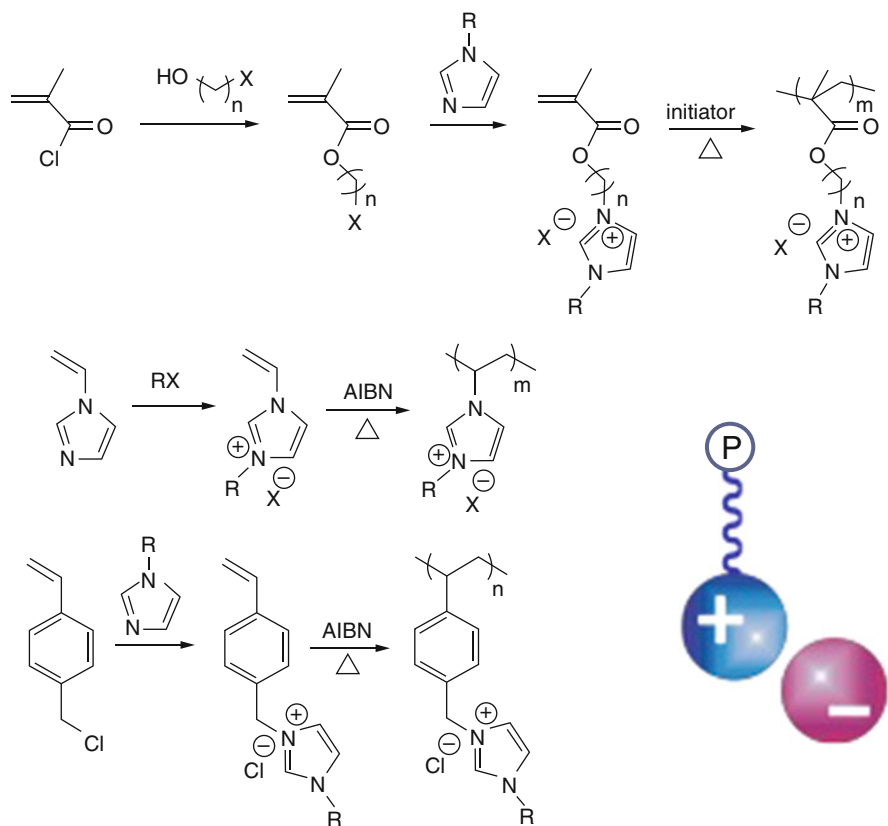


Fig. 3.3 General synthetic route to PILs from methacryloyl, vinylimidazolium, and styrenic IL monomers bearing an imidazolium species (R alkyl chain, X halide)

is quite easy, generating no by-product and can be readily extended to other acids, such as hexafluorophosphoric acid and alkane sulfonic acids. In this case, a non-halide anion is incorporated in the *N*-vinylimidazolium-based IL monomer simultaneously with the formation of the IL monomer without the aid of silver salts in a metathesis reaction.

Although less reported in literature than the cationic IL monomer, several examples of anionic IL monomers with a single polymerizing unit on the anion have been described. For instance, an IL monomer consisting of an acrylate-type anion and a 1-decyl-3-methylimidazolium cation has been synthesized by a metathesis reaction involving the treatment of an aqueous solution of 1-decyl-3-methylimidazolium bromide with silver acrylate [15]. In another example, a tris[2-(2-methoxyethoxy)ethyl]ammonium 2-acrylamido-2-methyl-1-propanesulfonate IL monomer has been reported via a simple step of neutralization reaction between 2-acrylamido-2-methyl-1-propanesulfonic acid and an equimolar quantity of tris[2-(2-methoxyethoxy)ethyl]amine [16]. There are also several other

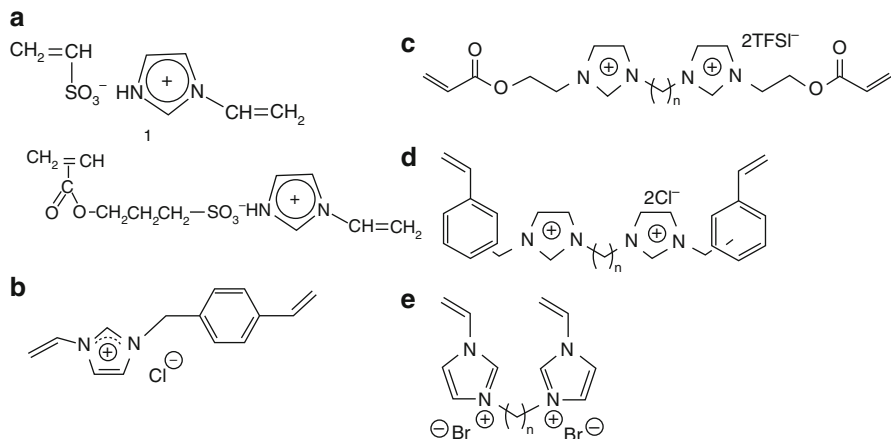


Fig. 3.4 Chemical structures of five types of cross-linkable IL monomers bearing two polymerizable functionalities in one monomer unit

types of IL monomers bearing a single polymerizable unit. Most of these examples deal with a neutralization reaction of vinyl acid with *N*-alkyl imidazole. For example, the synthesis of *N*-ethylimidazolium vinylsulfonate and *N*-ethylimidazolium vinylphosphate by neutralizing *N*-ethyl imidazole with vinyl sulfonic acid and vinyl phosphoric acid, respectively, has been reported in literature [6, 17].

As illustrated in Fig. 3.4, some structurally more complex IL monomers may contain two polymerizable groups in their chemical structures. Several of these cross-linkable IL monomers are displayed in Fig. 3.4. In Fig. 3.4a, an IL monomer with two types of vinyl groups localized separately on the IL cation and anion was prepared via a two-step synthetic protocol: (1) the alkali metal cations in sodium vinylsulfonate and 3-sulfopropyl acrylate potassium salt were replaced by protons by means of cation exchange resin to afford the corresponding acids and (2) aqueous solutions of these acids were slowly mixed with equimolar amount of *N*-vinyl imidazole in an ice bath [18]. The as-synthesized IL monomers (Fig. 3.4a) possessing an *N*-vinylimidazolium cation and a vinylsulfonate anion were thermally polymerized in the presence of AIBN in ethanol to yield a PIL network. Figure 3.4b displays an IL monomer *N*-vinyl-4-vinylbenzylimidazolium chloride with two polymerizable units confined on a single cation, here the imidazolium ring cation. This monomer is accessed in one-step quaternization reaction of *N*-vinyl imidazole with 4-vinylbenzyl chloride [19]. Figure 3.4c–e sketches three other IL monomers, in which two monovalent IL monomers of the same type are covalently bridged through an alkyl chain. They are commonly (meth)acryloyl-, styrenic-, or *N*-vinylimidazolium-based ILs. For example in Fig. 3.4c, an acryloyl-based monomer, 1,4-bis[3-[2-(acryloyloxy)ethyl]imidazolium-1-yl] butane bis[bis(trifluoromethylsulfonyl)imide], was obtained via an ester formation reaction between methacrylic acid and 1,4-bis[3-hydroxyethylimidazolium-1-yl] butane bis[bis(trifluoromethylsulfonyl)imide] [20]. In Fig. 3.4e, a *N*-vinylimidazolium-based

cross-linkable monomer was synthesized via quaternization reaction between *N*-vinyl imidazole and dibromoalkane in a molar ratio of 2:1 [21, 22].

An advantage of handling ILs by polymerization technique is the possibility to copolymerize an IL monomer with other common comonomers widely available in polymer chemistry. The formed PIL copolymers have broad chemical composition, function, and property window [23–25]. For example, a random copolymer of hexyl methacrylate (HMA) and a methacryloyl-based imidazolium IL monomer 1-[2-(methacryloyloxy)ethyl]-3-butylimidazolium tetrafluoroborate (MEBIm-BF₄) were synthesized via radical polymerization [26]. It was found that a high content of nonionic comonomer, here HMA in the copolymer chain, though diluting the charge density, increases the ionic conductivity over an order of magnitude. This is because the HMA fraction significantly lowers down the glass transition temperature of the copolymer. This in turn improves dramatically the ion mobility in the bulk copolymer matrix. The accelerating kinetic effect of the ion motions surpasses the effect of low ion density, thus contributes positively to the overall ion conductivity.

Controlled/Living Radical Polymerization

Controlled/living radical polymerization techniques have been a very active field in the last 15 years. New polymerization techniques such as atom transfer radical polymerization (ATRP), reversible addition–fragmentation chain transfer (RAFT) polymerization, and nitroxide-mediated polymerization (NMP) have been rapidly developed and widely applied to polymerize various monomers. These polymerization techniques have been used to polymerize IL monomers, demonstrating an unprecedented opportunity to precisely design and control macromolecular architecture of IL species on a nanoscale in a polymer entity. ATRP was the first method in this group to be tested for IL monomers. It was used to polymerize a methacryloyl-based IL monomer, 2-(1-butylimidazolium-3-yl)ethyl methacrylate tetrafluoroborate [27], and styrenic IL monomers of 1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate and 1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate [28]. In these attempts, due to the complexation of the copper salt by the formed PIL polymers and the coexisting ion exchange between the used copper cation and the IL species, the controllability over the molecular weight and the molecular weight distribution is a very challenging issue. The real breakthrough in the molecular structure control of PILs comes along the polymerization of IL monomers by RAFT method, because the aforementioned problems are avoidable in the case of RAFT. In RAFT method, no metal salt is involved. The same is true for NMP as well [29]. Taking advantage of the living character of the RAFT process, block copolymers with a PIL segment are accessible [30]. For example, the RAFT polymerization using dithioate esters as chain transfer agent (CTA) was applied to methacryloyl-based IL monomers in methanolic solutions and led to well-defined PILs with CTA at the chain end. The functional chain end can grow a second block of common comonomers, such as methyl methacrylate.

It should be mentioned that the chemical structure of the IL monomer has a decisive influence on the choice of the chain transfer agents (CTAs). For methacryloyl-based IL monomers, the imidazolium cation is separated from the polymerizing unit by an alkyl

spacer. The radical polymerization thus can proceed with less to no disturbance from the imidazolium cation ring. Controlled radical polymerization of *N*-vinylimidazolium-based IL monomers is more challenging, since the generated radical species are highly reactive due to their nonconjugated nature. The dithioate esters as CTA work very well for methacrylate and styrenic IL monomer, yet for vinylimidazolium-based IL monomer, no PILs of well-controlled molecular weight were obtained. The controlled polymerization of vinylimidazolium-based IL monomer requires a RAFT/MADIX (macromolecular design via the interchange of xanthates) process for the synthesis of well-defined polymer architectures, since this process is tolerant to radical polymerization of nonconjugated monomers. The synthesis of *N*-vinylimidazolium-based PILs and their copolymers with controlled molecular weights and narrow polydispersity by RAFT/MADIX polymerization has been demonstrated [31]. It should be mentioned that apart from ATRP, RAFT, and NMP, other radical polymerization techniques that can polymerize IL monomers in a controlled manner have also been reported [32].

Other Polymerizations

There exist also other polymerization techniques for the synthesis of PILs. This includes electrochemical polymerization, polycondensation, etc. The electropolymerization approach has attracted special interest due to the advantage over chemical polymerization approaches, including facile generation of thin polymer films on a variety of complex surfaces and the ability to modify and/or engineer surfaces with redox-active molecules. Oxidative polymerization and electropolymerization have been involved for the synthesis of thiophene-based conductive PILs that bear an IL pendant unit along the polythiophene backbone [33]. Polycondensation reaction has been applied to prepare a polysilsesquioxane-structured PIL organic–inorganic composite from an IL monomer, 1-methyl-3-[3-(trimethoxy- λ^4 -silyl)propyl]-1H-imidazolium iodide [34]. PILs bearing an organoboron unit in the repeating unit along the main chain for the purpose of selective lithium cation transport were prepared via hydroboration reaction [35]. In addition, poly(norbornene)-based PILs with pendant imidazolium moieties with three different counter anions of TFSI[−], BF₄[−], and PF₆[−] have been recently prepared via ring-opening metathesis polymerization of norbornyl-based IL monomers in IL as a reaction medium [36].

PILs by Polymer Modifications

The chemical structure of PILs can be alternatively accessed by chemical modification of existent polymers, i.e., using a polymeric template and grafting/introducing the IL species to it. The advantage of this synthetic approach is that the as-synthesized PILs will adopt the same polymerization degree, macromolecular architecture, and molecular weight distribution as the polymer precursor. Taking into account that there are many uniquely structured macromolecules, PILs possessing very unusual architectures and composition can be easily prepared from their precursors without switching to complicated monomer synthesis and tedious polymerization reactions. This is especially important when the desired PIL structures cannot be prepared by direct

polymerization route. For example, PILs with ultra-high molecular weight remain a challenge currently. This problem can be tackled in principle by converting the high molecular weight polymer precursors, which are either commercially available or can be easily synthesized, into desired PILs.

Currently, this method is mostly applied to imidazolium-based PILs in two major paths. In the first one, excessive *N*-alkyl imidazole or its derivatives can react with the alkyl halide (mostly chloride or bromide) functionalities along the polymer backbone to form imidazolium halide moieties as pendant groups. In the second path, excessive halo-alkanes can react with the imidazole functionalities along the polymer backbone. In comparison, the first path is more popular than the second, due to the much richer source of halogen-containing polymers than that of the imidazole-containing polymers. Yet, a drawback associated with the first path is the dehydrochlorination or dehydrobromination as a competing side reaction to the quaternization process. This side reaction forms dead alkene units that can hardly be converted into IL species. There are also some halogen-containing polymers that are free of this problem. A classic example is the synthesis of poly(1-butyl-3-vinylbenzylimidazolium chloride) by postpolymerization modification of poly(*p*-chloromethylstyrene) (PCMS) with 1-butylimidazole [28]. The precursor polymer, PCMS, with controlled molecular weight and narrow molecular weight distribution was prepared by RAFT polymerization of *p*-chloromethylstyrene. The quaternization of the chloromethyl units with 1-butylimidazole was proved to be a very quantitative reaction and proceeded to 100 % at 80 °C in DMF. In this modification process, the dehydrochlorination side reaction is excluded, since there is no β hydrogen atom close to the chlorine atom.

Versatile Applications in Materials Science

The research activities on PILs have been initially driven by the pursuit of solid polymer electrolytes as new candidate for ion conductors, as discussed in the next chapter. That is, from its beginning, the PIL research is strongly application oriented. Even nowadays, PILs are still considered as important technological materials for many systems. This also defines the interdisciplinary character of the PIL research, which shapes the current research scope of PILs. The application of PILs includes polymer electrolytes, powerful stabilizers, anion active materials, carbon production, catalysis, CO₂ separation, and more. Some of them will be briefly introduced here.

Solid Ion Conductors

ILs feature high ion conductivity due to the liquid state and the high ion concentration. This favors their broad electrochemical usages. However, the liquid state causes sometimes a leakage problem that further raises safety concerns. PILs as solid-state polymeric electrolytes are of significant interest in the field of electrochemistry because they are solid at room temperature and have high ion concentration as well. In addition, the polymer nature of PIL potentially permits

production of materials with defined size, shape, and geometry, such as thin films, fibers, coatings, and even complete circuits. Therefore, there have been intensive studies to make highly ion conductive PILs. The relationship of PIL chemical structure and ion conductivity has been systematically studied using (meth)acryloyl- and *N*-vinylimidazolium-based PILs as model examples. It was found that polymerization of IL monomers in general decreases ion conductivity compared to the IL monomers due to the considerable elevation of the glass transition temperature (T_g). Meanwhile, after polymerization, the cation or anion constraint to the polymer backbone loses its mobility and contributes negligible ion conductivity. Thus, PILs in this case are often considered as a single-ion conductor. The decrease in the carrier density is therefore another reason for the decreased ion conductivity in the PIL system. The structural parameters of PILs that influence the ion conductivity include types of IL monomers, cations [11], anions, the spacer between the polymerizable group and the cation (for methacryloyl-based IL monomers) [17, 37], the alkyl chain length on the imidazolium ring (for *N*-vinylimidazolium-based IL monomers), the presence of networks, and the backbone rigidity. For example, the effect of different anions on the polymer T_g and ion conductivity was examined in detail. Maximum ion conductivity was attained for the TFSI[−] anion-containing polymers, since the large-sized TFSI[−] anion significantly lowered the glass transition temperature of the polymer.

To enhance the ion conductivity, doping PILs with ILs has been attempted. In the right doping range, the mixture remains solid and nonflowable, yet a high conductivity value is achieved. The addition of ILs into PILs on the one hand pumps in more charge carriers; on the other hand, they lower down the T_g of the IL/PIL mixture due to the plasticizing effect. PIL networks or gels prepared from cross-linkable IL monomers often showed very poor ion conductivity due to its lack of both mobile cations and anions. However, in the presence of IL or salt doping, a relative high ion conductivity of the PIL networks in the temperature range from 25 °C to 125 °C was observed [38].

Dispersants

Imidazolium-containing PILs are surface-active materials, which have been frequently used as dispersants for nanomaterials in aqueous and organic solution. The aromatic nitrogen-containing five-membered cation ring cannot only coordinate with metal ion but also undergo cation- π interaction with aromatic carbon nanostructures, for example, single-wall carbon nanotubes (SWCTs), multi-wall carbon nanotubes (MWCTs), and graphene sheets. The cation- π interaction between the conjugated carbon network and the imidazolium cation ring has been evidenced in the FTIR spectrum of a 1:1 mixture of imidazolium IL-treated MWCTs [39]. The dispersion process is commonly conducted via sonication of the carbons in aqueous solution of the imidazolium-based PILs. Poly(1-vinyl-3-ethylimidazolium bromide) is one of the most widely used PIL dispersants [40]. It has been used to stabilize isolated graphene sheets and further provided a functionality to transfer graphene sheets from the aqueous phase to organic solvents

via exchanging the Br^- with other hydrophobic ones, such as bis(trifluoromethane sulfonylimide) [41]. This anion exchange process could also be reversed from hydrophobic anions to bromide. For example, SWCNTs could be dispersed by poly(1-vinyl-3-ethylimidazolium bromide) in water. Upon addition of excessive bispentafluoromethanesulfonimide lithium salt, the dispersed SWNTS formed a precipitate. This precipitate was dissolved in acetone. Its dispersion in acetone, when added into an aqueous solution of excessive tetrabutylammonium bromide, built up a precipitate. Upon filtration, the SWCNTs bearing bromide could be redissolved in water. Instead of dispersing CNTs by PILs directly, an alternative way is to first stabilize CNTs in liquid IL monomer. This forms a CNT Bucky gel [42]. In situ free radical polymerization of the IL monomers in the IL/CNT mixture generated polymeric Bucky gels or Bucky plastics with a high content of SWCNTs and a high electrical conductivity [43].

The stabilization power of the imidazolium-based PILs can be extended from their homogeneous solution to their colloidal suspension. For example, a nanolatex copolymer (25–30 nm) of an imidazolium bromide acrylate and methyl methacrylate could build up stable waterborne dispersions of SWCNTs. Such stable dispersion was used to construct thermally and electrically conducting coatings that adhered to plastics [44]. The PILs in this case acted as a stabilizer and a binder simultaneously.

It should be noted that the stabilizing power of PILs is universal. In parallel with the intense activities in using PIL as CNT stabilizers, poly(1-vinyl-3-ethylimidazolium bromide) shows a strong dispersion effect in nonaqueous media for electrically conducting polymers, such as polypyrrole, polyaniline, and poly(3,4-ethylenedioxythiophene) [45, 46]. By combining the stabilizing effect of PILs to SWCNTs as well as conducting polymers, a practical approach for the hybridization of SWNTs by conducting polymers was developed [47]. The PIL acted as a glue to closely hold SWNTs and the conducting polymers firmly together. Stabilization of inorganic nanoparticles is another active part of PIL dispersants. For example, the aforementioned copolymer PIL nanolatexes of imidazolium bromide-based acrylate and methyl methacrylate have been employed to stabilize tungsten carbide nanoparticles in aqueous solution [48]. In some examples, the stabilizing power of PILs toward CNTs and nanoparticles can be synergistically combined. It has been reported that a PIL was first prepared by thermally initiated free radical polymerization of 1-vinyl-3-ethylimidazolium tetrafluoroborate in the presence of MWCTs [49]. This reaction coated a uniform and dense thin PIL layer on the surface of MWCTs. Metal (Pt/Ru and Pt) nanoparticles could be further grown in the PIL layer on the surface of MWCNTs, leading to the formation of a nanoparticle/PIL/CNT ternary hybrid. An enhanced catalytic performance in the electrooxidation of methanol was achieved from this hybrid system.

Sorbents and Separation

The interest on using PILs as absorbent was motivated by the finding that imidazolium-containing PILs exhibited surprisingly higher CO_2 sorption capacity

and faster kinetics than the corresponding ILs [50]. The sorption and desorption process is fully reversible and can be cycled many times. This high capacity and fast kinetics is related to the free volume in the polymer chains, which act as the highway for CO₂ transport and in addition the storage site for CO₂. These factors enable PILs as potential candidate for industrial CO₂ capture, storage, and conversion. Many PILs have been studied to reveal the fundamental sorption mechanism(s). From the experimental results, the effect of the cation's structure seems to be more dominant. This is different from conventional ILs, in which anions are more decisive in CO₂ sorption [51–53]. The CO₂ absorption capacities in PILs containing different cations have been observed to decrease in the order of ammonium > pyridinium > phosphonium > imidazolium, although the underlying mechanism of gas adsorption remained not fully clear. PILs containing different anions decrease in the order of BF₄[−] > PF₆[−] > TFSI[−]. As for the backbone, PILs containing the same ion pair but a polystyrene backbone rather than a polyvinylimidazolium or polymethacrylate backbone have been found to exhibit higher CO₂ absorption capacities. Long alkyl substituents on the cation as well as a high cross-linking degree have been found to decrease the CO₂ absorption capacity.

An isothermal CO₂ sorption experiment, involving PILs with different chemical structures at low CO₂ pressure, has found that CO₂ absorption into PILs fits well to a dual-mode model [54]. Two CO₂ storage mechanisms have been suggested by this study. The first one deals with the dissolution of CO₂ in the matrix phase, while the second deals with the CO₂ storage via a Langmuir hole-filling process in the microvoids, which are known as free volume created by the polymer chain entanglement.

Many modifications in PIL chemical structure have attempted to increase CO₂ uptake. An orthogonal approach is to make nanostructured PILs with rather large specific surface areas, thereby enhancing sorption kinetics and capacities. Several mesoporous PILs have been recently reported. A detail kinetic study indicates that mesoporous PILs reached the CO₂ absorption equilibrium state faster than IL monomers and the bulk PIL. Meanwhile a higher CO₂ sorption capacity was observed as well [55]. Currently, there are intensive ongoing efforts to push the CO₂ absorption capacity limit on PIL-based materials [56, 57], because the CO₂ uptake of PILs is notably high for polymers but not yet comparable to commercial absorbents. Although a recent report has demonstrated that a tetraalkylammonium-based PIL can absorb up to 77 wt% of CO₂, these data have not been verified by other groups [58].

Another usage of PILs on CO₂ is the separation from light gases, such as nitrogen or CH₄. This process requires a PIL membrane for high CO₂ flux and simultaneously selectivity and stability at processing temperatures and pressures. PIL membranes containing IL moieties can specifically interact with CO₂ to afford high selectivity and meanwhile avoid the “blowout” problem due to their solid nature and physical resistance to high pressures. However, the PIL membranes with various chemical structures suffered from the difficulty associated with the rather low CO₂ permeability. This problem forced the community to reexamine the value of ILs with regard to CO₂ enrichment and separation, this time by dissolving them in PILs. Indeed, dramatic improvements in CO₂ permeability have been

accomplished by blending up to 20 mol% of room-temperature ILs with PILs [59, 60]. The small fraction of ILs in the blend acts as a plasticizer and does not hamper the physical state of the membrane, eliminating the “blowout” problem. Current studies concentrate on understanding the influence of various chemical structures on the performance of the blend system [61, 62].

In the field of separation science, PILs have been examined for use in solid-phase extraction and chromatography [63, 64]. The introduction of PILs was initially aimed to increase the chromatographic efficiency of ILs at elevated temperatures, since at high temperature IL viscosities decrease significantly, thus destroying the homogeneous IL film coated on the solid surface. When using IL monomers instead of common ILs, the surface IL film can be polymerized into a polymeric cross-linked layer that permanently sticks to the surface even at high temperatures. In this direction, an in-column polymerization of cross-linkable dicationic vinylimidazolium IL monomers was adopted to further enhance the chromatographic efficiency and avoid column bleed problem at high temperature.

Carbon Materials

Carbon plays a very important role in the current energy generation, storage, and conversion. Imidazolium- and pyridinium-based ILs are an important class of precursors for nitrogen-doped carbons. The atomic incorporation of nitrogen into the carbon framework is responsible for enhanced electronic conductivity, basicity, and catalytic activity. PILs similar to ILs are a class of important carbon precursors. In addition to homopolymers, PIL random and block copolymers were also reported to serve as carbon precursors [65, 66]. Taking the polymeric nature into consideration, PILs are especially useful for the production of shaped, nitrogen-doped carbon nanostructures.

In the initial carbonization example of PILs, it was found that the metal salts, such as iron chloride, would form layered graphitic mesoporous carbon nanostructure but eliminate all nitrogen atoms from the carbon structure as well [67]. During the carbonization, the metal salts were reduced to iron metal to catalyze the growth of curved and randomly oriented carbon nanosheets via a dissolution–precipitation process. To keep nitrogen atoms in the final products, metal salts were excluded from the carbonization process. In an attempt to use PILs for the synthesis of nitrogen-doped carbon fibers and membranes, the electrospinning technique was employed to process PILs into fibers. Electrospinning is a robust processing technique to shape polymers or polymer-based hybrids into one-dimensional objects with the fiber diameter down to several nanometers [68]. The electrospun PIL fibers were first radically cross-linked at 80 °C under vacuum to lock the fiber structure. In a following step, the fibers and membranes were carbonized at 1,000 °C to produce nitrogen-doped carbon fibers and membranes.

Beside fibers, hollow spheres are another unique carbon architecture possessing a high surface-to-volume ratio, high thermal and chemical stability, low apparent density, and low percolation threshold. Nitrogen-doped carbon hollow spheres

could be achieved from PILs in two approaches: (a) Silica hard-templating method. In this method, silica (nano)particles from 70 nm to micron size act as solid substrate, the surface of which is coated by a thin layer of PILs or PIL containing polymers. For example, silica nanoparticles as hard templates can be homogeneous coated by poly(1-ethyl-3-vinylimidazolium tetrafluoroborate) in a simple free radical polymerization step [69]. During the polymerization, the IL monomer soluble in ethanol was polymerized into insoluble polymer, which preferentially deposited on the silica surface due to the attractive interaction between PIL and silica. Layer-by-layer is another technique useful to deposit PILs onto silica surface. The layer-by-layer assembly technique is a well-known method to engineer surfaces with oppositely charged polyelectrolytes. To coat silica particle surface, a cationic PIL poly(3-cyanomethyl-1-vinylimidazolium bromide) and an anionic poly(ammonium acrylate) were employed as the deposition pair. Either the in-situ polymerization or the LbL technique can provide a dense PIL layer on the silica particle surface. Upon carbonization, the PIL polymer layer was in situ converted into nitrogen-doped carbon film. Carbon hollow spheres from 70 nm to micron meter size were prepared. All these carbon hollow spheres are microporous or mesoporous and containing ca. 7 wt% of nitrogen in the carbon framework. (b) Nanoconfinement carbonization. PIL colloid nanoparticles of 25 nm in size were employed. By reaction with tetramethoxysilane in water, these PIL nanoparticles were individually embedded in a compact silica matrix, a process called silica nanocasting. By carbonization under nitrogen atmosphere, the PIL nanoparticles confined in the silica matrix were converted into hollow carbon nanospheres. The size of the carbon nanospheres can be modulated in the range of 25–90 nm, depending on the silica nanocasting conditions. Very much different from common ones, these carbon hollow spheres prepared from the silica nanocasting technique are fairly dispersible in water and highly graphitic.

Catalysis

The enhanced mechanical stability of PILs by several orders of magnitude compared to ILs has enabled many catalytic reactions performed in a simple manner by using PILs. The application of PILs in catalysis can be classified into three types according to their function in the reactions as catalyst, pre-catalyst, and catalyst support. The freedom to choose the cation and anion, the tunable form in the macromolecular structures, and the modern polymer-processing techniques can be synergistically combined to amplify the catalytic effect and in addition facilitate the recycling and reuse of the catalysts. Currently, there is a strong tendency in some groups to exploit PILs as a heterogeneous catalyst to replace IL-grafted solid systems, so-called supported ionic liquid phases (SILPs).

As catalyst the chemical fixation of CO₂ by PILs is of significant interest and importance because of its potential impact on the chemical storage of CO₂ by capturing it as a building block in C1 chemistry. Very often, CO₂ is captured and in situ utilized in the direct synthesis of cyclic carbonates via the coupling of CO₂ with

epoxides. In several reports [70, 71], cross-linked PIL nanoparticles were used because of high surface-to-volume ratio and their easy recycling. Furthermore, unlike the normal ILs, the cross-linked PILs hold firmly the nanoparticle morphology despite partial swelling under vigorous reaction conditions, such as high CO₂ pressure and high reaction temperature. For example, cross-linked PIL nanoparticles could be prepared via dispersion polymerization of a phosphorous IL monomer tributyl-4-vinylbenzylphosphonium chloride using AIBN as a radical initiator in the presence of an ethylene dimethacrylate cross-linker [72]. The formed nanoparticles were in the range of 10–50 nm. The catalytic experiments were conducted by mixing the dried PIL nanoparticles and CO₂ under 3 MPa at 140 °C for 3 h without any solvents or cocatalysts. Both high activity and selectivity were achieved for the cycloaddition between CO₂ and several epoxides, such as allyl glycidyl ether, styrene oxide, methyl chloroacetate, propylene oxide, and epichlorohydrin.

Besides the major interest in chemical fixation of CO₂, PILs have served as a catalyst in several other systems. The oxidative carbonylation of aniline using poly(1-methyl-3-vinylimidazolium methylselenite) or poly(1-ethyl-3-vinylimidazolium methylselenite) as a heterogeneous catalyst has been introduced [73]. A cross-linked PIL shell coated onto the magnetite nanoparticle has been used as an acidic catalyst for the synthesis of 1,1-diacetyl from aldehydes under solvent-free conditions at room temperature in high yields [74]. A microgel based on vinylimidazolium-type PILs with paramagnetic anions of tetrachloroferrate (III) or tetrabromoferrate (III) successfully catalyzed the Friedel–Crafts alkylation reactions. Some PILs could assemble themselves with a macrocyclic polyoxometalate to create a water-insoluble and visible-light-photosensitive catalyst for photocatalytic reactions [75].

PILs can complex and stabilize metal and metal oxide nanoparticles that are catalytically active. This feature is related to the high charge density as well as the dynamic polymer chain structure. Instead of monovalent IL as stabilizers for metal or metal oxide nanoparticles, the stabilizing power of PILs is multivalent, strong, and permanent. Copolymerization of *N*-vinyl-2-pyrrolidone and 1-butyl-3-vinylimidazolium bromide in IL 1-butyl-3-methylimidazolium tetrafluoroborate has been used for the stabilization of rhodium nanoparticles [76]. The metal catalyst showed a long lifetime for benzene hydrogenation. Furthermore, PILs grafted onto carbon nanotubes could effectively support PtRu nanoparticles, which showed improved catalytic performance over the PtRu/CNT binary systems toward the electrocatalytic oxidation of methanol [49]. In general, PIL-based systems as supports facilitate the recovery, recycling, and further use of the catalyst.

PILs could act as pre-catalyst for poly(*N*-heterocyclic carbene)s (poly(NHC)s) [77–79]. For example, poly(3-vinyl-1-alkylimidazolium TFSI) was first deprotonated in THF at –80 °C by a strong base potassium butoxide under moisture-free conditions. This produced the poly(NHC)s, which can react with carbon dioxide, forming relatively air-stable and thermolabile poly(NHC–CO₂) adducts. At high temperature, poly(NHC–CO₂) could decompose back to poly(NHC). Thus, through carbon dioxide, poly(NHC) and poly(NHC–CO₂) could be reversibly converted to each other. Both were proven to be active, soluble, and homogeneous polymer-supported organic

catalysts for the transesterification and benzoin condensation reactions. The advantage of using poly(NHC-CO₂) instead of poly(NHC) is the enhanced tolerance of the catalyst toward the external environment. This design makes the practical carbene-related catalytic reactions easier to implement.

Other Applications

The application spectrum of PILs is currently under significant expansion. Apart from those mentioned above, many newly emerging applications have been demonstrated recently. Among them, PIL for energy harvesting and storage is one of the fastest growing fields. Several groups have investigated PIL-based electrolyte membranes for use in alkaline fuel cell operation [80–84]. In parallel, there have also been reports on PIL-based quasi-solid-state dye-sensitized solar cells [85, 86] and lithium ion batteries [87, 88]. In addition to energy-related application, some other applications are right now under development. For example, there are very intensive studies in porous PIL production, which have high specific surface area. These porous PILs have been used as sensors [12], coatings [89], and catalytic supports. Other applications of PILs include microwave-absorbing materials [50], actuators in electric fields [16], and DNA vectors [90, 91]. With the rapid progress in the PIL chemistry and physics, a further expansion in the application spectrum of PILs is expected.

Conclusion

This chapter introduces the basic knowledge of PILs, including possible chemical structures, their synthesis strategies, and materials applications in a variety of fields. As the polymeric form of ILs, PILs have enhanced mechanical stability and superior processability. The macromolecular architecture also allows for controlled ordering of the IL species in a three-dimensional space. Therefore, the study on PILs has further broadened the research scope of ILs in many directions. Compared to common polyelectrolytes, the fundamental transport phenomenon and interfacial activity in bulk PILs are very unique and deserve more efforts in the future. Generally speaking, PIL research is right now still in its infancy and plenty of research activities are running simultaneously to the writing of this chapter. The fast advance in this field is evidenced by massive scientific publications, newly reported chemical structures, and novel properties and functions. In addition, unlike other topics in polymer science, PIL research is very much application driven and spans a plethora of notably different fields of study. This requires a close collaboration of scientists from various fields. The interdisciplinary character of PILs is expected to be stronger in the future.

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Imidazolium-Based Poly(Ionic Liquid) Block Copolymers

4

Paul Coupillaud and Daniel Taton

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Abstract

Poly(ionic liquid)s (PILs) have been recently introduced into block copolymer (BCP) architectures to combine the specific properties of PILs, such as responsiveness to ion exchange, ionic conductivity, and/or gas transport, with the self-assembling properties of BCPs, enabling the access to a wide range of robust nanostructured morphologies, either in solution or at the solid state. This chapter describes synthetic strategies to such PIL BCPs utilizing “controlled/living”

P. Coupillaud (✉) • D. Taton

Laboratoire de Chimie des Polymères Organiques, Université de Bordeaux & Centre National de la Recherche Scientifique, Pessac, France

e-mail: Paul.Coupillaud@enscbp.fr; taton@enscbp.fr

polymerization methods and/or post-chemical modification of preformed copolymers, as well as their self-assembling properties in a selective solvent and in bulk. Potential applications of this emerging class of materials, for instance, in energy conversion devices or in gas separation membranes, are also briefly presented.

Keywords

Block copolymer • Poly(ionic liquid) • Imidazolium • Controlled polymerization • Self-assembly • Nanostructures • Ionic conductivity

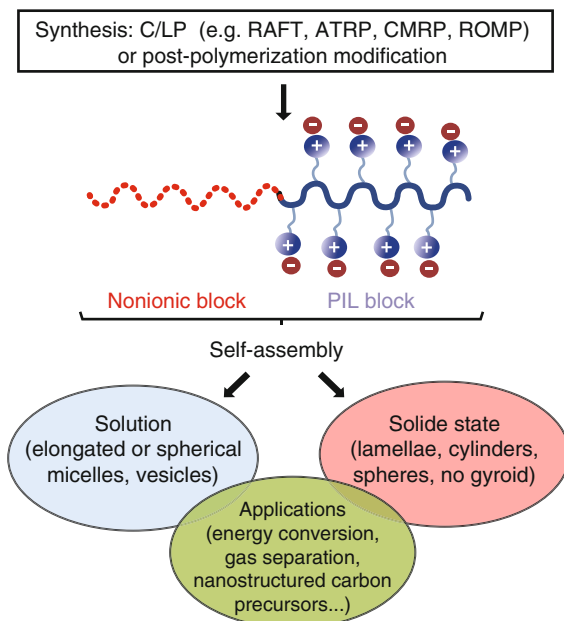
Introduction

Engineering of block copolymers (BCPs) is a major item of polymer science, spanning aspects of macromolecular chemistry through the molecular design of active species, to theoretical and physicochemical studies [1–3]. Some BCPs are practically used in our daily life as specialty polymers, e.g., as compatibilizers, dispersants, and adhesives, in microelectronics, or drug delivery systems [4–12]. The success of BCPs is due to their self-assembling properties, either at the solid state or in a selective solvent of one block, which provides a wide range of morphologies in the submicron size range [13–16]. Miscellaneous BCP architectures and compositions can be achieved by resorting to “controlled/living polymerization” (C/LP) techniques, which can be combined with modern synthetic tools, such as “click chemistry” [17], post-polymerization modification of preformed and reactive (co)polymers [18–20], or supramolecular chemistry [21, 22].

In recent years, ionic liquids (ILs) have been introduced as doping agents in nonionic (nonconducting) BCPs as a means to tune nanostructured morphologies and impart ionic conductivity or gas transport in nanodomains [23–33]. This is because ILs exhibit a high intrinsic CO₂ solubility as well as a high ion conductivity [25, 34–38]. For instance, ionic nanodomains of continuous morphology prove more conductive than morphologies in which grain boundaries impede ion mobility [39, 40]. An anisotropic ionic conductivity can be achieved from IL-doped BCPs exhibiting a lamellar mesophase [41], while BCPs with a three-dimensional network morphology can lead to a direction-independent ionic conductivity, due to well-connected ion-conducting pathways [31].

However, blends between an exogenous liquid electrolyte and a polymer matrix are prone to electrolyte leakages. To alleviate this problem, one solution may be to resort to polymerized ionic liquid – also referred to as poly(ionic liquid)s (PILs) – instead of molecular ILs. As described in other chapters, PILs have emerged as a special class of polyelectrolytes combining inherent features of ionic liquids (ILs), including thermal stability, high solid-state ionic conductivity, high CO₂ permeability, and adjustable solubility, with specific properties of polymers, such as film formation and processability [42–47].

Fig. 4.1 Illustration of poly(ionic liquid) block copolymers (PIL BCPs) and their potential for self-assembly and their use in various applications



In the past 5–6 years, design and self-assembling properties of BCPs constituted of a PIL block have been the topic of detailed studies. This novel family of BCPs combines the attributes of PILs, such as ionic sensitivity, with the self-assembling properties of BCPs, which provides access to a range of nanostructured morphologies in solution and at the solid state. In bulk, ionic and nonionic blocks segregate in highly ordered nanodomains, due to the strong incompatibility of the two blocks [48]. This is expected to impart complementary features to these ion-conducting materials, such as structural stability and bulk mechanical properties, while affording tunable transport performance [49, 50] (Fig. 4.1).

Most of BCPs featuring a PIL block reported so far are polyelectrolytes based on the cationic imidazolium or pyridinium ring, associated with various counter-anions. The present chapter is devoted to such PIL BCPs, covering their synthetic strategies by C/LP (section “[Synthetic Developments to PIL BCPs](#)”), their self-assembling properties in solution (section “[Self-assembly in Solution](#)”) and in bulk in correlation with their transport capabilities (ions or gas, see section “[Self-assembly at the Solid State and Related Transport Properties](#)”), as well as their potential applications (section “[Potential Applications of PIL BCPs](#)”). Minor exceptions to this scope, and that we have considered of particular interest, have been however included. For instance, an example of an anionic BCP with trifluorosulfonylimide units and lithium counter-anions will be described. In contrast, BCPs that are issued from alkylation of tertiary amino-containing units, i.e., quaternization reaction of, e.g., dialkylaminoethyl (meth)acrylate, will not be covered here, and information regarding such materials can be found elsewhere [51, 52].

Synthetic Developments to PIL BCPs

The traditional synthetic route to linear AB-type BCPs is by sequential addition of monomers, following a same CLP mechanism. After the first monomer (A) is consumed, active species are still “alive” to initiate the polymerization of monomer B. However, monomers may not be polymerized in an indiscriminate sequence, and order of monomer addition often matters so as to achieve well-defined compounds. Various PIL BCPs have been directly synthesized by CLP of imidazolium-type IL monomers featuring a halide counter-anion (see Table 4.1), which includes not only radical methods by reversible addition-fragmentation chain transfer (RAFT), atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and cobalt-mediated radical polymerization (CMRP) but also ring-opening metathesis polymerization (ROMP). Facile anion exchange (metathesis reaction) can be achieved to introduce anions, such as bis(trifluoromethanesulfonyl)imide (Tf_2N^- or TFSI) or tetrafluoroborate (BF_4^-) in PIL BCPs [48, 53–68].

Besides direct sequential polymerization, PIL BCPs can be accessed by post-polymerization modification of preformed BCP precursors [17, 20, 69]. First examples based on imidazolium units were actually made in this way, as reported by Waymouth, Gast et al. in 2003 [70]. The resulting compounds were found to self-assemble in toluene into elongated micelles with PIL block at the core (see section “Self-assembly in Solution”).

Table 4.1 gathers the different imidazolium-based PIL BCP structures that were reported so far, including the nature of the anions and that of the alkyl chains on the imidazole ring, as well as the associated synthetic methods. In this section are described the synthetic aspects, while sections “Self-assembly in Solution” and “Self-assembly at the Solid State and Related Transport Properties” will discuss the self-assembling properties in solution and at the solid state of these materials.

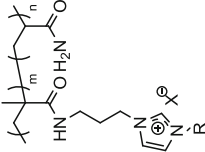
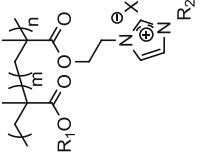
Note that the determination by direct methods of the molar mass and dispersity of PILs in general and of BCPs, e.g., by size exclusion chromatography (SEC) or by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI ToF), is most often inconclusive, likely due to strong interactions of these cationic polyelectrolytes with SEC columns. Very recently, however, Matyjaszewski et al. proposed a “universal” method to analyze imidazolium-based PILs with Tf_2N^- counter-anions by employing THF as eluent in the presence of LiNTf_2 [71].

Reversible Addition Fragmentation Chain Transfer (RAFT)

Main chain transfer agents (CTAs) used in the RAFT process to achieve imidazolium-based PIL BCPs are shown in Fig. 4.2, and a typical synthesis is illustrated in Scheme 4.1 [72–75].

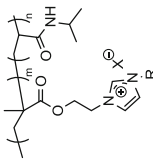
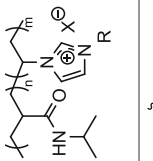
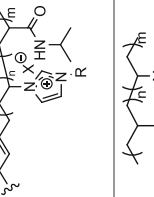
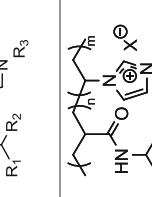
The first example was reported by Mecerreyes, Taton, Gnanou et al. in 2008 [53]. Methacrylamido- and methacrylate-type monomers were purposely designed to this end. RAFT polymerization was conducted in methanolic solutions at 70 °C,

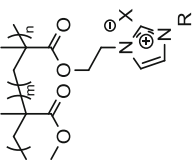
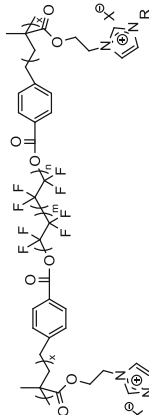
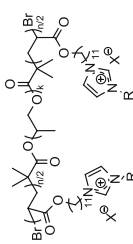
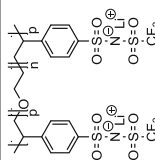
Table 4.1 Representative PIL BCP structures, related synthetic and characterization methods, morphologies observed at the solid state, and conductivity. Entries 11 and 23–24 correspond to non-imidazolium PIL BCPs

Entry	Structure	X [−] = Anion	R-groups	Polym. method	Charact.	S.A. in solution	S.A. in bulk	Morph. ^a	Conductivity range (S cm ^{−1})	Ref.
1		Br [−]	−CH ₂ CH ₃	RAFT	¹ H NMR, SEC in THF	DLS, SLS, TEM	n.i. ^b	n.i. ^b	n.i. ^b	[53]
2		Br [−]	R ₁ = H; R ₂ = CH ₃ , R ₁ = CH ₃ , R ₂ = CH ₃ , R ₁ = CH ₃ , R ₂ = CH ₂ CH ₃	RAFT	¹ H NMR, SEC in THF	DLS, SLS, TEM	n.i. ^b	n.i. ^b	n.i. ^b	[54]

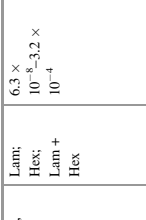
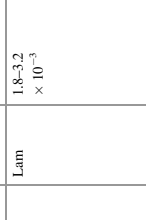
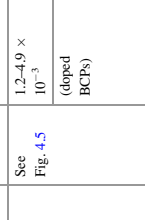
(continued)

Table 4.1 (continued)

Entry	Structure	X [−] = Anion	R-groups	Polym. method	Charact.	S.A. in solution	S.A. in bulk	Morph. ^a	Conductivity range (S cm ^{−1})	Ref.
3		BF ₄ [−]	−(CH ₂) ₃ CH ₃	RAFT	¹ H NMR, SEC	DLS, cryoTEM, fluorometry	n.i. ^b	n.i. ^b	n.i. ^b	[55]
4		Br [−]	−(CH ₂) ₇ −(C ₆ H ₅)	RAFT	¹ H NMR, SEC in acetonitrile/water (1:1)	n.i. ^b	n.i. ^b	n.i. ^b	n.i. ^b	[56]
5		Br [−]	−CH ₂ CH ₃	RAFT	¹ H NMR, ¹³ C NMR, SEC in acetonitrile/water (1:1), FTIR	DLS, AFM	n.i. ^b	n.i. ^b	n.i. ^b	[57]
6		Br [−] , (CN) ₂ N [−]	R ₁ = −H, −CH ₃ R ₂ = −CH ₃ , −CH(CH ₃) ₂ R ₃ = −CH ₂ CH ₃ , −CH ₂ CN, −(CH ₂) ₃ CN	RAFT	¹ H NMR, SEC in NMP, FTIR, UV, TGA, DSC	AUC, TEM, XRD, FT-IR, nitrogen sorption	n.i. ^b	n.i. ^b	n.i. ^b	[58]
7		Br [−]	−(CH ₂) ₃ CH ₃	RAFT	¹ H NMR, FTIR	DLS	n.i. ^b	n.i. ^b	n.i. ^b	[59]

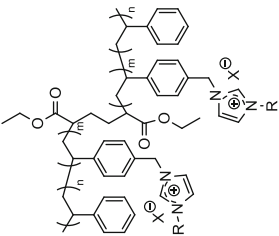
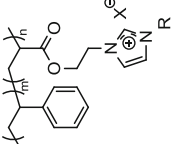
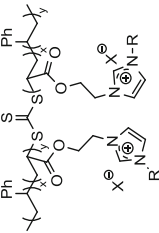
8		Br^- , Ti_2N^- , HO^-	$-(\text{CH}_2)_9\text{CH}_3$	RAFT	^1H NMR, DSC, TGA, FTIR, elemental analysis	n.i. ^b	TEM, SAXS EIS, dynamic vapor sorption (DVS)	Lam	10^{-4} – 10^{-2} ; 1.0×10^{-3} – 2.5×10^{-2} until 90 % of relative humidity	[60], [61]
9		BF_4^- , Ti_2N^-	$-(\text{CH}_2)_9\text{CH}_3$	RAFT	^1H NMR, SEC in THF, TGA, DSC	n.i. ^b	WAXS, SAXS, dielectric relaxation spectroscopy (DRS)	Unord	10^{-12} – 10^{-4}	[62]
10		Br^-	$-\text{CH}_3$	ATRP	^1H NMR, SEC in HEP, FTIR, UV, TGA, DSC	Dynamic contact angle	n.i. ^b	n.i. ^b	n.i. ^b	[63]
11		–	–	NMP	^1H NMR, SEC in H_2O + acetonitrile, TGA, DSC, DMA	n.i. ^b	EIS	n.i. ^b	2×10^{-8} – 5×10^{-5}	[50]

(continued)

16		Ti_2N^-	$-(\text{CH}_2)_5\text{CH}_3$	NMP + post modif	^1H NMR, SEC in THF, DSC	n.i. ^b	SAXS, TEM, EIS	Lam; Hex; Lam + Hex	6.3×10^{-8} – 3.2×10^{-4}	[39]
17		Cl^- , HO^-	$-(\text{CH}_2)_5\text{CH}_3$	NMP + post modif	^1H NMR, SEC in DMF, TGA, DSC	n.i. ^b	SAXS, EIS, galvanodyna	Lam	1.8 – 3.2×10^{-3}	[83]
18		Br^-	$-\text{CH}_2\text{CH}_3$	NMP + post modif	^1H NMR, SEC in THF, DSC, TGA, DMA, EIS	n.i. ^b	SAXS, TEM	See Fig. 4.5	1.2 – 4.9×10^{-3} (doped BCPs)	[84]

(continued)

Table 4.1 (continued)

Entry	Structure	X [−] = Anion	R ₂ groups	Polym. method	Charact.	S.A. in solution	S.A. in bulk	Morph. ^a	Conductivity range (S cm ^{−1})	Ref.
19		Tf ₂ N [−]	−CH ₂ CH ₃	NMP + post modif	¹ H NMR, SEC in THF, DSC, TGA, DMA	n.i. ^b	EIS	Unord	5 × 10 ^{−7} –5 × 10 ^{−4} , 8 × 10 ^{−5} –2 × 10 ^{−2} (doped BCPs)	[49]
20		Br [−] , Tf ₂ N [−]	−(CH ₂) ₃ CH ₃	RAFT + post modif	¹ H NMR, SEC in THF, TGA, DSC	n.i. ^b	SAXS, TEM, EIS	Hex; Lam + Net; Unord; Lam	10 ^{−6} –10 ^{−3}	[85]
21		Cl [−] , TfSA	−(CH ₂) ₃ CH ₃	RAFT + post modif	¹ H NMR, SEC in THF, elemental analysis	n.i. ^b	n.i. ^b	n.i. ^b	n.i. ^b	[86]

22		CF_3COO^-		ATR-FTIR + post modif	^1H NMR, SEC in THF	n.i. ^b	SAXS, TEM	Hex; Lam	5×10^{-4} – 1.2×10^{-2}	[87]
23		Br^- , Ti_2N^- , $\text{CF}_3(\text{CF}_2)_3^-$, SO_3^-	$-\text{CH}_2\text{CH}_3$	Anionic + post modif	^1H NMR, SEC in DMF, TGA, FTIR	n.i. ^b	AFM, TEM	Lam	n.i. ^b	[88]
24		Br^- , $\text{Fe}_3\text{Br}_{10}^-$	$-\text{CH}_2\text{CH}_3$	Anionic + post modif	^1H NMR, SEC in THF, TGA, DSC, FTIR	n.i. ^b	TEM, osmometry, magnetic character	n.i. ^b	n.i. ^b	[89]

^aMorphology abbreviations: *Lam* Lamellae, *Hex* hexagonally packed cylinders, *Lam* + *Hex* coexisting *Lam* + *Hex*, *S_{6CC}* spheres on a body-centered cubic lattice, *LLP* liquid-like packing, *Unord* unordered separated microphase, *Net* network
^bn.i. not investigated

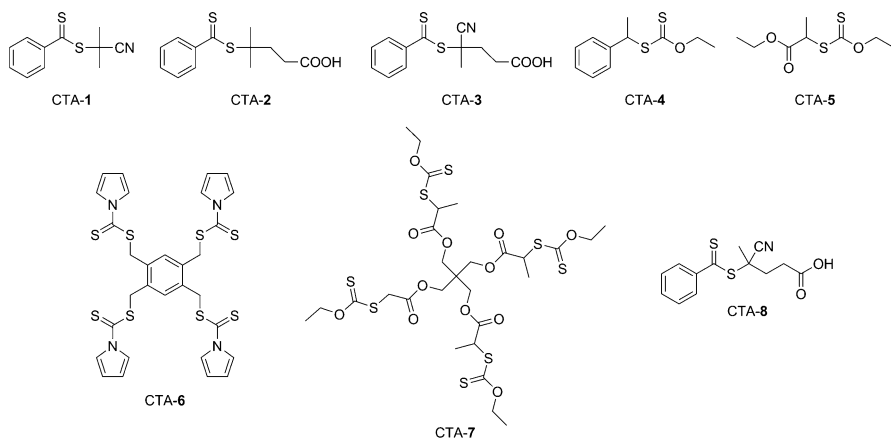
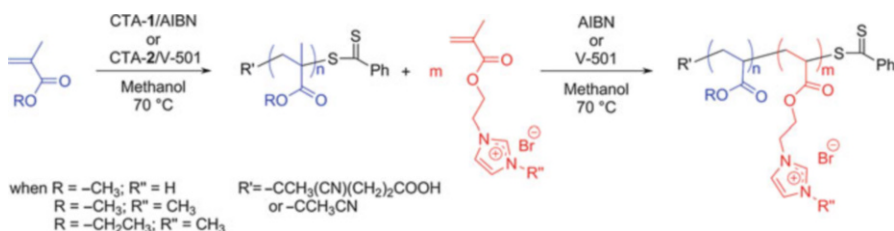


Fig. 4.2 Chain transfer agents (CTAs) used for PIL BCP synthesis by RAFT polymerization [53–61]



Scheme 4.1 First example of PIL BCP synthesis by RAFT polymerization [53]

in the presence of either 2-cyanopropyl dithiobenzoate (CTA-1) or (4-cyanopentanoic acid)-4-dithiobenzoate (CTA-2) as CTAs and a radical source. It was first established that RAFT-mediated polymerization of IL-based monomers in methanolic solutions led to well-defined PILs. Polymers did exhibit molar masses predetermined by the initial molar ratio of the monomers to the dithioester precursor, as evidenced by ^1H NMR spectroscopy from polymer chain-end analysis. Polyacrylamide (PAm) and poly(methacrylic acid) (PMAA) were also pre-synthesized by RAFT to serve as macro-CTAs for block copolymer synthesis [53, 54]. Chain extension experiments were carried out in aqueous or in alcoholic solutions, affording double hydrophilic PIL BCPs with bromide anions (PMAA-*b*-PIL(Br) and PAm-*b*-PIL(Br); Entries 1 and 2, Table 4.1). These compounds were further manipulated and made to self-assemble in micelle-like structures, either by anion exchange or by chemical modification of PMAA (see section “[Synthetic Developments to PIL BCPs](#)”).

Sequential RAFT polymerization was also employed to achieve copolymers based on PIL and poly(*N*-isopropylacrylamide) (PNIPAM), thus exhibiting both an ionic and a thermal responsiveness (Entry 3) [55]. Dithioester CTA-3 was used

and the length of the PIL block was kept constant, while that of PNIPAM was varied ($\overline{M}_n$ values from 5,500 to 38,600 g mol⁻¹, with $\overline{M}_w/\overline{M}_n < 1.13$). The selected PIL, namely, poly(2-(1-butylimidazolium-3-yl)ethyl methacrylate tetrafluoroborate), was insoluble in water (anion exchange from bromide (Br⁻) to tetrafluoroborate (BF₄⁻) was carried out with the IL monomer prior to RAFT polymerization).

Similar RAFT-derived BCPs based on PIL and PNIPAM (Entry 4, Table 4.1) were previously reported by Endo, Mori et al., from xanthates (CTA-4 and CTA-5, Fig. 4.2) [56]. Polymerization of the *N*-vinylimidazolium salt was accomplished from a xanthate-functionalized PNIPAM, leading to a reasonably well-defined PIL BCP ($\overline{M}_w/\overline{M}_n < 1.5$). The same group also synthesized four-armed star-block copolymer homologues, using tetrafunctional dithiocarbamate CTAs (CTA-6 and CTA-7, Fig. 4.2; Entry 5, Table 4.1) [57]. Two types of star-block compounds were prepared: one consisting of PNIPAM blocks forming the core surrounded by the PIL layer and the other with the reverse structure. A lower dispersity was noted when using a four-armed PIL as macro-CTA: $\overline{M}_w/\overline{M}_n < 1.22$ versus 1.57, when starting by RAFT polymerization of NiPAm.

Antonietti and Yuan also resorted to the xanthate chemistry to derive a series of double hydrophilic PIL BCPs ($\overline{M}_w/\overline{M}_n \sim 1.20$ – 2.19 ; Entry 6, Table 4.1), from four different *N*-vinylimidazolium IL monomers possessing different alkyl substituents and anions [58]. PNIPAM or poly(*N,N*-dimethylacrylamide) (PDMA) was selected as the nonionic polymer associated with the PIL block. The use of dicyanamide, (CN)₂N⁻, as counter-anion was found to favor ion pair dissociation (increasing the distance between the imidazolium and the dicyanamide ions). However, polymerization of corresponding IL monomers proved energetically unfavorable (conversion $\sim 10\%$) in contrast to monomers featuring other anions. Hence, reactivity of *N*-vinylimidazolium IL monomers might be adjusted by a proper selection of this structural parameter.

PNIPAM and PIL segments were also associated in BCP architectures obtained by sequential RAFT in the works by Wu et al. (Entry 7, Table 4.1) [59]. Self-assembling properties in solution were studied by dynamic FTIR, which evidenced the occurrence of interactions by H-bonding (see section “Self-assembly in Solution”).

More recently, Elabd et al. described the synthesis of a series of well-defined PIL BCPs based on poly(methyl methacrylate) (PMMA), with various PIL compositions ($\overline{M}_n$ values from 16,100 to 25,700 g mol⁻¹ with 4.3–15.7 mol% PIL, $\overline{M}_w/\overline{M}_n < 1.6$; Entry 8, Table 4.1) [60, 61]. The aim of this study was to provide an understanding of the influence of morphology on ion transport after anion exchange, from bromide to Tf₂N⁻ or hydroxide (HO⁻), as discussed in section “Self-assembly in Solution”.

Wang et al. developed a synthetic strategy to ABA-type triblock copolymers ($\overline{M}_n$ values from 21 to 29 kg mol⁻¹ with 6.8–13.5 mol% PIL; Entry 9, Table 4.1) [62]. A telechelic poly(vinylidene fluoride-*co*-hexafluoropropylene) [P(VDF-HFP)] macro-RAFT agent was first designed before the polymerization of the methacrylate imidazolium monomer. No microphase separation was observed with this particular triblock PIL BCPs, presumably owing to the compatibility of the PIL

and the fluoropolymer matrix. The compounds with Tf_2N^- counterions showed higher ionic conductivities than those with BF_4^- , which was attributed to a higher segmental mobility.

Atom Transfer Radical Polymerization (ATRP)

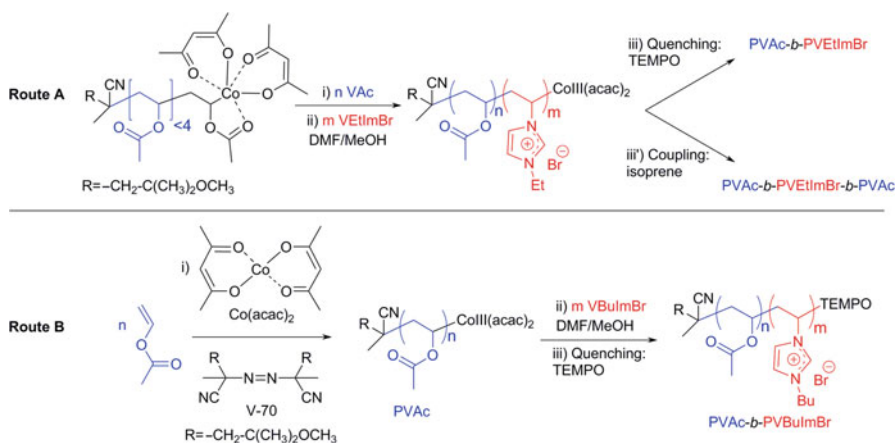
Only a very few examples of PILs and PIL BCPs were prepared by ATRP (see also ► Chap. 13 for the synthesis of homoPILs by controlled radical polymerization) [76–78]. In 2012, Texter et al. reported the synthesis of ABA-type symmetric triblock copolymers with a central poly(propylene oxide) block and poly(1-[11-acryloylundecyl]-3-methyl-imidazolium): $\overline{M}_n \sim 9,600 \text{ g mol}^{-1}$, $\overline{M}_w/\overline{M}_n \sim 1.5$, after chemical modification of a telechelic PPO precursor (Entry 10, Table 4.1) [63].

Nitroxide-Mediated Polymerization (NMP)

Recently, Armand, Gigmes et al. elaborated one of the most efficient copolymer materials in terms of ionic conductivity and mechanical properties [79]. Based on a polyanionic backbone with lithium as counter-cation, a series of BAB triblock poly(4-styrenesulphonyl(trifluoromethylsulfonyl) imide lithium)-*b*-poly(ethylene oxide)-*b*-poly(4-styrenesulphonyl(trifluoromethylsulfonyl) imide lithium), denoted P(STFSILi)-*b*-PEO-*b*-P(STFSILi), with various ratios of P(STFSILi)/PEO (10–40 wt% P(STFSILi), were designed by NMP ranged from 38,700 to 61,400 g mol^{-1} (Entry 11, Table 4.1) [50].

Cobalt-Mediated Radical Polymerization (CMRP)

CMRP has been developed by the group in Liège [80] as a powerful method to control the polymerization of conjugated vinyl monomers, such as acrylonitriles or acrylates, and nonconjugated vinyl monomers as well, including vinyl acetate (VAc) or *N*-vinylpyrrolidone. In 2011, Detrembleur, Taton et al. introduced a new family of PIL BCPs based on poly(*N*-vinyl-3-ethylimidazolium bromide) (PVEtImBr) and PVAc; the synthesis of which was achieved by sequential CMRP (see Scheme 4.2, Route A; Entry 12, Table 4.1) [64]. Polymerizations were typically carried out either in dimethylformamide or in methanol solution, using a preformed alkyl-cobalt(III) adduct as both the polymerization initiator and controlling agent upon dissociation. Excellent control over molar masses and dispersities ($\overline{M}_w/\overline{M}_n \sim 1.05\text{--}1.06$) were achieved in MeOH. Substituting methanol for DMF induced much faster polymerization process, even under quite high dilute conditions. Well-defined PVAc-*b*-PVEtImBr PIL BCPs were synthesized from a CMRP-derived PVAc-Co(acac)₂ macroinitiator, in a mixture of DMF and MeOH (2/1: v/v) at 30 °C. Finally cobalt-mediated radical coupling of such PIL BCPs, in the presence of isoprene, readily led to PVAc-*b*-PVEtImBr-*b*-PVAc symmetrical triblock copolymers.



Scheme 4.2 **Route A.** Synthesis of PVAc-*b*-PVETImBr and PVAc-*b*-PVETImBr-*b*-PVAc by sequential CMRP using alkyl-cobalt(III) adduct as a mediating agent [64]. **Route B.** Synthesis of PVAc-*b*-PVBulmBr by sequential CMRP using Co(acac)₂ and V-70 [65]

Though straightforward, this method required the prior synthesis of the alkyl-cobalt(III) adduct. Very recently, the same team reported an alternative strategy to CMRP-derived PIL BCPs by using a commercially available controlling agent, namely, *bis*(acetylacetonato)cobalt(II) (Co(acac)₂) in conjunction with 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70). In this way, a PVAc precursor could be grown by CMRP ([VAc]/[V-70]/[Co(acac)₂] = 281/6.5/1) [65]. Crossing over from PVAc to poly(*N*-vinyl-3-butyliimidazolium) allowed for an easy access to PVAc-*b*-PIL BCPs (Entry 12, Table 4.1). Growth of the PVBulmBr block from PVAc-Co(acac)₂ was again accomplished by CMRP in DMF/MeOH (2/1: v/v). Analysis of compounds by ¹H NMR showed the presence of both blocks in methylene chloride. Formation of micelle-like structures was then evidenced after adding few drops of a non-solvent of one block. In addition, only one diffusion coefficient was observed by DOSY NMR, which allowed the authors to conclude that a pure diblock copolymer was present, free of any homopolymer contaminant, validating their synthetic approach utilizing Co(acac)₂.

Ring-Opening Metathesis Polymerization (ROMP)

In a series of papers, Gin, Bailey et al. investigated the synthesis and self-assembling properties in bulk of PIL BCPs obtained by ROMP of norbornyl-type monomers, using Grubbs' first-generation catalyst (Entry 13, Table 4.1) [48, 66]. Control over the ROMP process allowed them to vary the relative volume fraction of the poly(norbornene dodecyl ester) block (*f*_{DOD} = 0.42–0.96) and the overall molar masses of PIL BCPs (*M_n* values from 5,000 to 20,100 g mol⁻¹). As indirect evidence for the formation of copolymers with no apparent homopolymer contaminant, analysis by

NMR DOSY showed only one room-temperature diffusion coefficient in CD_2Cl_2 , whereas a physical blend of the two homopolymers gave rise to two distinct diffusion coefficients.

The same team also reported the synthesis of ABC-type triblock copolymers by sequential ROMP (Entry 14, Table 4.1) [67, 68]. Triblock copolymers of similar composition (mass fraction: 26.4 wt% for the hydrophobic block A, 46.1 wt% for the PIL block B, and 27.5 wt% for the hydrophilic block C) and total chain length ($\overline{M}_n$ values from 20.8 to 22.8 kg mol^{-1}), but with different block sequences (ABC, CAB, ACB), were designed in this way. The two former compounds were used as membranes in gas permeation application (see section “Self-assembly at the Solid State and Related Transport Properties”).

Chemical Modification of Preformed Block Copolymers

This method uses well-defined and reactive BCP precursors; the structural characterization of which can be generally achieved prior to the modification of one block. As mentioned above, first PILs arranged in a BCP architecture were synthesized in this way, as reported in 2003 by Waymouth, Gast et al. (Entry 15, Table 4.1) [70, 81]. This was achieved from neutral polystyrene-*b*-poly(chloromethyl styrene) (PS-*b*-PCMS) BCPs ($\overline{M}_w/\overline{M}_n < 1.2$) obtained by NMP [79, 82], followed by functionalization with 1-methylimidazole. The obtained PIL BCPs were then subjected to anion exchange using sodium tetrafluoroborate (NaBF_4).

Later on, a few groups employed similar NMP-derived PS-*b*-PCMS BCP precursors to achieve PIL BCPs of different composition and study their self-assembling properties in bulk. For instance, Elabd et al. described a series of poly(styrene-*b*-4-vinylbenzyl-alkylimidazolium bis(trifluorosulfonyl)imide) (PS-*b*-PVBn-(alkyl)-ImTFSI) of various compositions ($\overline{M}_n$ ranging from 20,000 to 25,000 g mol^{-1} with 2.7–17.0 mol% PIL, $\overline{M}_w/\overline{M}_n < 1.26$) and carrying different alkyl groups (CH_3 , *n*- C_4H_9 , *n*- C_6H_{13}) (Entry 16, Table 4.1) [39]. Balsara et al. synthesized PS-*b*-PVBnBuImCl BCPs, with molar masses varying from 4 to 60 kg mol^{-1} ($\overline{M}_w/\overline{M}_n \sim 1.09$ –1.45) and that were further quaternized with *n*-butylimidazole (Entry 17, Table 4.1) [83].

By combining NMP and post-polymerization modification, Long et al. reported a series of papers on ABA-type triblock copolymer synthesis, with PIL as the mid-block, with a view at developing electromechanical transducers. For instance, imidazole groups of poly(styrene-*b*-[vinylbenzyl imidazole-*co*-*n*-butyl acrylate]-*b*-styrene) triblock copolymer were quaternized to introduce IL units (Entry 18, Table 4.1) [84]. The charge content was varied so as to tune the glass transition temperature (T_g) and the Young modulus of the material. Another example concerned the prior synthesis of difunctional poly(VBIm) ($\overline{M}_n$ value = 204 kg mol^{-1} , $\overline{M}_w/\overline{M}_n \sim 1.2$) from a difunctional NMP initiator, followed by the quaternization with an alkyl imidazole (Entry 19, Table 4.1) [49]. After anion exchange, from Br^- to Tf_2N^- , chain extension of this PIL precursor with styrene produced the targeted ABA triblock copolymer.

Elabd et al. quaternized poly(styrene-*b*-1-((2-acryloyloxy)ethyl)-3-butyl bromide) (PS-*b*-PBrEA) made by RAFT polymerization into poly(styrene-*b*-1-((2-acryloyloxy)ethyl)-3-butylimidazolium bis(trifluorosulfonyl)imide) (poly(S-*b*-AEBIm-TFSI) with *n*-butylimidazole (Entry 20, Table 4.1), which was followed by anion exchange [85]. $\bar{M}_n$ values of the resulting PIL BCPs ranged from 9,950 to 18,800 g mol⁻¹ with 6.6–23.6 mol% PIL, $\bar{M}_w/\bar{M}_n < 1.31$).

Combination of RAFT polymerization and post-chemical modification allowed Lodge et al. to derive ABA triblock copolymers. PS-*b*-PBrEA-*b*-PS copolymers, with BrEA corresponding to 2-bromoethyl acrylate, were first synthesized using a difunctional CTA [86]. The quaternization reaction was then performed using 1-butylimidazole to introduce the IL groups (Entry 21, Table 4.1). The final PS-*b*-PIL-*b*-PS triblock copolymers were characterized by an overall molar mass of 260 kg mol⁻¹ and a dispersity index of 1.21.

Segalman et al. modified an ATRP-derived poly(styrene-*b*-histamine methacrylamide) (PS-*b*-PHMA; $\bar{M}_n$ in the range 24,000–53,000 g mol⁻¹, $\bar{M}_w/\bar{M}_n < 1.3$) with trifluoroacetic acid, so as to generate a protic PIL (PS-*b*-PIL) featuring trifluoroacetate counter-anions for a use as ion-conducting materials (Entry 22, Table 4.1) [87].

As for Garcia et al., they chemically modified poly(styrene-*b*-2-vinylpyridine) (PS-*b*-P2VP; $\bar{M}_w/\bar{M}_n = 68,600$ g mol⁻¹ with a dispersity of 1.09; Entry 23, Table 4.1) by partial quaternization of the P2VP block with ethyl bromide [88]. Note that in this case, the resulting PIL BCP is a non-imidazolium-type compound. The same was true for the post-chemical modification of poly(2-vinylpyridine)-*b*-poly(methyl methacrylate) P2VP-*b*-PMMA (Entry 24, Table 4.1), grown by anionic polymerization and whose degree of substitution was varied [89]. The extent of quaternization of resulting compounds, denoted as [(P2VP-*r*-poly(1-ethyl-2-vinylpyridinium bromide))-*b*-PMMA], was in the range 7.5–37 %. Adding a methanolic solution of FeBr₃ onto the latter PIL BCPs led to paramagnetic materials, [(P2VP-*r*-poly(1-ethyl-2-vinylpyridinium Fe₃Br₁₀⁻))-*b*-PMMA].

Self-assembly in Solution

Only a handful of studies have focused on the self-assembly in solution of PIL BCPs. Use of a selective solvent of one block gives rise to micelle-like nanostructures. Interestingly, self-assembly of PIL BCPs can be triggered by a simple ion exchange, which relates to the ionic sensitivity of PILs [45, 90].

Pioneer works by Waymouth, Gast et al. evidenced the formation of elongated micelles in dilute toluene solution, from styrenic-based PIL BCPs shown in Entry 15, the PIL block arranging in a cylindrical morphology at the core [70, 81]. This was investigated both by small-angle neutron scattering (SANS) and dynamic light scattering (DLS). As the length of the IL core-forming block was increased, the conformation of the PS shell changed from a starlike to a brushlike arrangement, as depicted in Fig. 4.3. It was also shown that these micelles could sequester a few water molecules for each IL repeating unit.

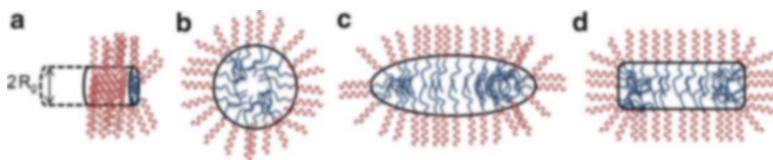


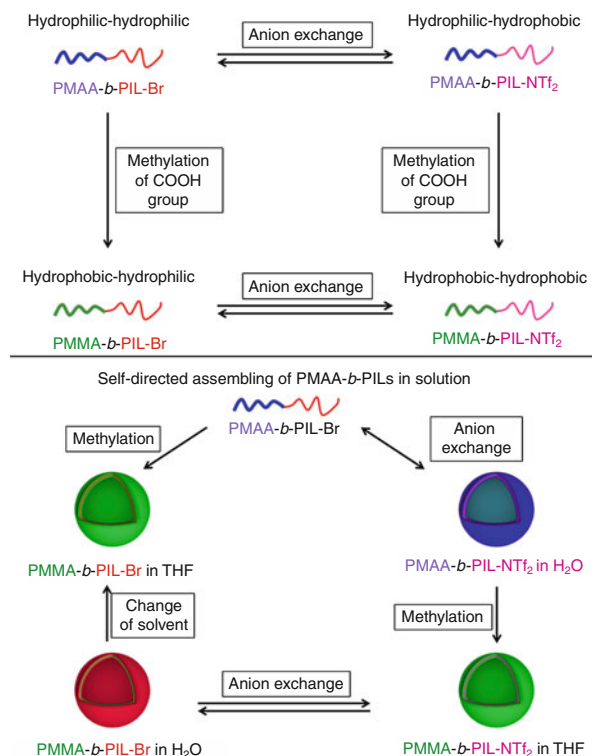
Fig. 4.3 Nanoassemblies obtained from PIL BCP (Entry 15, Table 4.1; PIL in red, PS in blue): (a) PS-PIL elongated micelles with (b) circular, (c) ellipsoidal, or (d) tablet-shaped cross sections (Adapted from Ref. [81])

Gnanou, Taton et al. investigated in details the self-assembly in solution of PIL BCPs shown in Entries 1 and 2 (Table 4.1) and took benefit of their anion-responsive behavior [53, 54]. Thus, anion exchange from Br^- to Tf_2N^- turned the solution properties of PIL blocks from hydrophilic to hydrophobic, forming water-soluble micellar aggregates. Studies by ^1H NMR, light scattering, and transmission electron microscopy (TEM) evidenced that compounds consisting of a hydrophilic mass fraction (f) around 35 ± 10 self-organized into direct or reverse polymersomes (=polymeric vesicles), as a function of the selective solvent used (water, methanol, or THF). Hydrodynamic radius of polymersomes ranged from 17 to 150 nm, depending on the composition of the copolymer. Compounds with $f > 45$ self-assembled into polymeric spherical micelles. For instance, anion exchange of the PIL block, from Br^- to Tf_2N^- – also referred to as TFSI – led to a vesicular morphology consisting of TFSI-based PIL blocks as the hydrophobic membrane stabilized by water-soluble PAm (or PMAA). The $\text{PAm}_{135}\text{-}b\text{-(PIL-TFSI)}_{12}$ sample possessing a hydrophilic mass fraction higher than 45 was found to self-assemble into spherical polymeric micelles. All these observations were consistent with the empirical classification of Discher and Eisenberg regarding the type of nanoparticles obtained by self-assembly of amphiphilic block copolymers of coil-coil type, as a function of the hydrophilic mass fraction [91]. Interestingly, this variation in solubility due to anion exchange was found to occur reversibly, so that a given self-assembled morphology could be unassembled and/or reassembled into another nanostructure. Moreover, chemical modification of the hydrophilic PMAA block allowed generating a hydrophobic PMMA, offering another means to manipulate nanostructures, not only in water but also in organic media, through a proper selection of the selective solvent of one block (Fig. 4.4).

More recently, Taton et al. looked at the self-assembling properties in solution of a particular *N*-vinylimidazolium-based and CMRP-derived PIL BCP, $\text{PVAc}_{213}\text{-}b\text{-PVBuImBr}_{33}$ (Entry 12, Table 4.1) [65]. This compound was found to generate aggregated spherical micelles in THF as selective solvent, with PIL blocks forming the core of these micelles, whereas the same diblock self-assembled into polymeric vesicles in water with PVAc blocks forming the hydrophobic membrane. The observed sizes indicated were very close to those determined by DLS in the same selective solvent (THF or H_2O).

The first example of a doubly responsive PIL/PNIPAM BCP was reported by Endo, Mori et al. (Entry 4, Table 4.1) [56]. As expected, introduction of poly

Fig. 4.4 Chemical manipulation either by anion exchange or by chemical modification of the PMAA block of PIL BCPs (Entries 1–2, Table 4.1) (Adapted from Ref. [54])

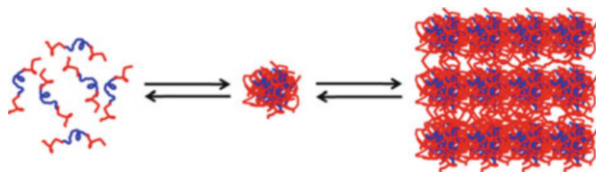


(1-(2-ethoxyethyl)-3-vinylimidazolium bromide) (PEtOEVI-Br) hydrophilic segment increased the LCST of the compound. In contrast, BCP containing more hydrophobic blocks, such as poly(1-(3-phenylpropyl)-3-vinylimidazolium bromide) (PPVI-Br) or poly(1-(6-ethoxycarbonylhexyl)-3-vinylimidazolium bromide) (PEHVI-Br), were insoluble in water at room temperature. The amphiphilic PNIPAM₉₁-*b*-PPVI-Br₉ BCP was found to self-organize into micelles consisting of a hydrophobic PIL core and hydrophilic shell of PNIPAM. In contrast, no detectable micelle was observed from the double hydrophilic PNIPAM-*b*-PEtOEVI-Br sample.

The same team evidenced that the star-block architecture shown in Entry 5 (Table 4.1) could form spherical micelles, which aggregated into dehydrated clusters at temperature above the LCST of PNIPAM [57]. The thermally induced phase separation behavior and self-assemblies in aqueous solution were found to depend on the sequence of each block (location of the thermoresponsive segment) along the arm star.

The ATRP-derived ABA-type symmetric PIL BCP (Entry 10, Table 4.1) reported by Texter et al. also exhibited both an ionic and a thermal responsive behavior, emanating from the PIL and the pluronic block, respectively [63]. In addition to exhibit “classical” surface activity, the amphiphilic compound also

Fig. 4.5 Multi-stimuli responsive micelle-like structures obtained from poly (ILBr-*b*-PO-*b*-ILBr) triblock copolymer (Adapted from Ref. [63])



immunized colloids against coagulation induced by electrostatic screening. It was also used as a wetting additive and was found to form a thermoreversible gel, with an LCST ranging from 0 °C to 50 °C (Fig. 4.5).

In the same vein, Tehnu et al. investigated the self-assembly in solution of their linear PIL BCPs shown in Entry 3 (Table 4.1) [55]. These compounds were not water soluble due to the bulky hydrophobic counter-anion. Core-shell micelles formed in pure water from amphiphilic samples featuring BF_4^- counterions, while double hydrophilic compounds with Br^- counterions showed a partial structural inversion in aqueous NaBF_4 , upon the thermal collapse of PNIPAM.

Investigations by DLS and turbidity measurements into the self-assembling properties of $\text{PNIPAM}_{50}\text{-}b\text{-PBVImBr}_{17}$ (Entry 7, Table 4.1) were reported by Wu et al. [59]. Furthermore, FTIR in combination with two-dimensional correlation spectroscopy (2Dcos) and the perturbation-correlation moving-window (PCMW) technique allowed studying the micro-dynamics of micelle-like structures. Micelle formation consisting of a core of PBVImBr and a shell of PNIPAM was again evidenced. The increase of the phase transition temperature was attributed to the dehydration of alkyl chains of the PIL. A greater hysteresis was also observed during the heating-cooling cycle. This was explained by the existence of hydrogen bonds among the micelles (intermicellar interactions) formed upon heating and that could be hardly disrupted. Hence, the recovery hydration process involving C–H groups upon cooling was prevented, due to the compact micellar structure. Intramicellar hydrogen bonding developing at room temperature was also suggested.

Another example of self-assembly from doubly responsive PIL/PNIPAM BCP was reported by Yuan, Antonietti et al. (Entry 6, Table 4.1) [58]. The authors took benefit of the $(\text{CN})_2\text{N}^-$ counter-anion generated by anion exchange from parent bromide-containing PIL and made use of the resulting dicyanamide-containing PIL as carbon precursor. With this counter-anion, indeed, polymeric carbon framework was better preserved at elevated temperatures during the carbonization step.

Self-assembly at the Solid State and Related Transport Properties

As already mentioned, PIL BCPs enable an access to a range of nanostructured morphologies at the solid state, where the ion-transporting and the nonionic blocks segregate in ordered nanodomains. In this regard, PILs behave as single-ion conductors with IL moieties as pendant groups and mobile counterions, making PILs good candidates as solid polymer electrolytes [46, 92]. For instance, strong

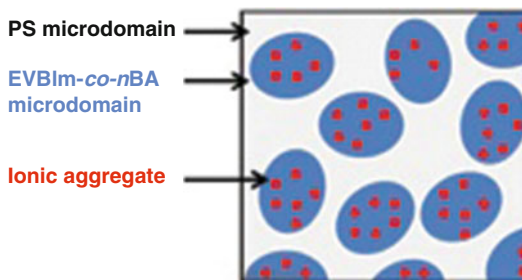
microphase separation and large nanodomain width (lower number of interfaces) are expected to favor high conductivity. However, optimal properties require that a balance between ionic conductivity and mechanical strength is found.

The ion conduction behavior of PS-*b*-poly(1-(4-vinylbenzyl)-3-alkylimidazolium TFSI; Entry 16, Table 4.1), as a function of morphology in the microphase-separated structure, was studied by Elabd, Mahanthappa et al. [39]. Morphologies at the solid state were examined both by temperature-dependent synchrotron small-angle X-ray scattering (SAXS) and TEM. These PIL BCPs were found to self-assemble into a hexagonally packed cylindrical morphology for a composition in PIL lower than 7.1 mol%. A lamellar morphology was observed above 17.0 mol%, and a blend of cylinders and lamellae was evidenced between these two compositions. Comparable values of ionic conductivity ($1.0 \times 10^{-4} \text{ S cm}^{-1}$ at 150°C) were determined by electrochemical impedance spectroscopy (EIS), regardless of the imidazolium alkyl substituent. However, ionic conductivity increased by an order of magnitude when the PIL content increased from 8.6 mol% to 17.0 mol%. Another fivefold conductivity enhancement was noted for higher mol. fraction in PIL. The conductivity dropped off by more than an order of magnitude, from the lamellar sample ($1.0 \times 10^{-6} \text{ S cm}^{-1}$ at 90°C) to the sample showing the coexistence of lamellae + hexagonally packed cylinders ($3.2 \times 10^{-7} \text{ S cm}^{-1}$ at 90°C ; 8.6 mol% in PIL). This was explained by the lack of connectivity of the discontinuous cylindrical mesophase, where grain boundaries might act as morphological defects impeding conductivity. Ionic conductivity values were also dramatically dependent on BCP processing method: solvent casting providing well-ordered morphologies versus melt pressing giving rise to more poorly ordered mesophases.

Similar PIL BCPs, but with chloride as counter-anion, i.e., PS-*b*-poly(1-(4-vinylbenzyl)-3-butylimidazolium chloride) (Entry 17, Table 4.1), were investigated by Balsara et al. [83]. These compounds were also compared with PS-*b*-poly(1-(4-vinylbenzyl)-3-trimethylammonium chloride) compounds. All samples exhibited a lamellar organization, regardless of the volume fraction (ϕ), which ranged from 0.35 to 0.60. The authors observed that the scaling of domain size with chain length was weakly dependent on the nature of the bound cation (trimethylammonium vs. butylimidazolium). Slightly higher conductivity values were determined compared to PIL BCPs studied by Elabd et al. [39]. For a given sample ($\overline{M}_n$, PS = 27 kg mol^{-1} and $\overline{M}_n$, PIL = 21 kg mol^{-1}), the conductivity increased with time and temperature, from $1.8 \times 10^{-3} \text{ S cm}^{-1}$ at 22°C to $3.1 \times 10^{-3} \text{ S cm}^{-1}$ at 40°C . Exchange from chloride to hydroxide anions allowed increasing the conductivity of PIL BCP membranes by a factor of 10. This result was explained by a higher diffusion of hydroxide ions (ratio of diffusion coefficients of HO^- and Cl^- in water: $D_{\text{HO}}/D_{\text{Cl}} \approx 3$) and also likely to some differences of condensation and hydration of counterions. However, some degradation was noted with PIL BCPs with the hydroxide ions, presumably owing to the formation of bicarbonate ions (HCO_3^-) formed in contact with atmospheric CO_2 .

Long et al. also evidenced microphase separation at the solid state for their poly(Sty-*b*-[EVBIIm-*co*-*n*BA]-*b*-Sty) ABA-type triblock copolymers (Entry 18, Table 4.1). A rather limited long-range order was yet noted, which was attributed to a relatively

Fig. 4.6 Proposed morphology of the self-assembled poly(Sty-*b*-[EVBI_m25%-co-*n*BA75%]-*b*-Sty) triblock copolymer (Adapted from Ref. [84])



high dispersity value ($\mathcal{D} \sim 1.40$) [84]. PS-type external A blocks allowed for mechanical reinforcement, while the central statistical copolymer B block provided ionic conductivity. These properties could also be tuned by doping the material with 20 % mol. of an exogenous molecular IL. Ionic conductivity values were in the range 5×10^{-4} – 5×10^{-6} S cm⁻¹ at 90 °C. Observation of a second scattering peak at $q \sim 1.8$ nm⁻¹ was ascribed to aggregation phenomena occurring between ion-rich domains. The proposed morphology is shown in Fig. 4.6.

The same team designed the poly(styrene-*b*-[vinylbenzyl imidazolium TFSI]-*b*-styrene) triblock copolymer (Entry 19, Table 4.1) for a use as electromechanical transducer [49]. A modulus of approximately 100 MPa at 23 °C was determined by dynamic mechanical analysis for this PIL BCP. Addition of 1-ethyl-3-methylimidazolium triflate, as molecular exogenous IL, allowed reducing the T_g of the central block and increasing ionic conductivity by an order of magnitude for 20 wt% and an additional order of magnitude for 40 wt% IL (a value of 1×10^{-2} S cm⁻¹ at 90 °C was determined in the latter case). In addition, actuator testing revealed superior curvature relative to Nafion®. It was found, however, that the presence of both homoPIL and diblock copolymer limited precise and long-range ordered microstructure formation.

With both PMMA-*b*-PIL BCPs having TFSI anions (Entry 8, Table 4.1), and random copolymer homologues as well, Elabd, Winey et al. studied the effect of the weak microphase separation in ion transport [60]. SAXS and TEM analyses evidenced a microphase-separated morphology for the PIL BCP, but with no long-range order, likely owing to the partial affinity between the PIL and the PMMA blocks. The interdomain distances were 18 nm and 21 nm, for BCPs made of 13.4 and 15.7 mol% in PIL, respectively. In contrast, random copolymer homologues did not show any microphase separation, as expected. At similar PIL compositions, the ionic conductivity of the PIL BCPs was 2 orders of magnitude higher than that of the random copolymers (6.3×10^{-6} vs. 1.0×10^{-7} S cm⁻¹ at 150 °C), demonstrating that local confinement of conducting ions in nanoscale ionic domains – despite a weak segregation regime – can favor ion transport.

In another contribution, the same PIL BCPs were evaluated for hydroxide (HO⁻) conductivity [61]. Parent compounds carrying bromide anions were employed to this end. A nanoscale morphology was observed at 30 °C, in both dry and relative humidity conditions (from 30 % to 90 % RH). Hydroxide-exchanged PIL BCPs

showed only two broader scattering peaks, compared to the bromide counterparts exhibiting four peaks. The HO^- conductivity ($25 \times 10^{-3} \text{ S cm}^{-1}$ at 80°C , 90 % RH) was one order of magnitude higher, not only than that of the random copolymer analogue but also than that of the homoPIL analogue with the same IL composition and water content. This was again explained by the ion-water confinement in nanodomains that might accelerate transport.

The same group showed that, at comparable PIL composition, acrylate-based poly(Sty-*b*-AEBIm-TFSI) PIL BCPs (Entry 20, Table 4.1) are strongly microphase separated. In addition, these compounds exhibited $\sim 1.5 - 2$ orders of magnitude higher ionic conductivity than their methacrylate-based homologues with weak microphase separation described above [85]. Hence, a higher degree of incompatibility between the low T_g PIL and the nonionic PS block improved ion transport properties. Hexagonally packed cylinders, lamellae, and coexisting lamellae and network morphologies were observed, as a function of PIL composition (6.6 – 23.6 PIL mol%). The measured interdomain distances of the lamellar morphology were in the range of 25–30 nm. These morphologies were also found sensitive to casting conditions. Increasing the PIL content increased the ionic conductivity, owing to a morphological transition, from hexagonally packed cylinders with 1-D conducting pathways to lamellae with 2-D conducting pathways. In addition, the transition from 2-D lamellar morphology to coexisting 2-D lamellae and 3-D continuous conducting network structures further increased ionic conductivity ($88 \times 10^{-5} \text{ S cm}^{-1}$ at 150°C in the latter case, corresponding to 23.6 PIL mol%). Overall, these acrylate-based PIL BCPs exhibited better conducting performances than PS-based PIL BCPs, highlighting the importance of the chemical nature of PIL.

Gin, Bailey et al. investigated in details the self-assembling properties in bulk of 16 ROMP-derived copolymers (Entry 13, Table 4.1) with variable volume fraction of the poly(norbornene dodecyl ester) block ($f_{\text{DOD}} = 0.42\text{--}0.96$; $\overline{M}_n$ values ranging from 5,000 to 20,100 g mol^{-1}) [48, 66]. SAXS and rheological measurements at 25°C showed the classic equilibrium self-assembled BCP morphologies, including lamellae, hexagonally packed cylinders, and spheres on a body-centered-cubic lattice. Even PIL BCPs having relatively low molecular weights exhibited a long-range ordered and stable morphology showing diffraction patterns with numerous higher order reflections by SAXS.

However, the bicontinuous gyroid phase occupying that region with traditional BCPs – and often sought for transport-related applications – was not observed in any sample. Instead, coexistence of cylinders and lamellae was identified at the intersection of hexagonal and lamellar regions. Poorly defined liquid-like packing of spheres was also noted in most asymmetric samples. The absence of the bicontinuous gyroid morphology and difficulties in accessing order-to-disorder transitions were attributed to the strong microphase separation of such PIL BCPs.

The first examples of self-assembled ABC-type triblock copolymers (A, hydrophobic block; B, PIL block; and C, hydrophilic block; Entry 14, Table 4.1) were described by Gin et al. [67]. SAXS analysis of these samples verified phase separation on the nanoscale and formation of different ordered morphologies,

depending on block sequence and compositions. ABC- and ACB-type triblock compounds were found to self-assemble into a lamellar phase, while the CAB-type BCP generated a hexagonally packed cylinder morphology. Interdomain spacings for the three compounds were very similar (i.e., ABC, 26.2 nm; CAB, 28.6 nm; ACB, 24.7 nm).

PIL BCPs reported by Segalman et al. were prepared by deprotonation of histidine moieties of nonPIL precursors based on PS and poly(histamine methacrylamide) (PHMA) with trifluoroacetic acid (TFA) [87]. SAXS and TEM analyses evidenced that, after thermal annealing above T_g (210 °C) under vacuum, hexagonally packed PHMA cylinders formed from the precursor materials containing between 8 and 20 wt% PHMA, while lamellar morphologies were observed for BCPs between 32 and 54 wt% PHMA. A change of domain sizes was noted after chemical modification with TFA, resulting in PIL BCPs shown in Entry 22 (Table 4.1). This was ascribed to a higher incompatibility between the PS and the PIL blocks, likely due chain stretching of histidinium-type chains, as well as to an increase in volume fraction of the as-derivatized PHMA. A higher water affinity of conducting blocks was also noted. While PS-*b*-PHMA membranes had conductivities up to $2 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature, conductivities resulting from PIL BCPs increased by an order of magnitude, presumably owing to a higher mobility of PIL chains.

SAXS patterns of the CMRP-derived PVAc₁₇₉-*b*-PVBuImBr₄₃ (Entry 12, Table 4.1) synthesized by Taton et al. showed a highly ordered lamellar organization [65]. The long-range order was also indicative of a strong microphase separation between the two blocks, with PIL chains likely exhibiting a high degree of chain stretching leading to rather large interdomain domain spacings (39 nm). TEM characterization of the PVAc₁₇₉-*b*-PVBuIm(Tf₂N)₄₃ PIL BCP obtained by anion exchange of the former compound also showed a lamellar mesostructure. Interestingly, suppression of the second order reflection in this sample, over a large temperature range, strongly suggested a symmetric volume fraction ($f_v \approx 0.5$) for this particular copolymer. Finally, SAXS experiments were also performed with both the di- and symmetric triblock copolymers, PVAc-*b*-PVEtImBr and PVAc-*b*-PVEtImBr-*b*-PVAc (see Entry 12). The presence of well-defined peaks at q/q_x ratios of 1, 2, 3, and 4 in a temperature range of 30–220 °C unambiguously indicated that, again, both architectures self-organized in bulk into lamellae, with a very similar phase behavior. However, a small difference in interdomain spacings (11.1 vs. 10.4 nm, for the triblock and its parent diblock sample, respectively) was determined, consistently with predictions by Matsen et al. [93].

In order to vary the lamellar interdomain sizes of their self-assembled pyridinium-type PIL BCPs (Entry 23, Table 4.1), Garcia et al. exploited the anion exchange method (see Fig. 4.7) [88]. Neutral PS-*b*-P2VP BCPs were first partially quaternized (20 mol% of the 2-VP units) with 1-bromoethane, and Br[−] anions were exchanged with larger-sized anions, such as TFSI[−] or CF₃(CF₂)₃SO₃[−]. All compounds, with Br[−], TFSI[−], and CF₃(CF₂)₃SO₃[−] anions, exhibited a lamellar morphology; the lamellar domain size of which varied from 34 nm to 48 nm and further to 73 nm, from the Br[−] to the TFSI[−] to CF₃(CF₂)₃SO₃[−] BCP compound, respectively.

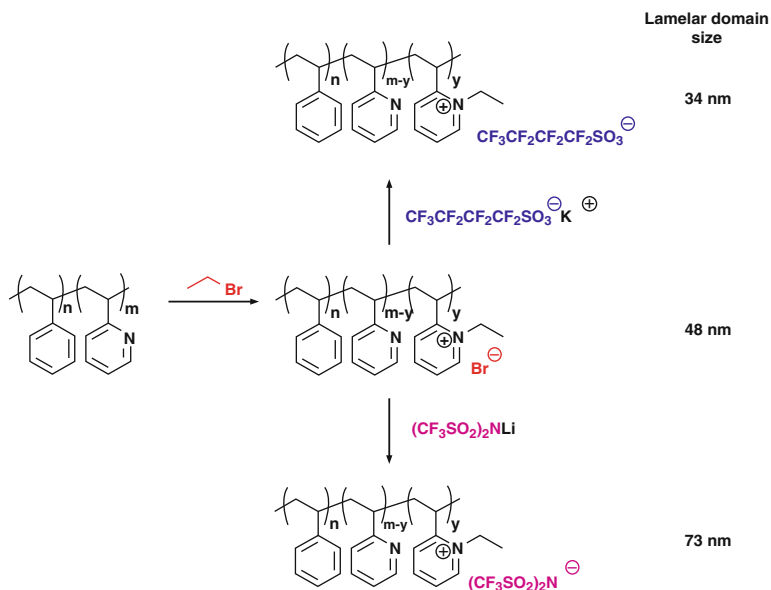


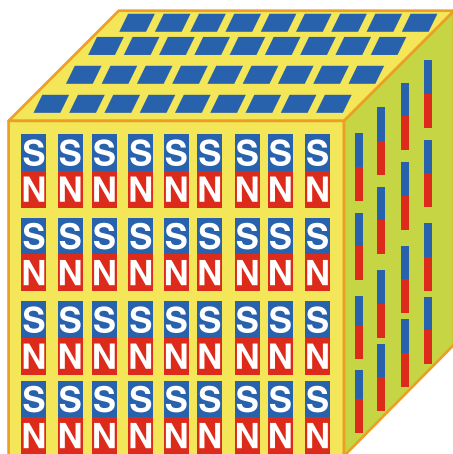
Fig. 4.7 Modification of lamellar domain sizes in pyridinium PIL BCP via anion exchange (Adapted from Ref. [88])

In another contribution, Garcia et al. used the same strategy by using FeBr_3 to obtain a paramagnetic $[(\text{P2VP}-r\text{-poly}(1\text{-ethyl-2-vinylpyridinium } \text{Fe}_3\text{Br}_{10}^-))\text{-}b\text{-PMMA}]$ (Entry 24, Table 4.1) [89]. This other non-imidazolium precursor was then blended with an epoxy resin (30 wt% relative to epoxy) and cured, which resulted in a spherical nanostructure, with sphere sizes of approximately 16 nm (by TEM). This led to the formation of a magnetic nanostructured thermoset material free of any kind of metal oxide or metal magnetic nanoparticles. The magnetic properties were measured by superconducting quantum interference device (SQUID). The spherical nanostructuration combined with confinement of magnetic anions (Fig. 4.8) allowed promoting strong dipolar interactions between the magnetic entities and the observed ferromagnetic ordering.

Potential Applications of PIL BCPs

As already emphasized, PILs and related BCPs have emerged as a versatile family of polyelectrolytes showing multiple advantages, such as tunable solubility, adjustable chain flexibility, relatively high ionic conductivity, or ionic responsiveness. This section briefly discusses the very few and preliminary investigations regarding PIL BCPs' applications in selected fields, such as energy harvesting, gas separation, or precursors for magnetic or nanostructured carbon materials.

Fig. 4.8 Schematic representation of the thermoset magnetic material based on PIL BCP (Adapted from Ref. [89])



Energy Conversion Devices

Due to their relatively high ionic conductivity, which can be tuned by a proper selection of both the alkyl substituent on the imidazolium ring and the counter-anion, PILs are promising materials as solid polymer electrolytes for various electrochemical devices (actuators, transducers, fuel cells, ion-conducting membranes, or solar cells) [94–102]. Ion-conducting membranes are key components in energy conversion devices, since they not only enable the transport of ionic species across physically separated reaction sites, but they also provide structural stability and barrier properties to the device. As emphasized in section “[Self-assembly at the Solid State and Related Transport Properties](#)”, microphase-separated PIL BCPs represent a promising method to develop mechanically robust nanostructured materials (via the nonionic block, preferentially of high T_g), while the PIL domains can form connecting paths for ion conduction (this is particularly favored with low T_g PILs). However, specific nanodomains (e.g., hexagonally packed cylinders) impede ionic conductivity due to grain boundaries [39], whereas larger size nanodomains (e.g., in lamellar morphologies) favor ion transport. Other parameters can influence conductivity of PIL BCPs, such as the type of counterion, relative humidity, temperature, or use of an exogenous IL. In different cases, the temperature dependence of the ionic conductivity was well described by the Vogel-Tamman-Fulcher (VFT) model, indicating a strong correlation between ion conduction and polymer segmental dynamics [39, 49, 60, 61, 83–85, 87]. These effects on ionic conductivity of some PIL BCPs have been discussed in section “[Self-assembly at the Solid State and Related Transport Properties](#)”.

Armand, Gimes et al. integrated their P(STFSiLi)-*b*-PEO-*b*-P(STFSiLi)s, BAB triblock copolymers (Entry 11), as solid polymer electrolytes in real lithium batteries [50]. Corresponding devices exhibited unprecedented performances in this application: the best ionic conductivity of $1.3 \times 10^{-5} \text{ S cm}^{-1}$ was obtained at about 20 wt% P(STFSiLi) (molar ratio [EO]/[Li] = 30) at 60 °C, and the mechanical properties were significantly improved compared to a neutral PS-*b*-PEO-*b*-PS triblock copolymer

electrolyte (10 MPa vs. 1 MPa at 40 °C, respectively). This work opens avenue for the development of energy device based on the PIL BCP discussed in this chapter.

PIL BCPs for Gas Separation

ILs and PILs represent promising materials for CO₂ capture, storage, and conversion and for gas separation applications in general [34–36, 103–106]. These features combined with the potential of nanophase separation on transport properties make PIL BCPs potential candidates for gas separation. Lodge et al. evaluated the separation performance of their triblock copolymer ion gel, PS-*b*-PBrEA-*b*-PS (Entry 21, Table 4.1), on a microporous PVDF membrane (0.45 μm pore size, 75 % porosity), at room temperature [86]. The pores of the PVDF membranes were filled with ion gels containing 15 wt% of the triblock to form a dense, dry membrane. The BCP ion gel showed a permselectivity of 19 for CO₂/CH₄ and 39 for CO₂/N₂ gas pairs. The permeability of each gas (CO₂, N₂, CH₄) was roughly the same in the presence or in the absence of another gas (e.g., CO₂ = 985 ± 29 vs. CO₂ in the presence of N₂ = 1030 ± 24 vs. CO₂ in the presence of CH₄ = 1040 ± 23).

Gas transport through phase-separated ROMP-derived PIL BCPs (71, 42, 31 and 18 wt% IL units, respectively; entry 14, Table 4.1) was also investigated by Gin, Noble et al. [67]. Preparation of defect-free, thin-film membrane composites, with a 3–20 μm thick nanostructured top layer of the BCP, could be achieved. The composition of the BCP top layer was found to impact the CO₂ permeability that could be increased by 2 orders of magnitude up to a value of 9,300 barrers. This beneficial effect on the CO₂ permeability was attributed to a higher gas diffusion coefficient of the ordered nanostructures arising from PIL BCPs, compared to amorphous BCP compounds. However, the selectivity was not improved since the diffusion of both CO₂ and N₂ was favored by the nanostructuration. The use of an additional molecular IL might be helpful to gain in selectivity.

The same group reported the first example of membrane nanocomposites issued from ABC PIL-based triblock copolymer (Entry 14, Table 4.1) [68]. Only the ABC- and CAB-type sequences were successfully coated onto the surface of a commercial porous poly(acrylonitrile) membrane support, forming hybrid membranes; the potential of which for CO₂/light gas separations was examined on a series of four gases (i.e., CO₂, N₂, CH₄, H₂). The two phase-separated systems showed different gas permeability values but similar selectivity values (Table 4.2). This was ascribed to different polymer nanostructures and/or nanodomain orientation.

Table 4.2 Gas permeabilities (in barrers) and selectivities of ABC- and CAB-type triblock copolymer composite membranes. Thickness of the active layers were, respectively, 12.4 μm and 12.6

	Perm (CO ₂) [barrers]	Perm (N ₂) [barrers]	Perm (CH ₄) [barrers]	Perm (H ₂) [barrers]	α(CO ₂ / N ₂)	α(CO ₂ / CH ₄)	α(CO ₂ / H ₂)
ABC	2,340	230	820	740	10.2	2.9	3.2
CAB	410	30	100	140	13.7	4.1	2.9

As Precursors for Nanostructured Carbon

Imidazolium-based ILs and PILs have been reported as effective precursors for functional carbon-based nanomaterials [107–109]. Incorporation of molecular ILs into porous templates, without the need for high pressure, can be easily achieved owing to the liquid state and the highly thermostability of ILs.

Antonietti et al. reported that PIL BCPs (Entry 6, Table 4.1) could serve as efficient precursors for the preparation of mesoporous graphitic nanostructures in the presence of metal salts [58]. The carbonization step was carried out in the presence of 10 wt% of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, leading to porous carbon products, after 2 h at 1,000 °C under N_2 atmosphere. Compounds prepared with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ exhibited a surface area of 150 and 175 m^2/g , respectively. TEM images revealed layered graphitic nanostructures, constructed from the stacking of graphene sheets with a d spacing of 0.34 nm. XRD characterizations revealed the existence of iron carbide phases as nanoparticles with a size range of 10–80 nm within the mesoporous graphitic carbon products. Same observations were made using chromium carbide. These mesoporous graphitic nanostructures are promising candidates for electrochemical applications.

Conclusion

In the past decade, the fields of ionic liquids (ILs) and of block copolymers (BCPs) have been cross-fertilized through the introduction of ILs and polymeric ionic liquid (PIL) segments into BCPs. PIL BCPs combine intrinsic properties of PILs, such as relatively high CO_2 gas solubility, ion conductivity, thermal stability, and tunable solubility, thanks to ion exchange, with the ordered phase-separated nanostructures formed by self-assembly of BCPs. From a synthetic viewpoint, structurally “tailor-made” PIL BCPs can be obtained either by direct, sequential “controlled/living” chain polymerization (e.g., ATRP, NMP, RAFT, CMRP, ROMP) of IL-type monomers or by post-chemical modification enabling the introduction of IL units side groups onto a preformed and reactive BCP precursor. These synthetic tools allow fine-tuning block composition, IL content, type of counterion, and alkyl chain. Both the thermomechanical properties and the ionic conductivity can thus be tailored by a judicious selection of these parameters.

On one hand, the possibility to achieve multiresponsive, robust, and stable nanostructures from PIL BCPs in solution opens avenues for their use in areas such as micellar catalysis and drug delivery systems. On the other hand, several studies have evidenced that transport properties of PIL BCPs correlate with their nanostructured morphologies resulting from their self-assembly at the solid state. As for traditional self-assembled materials, processing conditions (e.g., solvent casting vs. melt casting) influence phase segregation and resulting size and nature domains, which can have a significant impact on ionic conductivity and/or gas transport. Higher conductivities may be reached by increasing the size of the conducting channels, e.g., in lamellar domains where PIL chains can adopt a

stretched conformation. In contrast, PIL BCPs self-assembling into hexagonally packed cylinders may exhibit a rather a poor ionic conductivity owing to defects and grain boundaries of this peculiar morphology. None of the studies reported so far has established the existence of the bicontinuous gyroid morphology, which would be of particular interest for gas or ion transport-related applications. This is presumably due to the strong microphase segregation regime resulting from the covalent association of nonionic and PIL blocks that have been so far considered. However, further efforts may be needed to achieve the gyroid morphology, for instance, using specific solvent and/or thermomechanical treatments.

The field of PIL BCPs is still in its infancy, and pioneer works described in this chapter may help for an optimization of their transport and mechanical properties. There is still plenty of room to design and engineer novel compounds and, for instance, to introduce new functionalities via the PIL and/or the uncharged blocks toward specific applications. One can thus expect that this field will blossom in the next few years.

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Ionic Liquids and Polymeric Ionic Liquids as Stimuli-Responsive Functional Materials

5

John Texter

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Abstract

The anion recognition-based stimuli responsiveness of ionic liquids (ILs) and polymerized ionic liquids (PILs) is presented in the context of various association structures formed by these functional materials, and their responsiveness is characterized by ordered Hofmeister series. Gels and gelation, critical solution temperatures, and diverse applications including dispersion phase transfer and osmotic sphere and osmotic brush stabilization are discussed and illustrated.

Keywords

Anion recognition • Hofmeister series • Gels • Gelation • LCST • UCST • Osmotic sphere • Osmotic brush • Dispersion phase transfer • Dispersion stabilization

J. Texter (✉)

School of Engineering Technology, Eastern Michigan University, Ypsilanti, MI, USA

e-mail: jtexter@emich.edu

Introduction

Stimuli-responsive materials have been of intense interest now for many decades and have been referred to differently over these past several decades as smart materials, intelligent materials, designer materials, and functional materials, among other appellations. Such materials date back to the origins of photographic and magnetic storage materials, and the bioconjugation of diverse targeting moieties to nanoparticles carrying drug cargo represents the present frontier in nanoparticle research and development. In this volume we focus on ionic liquids, and in this review we focus on a subclass of ionic liquids and of polymeric ionic liquids (polymers derived from ionic liquid monomers) that are stimuli responsive and provide particular types of functionality.

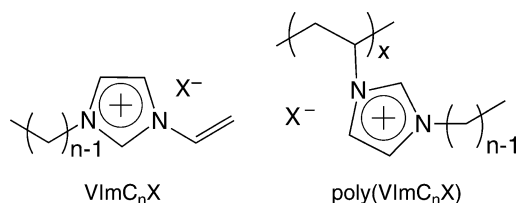
Ongoing efforts at creating smartness and stimuli responsiveness in polymer design and synthesis are providing basis for advanced materials that exhibit switchable poration in membranes and coatings, reversible particle formation, and thermodynamically stable nanoparticle dispersions, polymers that provide chemomechanical switching, and nanomaterials that adapt to changing environments. We focus on a subset of materials derived from ionic liquids (ILs) and polymerized ionic liquids (PILs) that exhibit stimuli responsiveness. By stimuli responsiveness we mean that some significant property of the associated materials changes upon exposure to some intensive (temperature, chemical potential) or extensive (stress) field (stimulus).

ILs and PILs have been intense research topics for about 20 and 10 years, respectively. The general topic of ionic liquids, organic salts that melt below 100 °C, has of this writing generated over 40,000 published documents and has been extensively reviewed [1–9]. Room-temperature ionic liquids (RTIL) [10–13] are of even greater interest because of their range of possible applications. Since such materials are composed of ion pairs (or multiple cation-anion pairings), they are intrinsically ion responsive because solubility can easily be tuned by varying ionic structure. A variety of other types of stimuli responsiveness can be associated with IL, and these include thermoreversibility, critical solution temperature, pH, magnetic, and other phenomena. When such ILs are used to compose new polymers, the resulting polymers will often also exhibit similarly responsive phenomena as well as new phenomena that do not emanate from the respective monomers, but only from their association structures or polymerized structures. The solvent and anion exchange stimuli responsiveness of PIL was recognized in the early work of Mecerreyes and co-workers [14] and of Yan and Texter [15, 16], wherein both the tendency for a particular anion to solvophilically or to solvophobically ion pair with an imidazolium counter ion [10] and the tendency for a particular anion-imidazolium ion pair to be solvated or not in a particular solvent [16] were observed to generate interesting stimuli responses, such as phase transfer following anion exchange and reversible gel-open cell porous material transitions by so-called spinodal decomposition. Many of these PILs and their applications have been reviewed [17–25]. In the following we partition our discussions into sections on association structures, ion sensing, gels, dispersion phenomena, wetting, magnetic ILs, and outlook.

Association Structures

Many of the most interesting responses exhibited by IL and PIL are related to the association structures formed by such moieties before and after being subjected to a stimulus. Since chemical potential is an intensive field variable [26], in addition to temperature and other fields (e.g., electrical and magnetic), the self-association of IL is itself a stimuli-responsive property. In this connection we can see how a basic property such as solubility is related to stimuli-responsive behaviors. While IL and PIL exhibit effectively no or very, very low vapor pressure, their behavior as solutes and as solvents may be thought of as classical. From this point of view, self-association, micellization [27], and microemulsion [28] formation is well founded experimentally and theoretically. Similarly, the formation of lamellar and other mesophases has been documented.

Solubility. The seminal paper of Mecerreyes and co-workers [14] set precedent for much of what is discussed in the sequel. They found that for two homopolymers, poly(VImC₂X) and poly(VImC₄X), that solubility varied significantly with the particular anion X[−] and with the particular solvent (water, methanol, acetone, THF, ethyl acetate, and VC₂ImTf₂N [Tf₂N[−] ↔ (CF₃SO₂)₂N[−]]). Of the anions examined, only Cl[−] and Br[−] yielded water-soluble homopolymers; BF₄[−], PF₆[−], ClO₄[−], CF₃SO₃[−] (Tf[−]), (CF₃SO₂)₂N[−], and (CF₃CF₂SO₂)₂N[−] yielded water-insoluble homopolymers. The homopolymer poly(VC₂ImX) was soluble in VC₂ImTf₂N for X[−] = Br[−], BF₄[−], and PF₆[−] and insoluble for X[−] = Tf[−], Tf₂N[−], and (CF₃CF₂SO₂)₂N[−].



Micellization. Imidazolium-based IL surfactants are known to be very sensitive to anions, and this sensitivity provides a significant form of stimuli responsiveness. The behavior of three imidazolium bromide surfactants, C_nImC₄Br (*n* = 8, 10, and 12) in EAN (ethylammonium nitrate, an RTIL), has been described [29], and effects of counterion basicity and chain length were investigated. The synthesis of C₁₄ImC₄Br has also been reported [30, 31]. The effects of various anions on the *cmc* and other aggregation-related effects of aqueous C₁₂ImC₁Br were found to follow a Hofmeister series in the order I[−] < Br[−] < NO₃[−] < Cl[−] with respect to increasing the *cmc* and micellar ionization [32]. Other important anions in modifying imidazolium surfactants include BF₄[−], PF₆[−], CF₃SO₃[−], and N(CN)₂[−] [22, 33]. These imidazolium-anion-based interactions have been examined in the context of various supramolecular complexes [34], exchange resins [35], and approaches to quantitative analyses [36] that emanate from imidazolium-anion pairing.

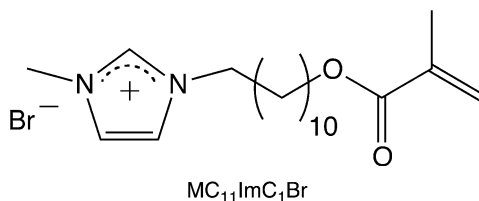
The micellar properties of 1-alkyl-3-methylimidazolium chlorides have been reported for C_nImC₁Cl with *n* = 10, 12, 14, and 16 [37]. The *cmc*'s ranged from

about 1–40 mM as chain length decreased. Bara et al. reported the characterization of 20 Gemini imidazolium-based surfactants [38]. Bromide and tetrafluoroborate salts were prepared, and the resulting liquid-crystalline phases were characterized by x-ray scattering and polarized light microscopy. Mono and Gemini imidazolium-based aromatic ether cationic surfactants have been prepared using 4-hydroxy benzoic acid [39], where the benzoic acid is converted to the methyl ester followed by *O*-alkylation with long-chain alcohols and by reduction and bromination to yield 4-alkoxy benzyl bromides. *N*-Methylimidazole is then quaternized with this benzyl bromide to obtain the mono-surfactants. Geminis are obtained by reacting the benzyl bromides with imidazole followed by quaternization with dibromoalkanes. The Gemini 1,4-bis(3-tetradecylimidazolium-1-yl) butane dibromide has been reported [31], and homologous decyl, dodecyl, and tetradecyl dibromides have been prepared and compared to the corresponding $C_n\text{ImC}_4\text{Br}$ for $n = 10, 12$, and 14 [40]. The *cmc*'s for the Geminis were much lower than the *cmc*'s of the mono imidazolium surfactants. Gemini imidazolium-based surfactants and pyridinium-based surfactants with thioether spacers have very recently been described and characterized [41, 42].

Polymerizable IL surfactants are a new type of surfmer, and these compounds are leading to the development of many new stimuli-responsive polymers and materials [17, 21]. These new materials include elastic conducting thin films, open cell porating monoliths [15, 16] and thin films, and stimuli-responsive block copolymers, including a new class of thermoreversible (LCST) gelating lyotropic liquid-crystalline mesophases [43].

Microemulsions. An early review of ionic liquids in microemulsions [28] included cases wherein IL was substituted for an oil in water/IL/surfactant microemulsions [44–46], IL was substituted for water in IL/oil/surfactant microemulsions [47–49], and IL was substituted for surfactant in water/oil/IL microemulsions [15, 16, 50, 51].

Yu et al. [52] have followed the IL-stabilized microemulsion polymerizations of Yan and Texter [15, 16] by synthesizing the methacrylate analogue of $\text{AC}_{11}\text{ImC}_1\text{Br}$, $\text{MC}_{11}\text{ImC}_1\text{Br}$. This new surfmer was used to stabilize microemulsions of styrene and $\text{C}_4\text{ImC}_1\text{BF}_4$. A microemulsion of these components comprising 30 % (w/w) $\text{C}_4\text{ImC}_1\text{BF}_4$, 47 % styrene, 23 % $\text{MC}_{11}\text{ImC}_1\text{Br}$, and about 3 % (relative to styrene and $\text{MC}_{11}\text{ImC}_1\text{Br}$) DVB (divinylbenzene) as cross-linker was polymerized at 60 °C using AIBN as thermal initiator. The resulting transparent and flexible membrane about 80 μm thick was physically characterized. Its intrinsic electrical conductivity exceeded 10 mS/cm at 140 °C.



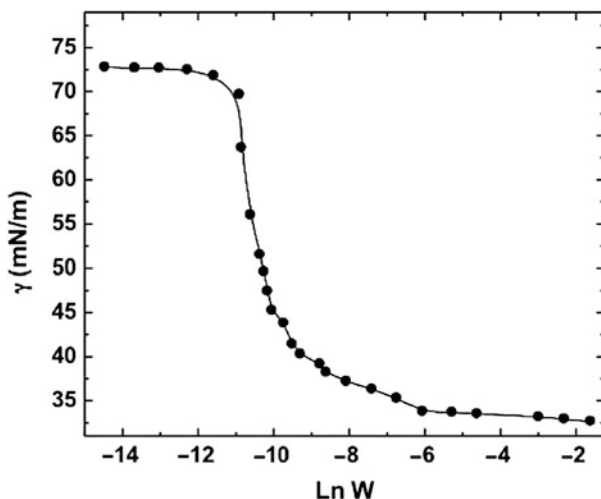


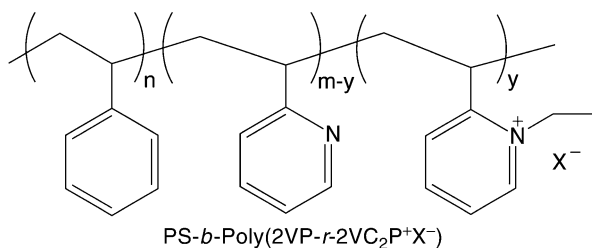
Fig. 5.1 Interfacial tension at the air–water interface of aqueous **TB** solutions at 25 °C as a function of $\ln w$, where w is **TB** weight fraction in water

The controlled ATRP (atom transfer radical polymerization) of a stimuli-responsive ionic liquid surfactant acrylate ($\text{AC}_{11}\text{ImC}_1\text{Br}$), from both ends of a telechelic poly(propylene oxide) (PPO) macroinitiator (BrX-PPO-XBr), wherein both ends of the PPO center block are esterified with bromoisobutyryl bromide (BrX), was done in aqueous methanol. The resulting highly water-soluble triblock copolymer, poly($\text{AC}_{11}\text{ImC}_1\text{Br-}b\text{-PO-}b\text{-AC}_{11}\text{ImC}_1\text{Br}$), is multi-stimuli responsive. Surface tensions of aqueous **TB** at the air–water interface are illustrated in Fig. 5.1 as a function of **TB** weight fraction. The primary cmc appears quite low at a weight fraction of 4.5×10^{-5} . A second cmc appears at $w \sim 0.0025$ ($\ln w \sim -6$). The high interfacial activity can be ascribed to the brush-like structure of the PILBr endblocks. Analysis of the steep transition leading to the first cmc according to the Gibbs adsorption isotherm indicates a surface saturation concentration corresponding to $50 \text{ \AA}^2/\text{ILBr/TB}$ assuming complete ion pair dissociation or $6.5 \text{ nm}^2/\text{TB}$, assuming 13 ILBr ionizing units/**TB**. This range is about 50 % of that reported for F108 adsorption at saturation on organic substrates [53]. This packing density also suggests essentially all of the PO groups are excluded from the aqueous phase and are extended as loops above the air–water interface, consistent with interfacial tensions of 33–40 mN/m.

Vesicles and Lamellar Phases. Yuan, Antonietti, and co-workers [54, 55] have synthesized a variety of such vinyl imidazolium bromide surfactants, including a bis-cross-linking agent (two vinyl imidazoles linked by quaternizing with 1,4-dibromobutane), and have demonstrated micellar (dispersion) polymerization of these monomers. Even-numbered carbon chain lengths of 8–18 were investigated. Latexes so formulated, after ion exchange (of bromide) with bis

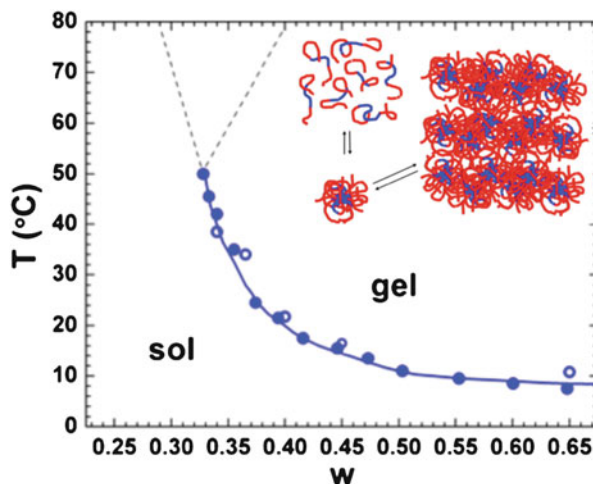
(trifluoromethylsulfonyl)imide, $(\text{CF}_3\text{SO}_2)\text{N}^-$, were stable in nonpolar solvents such as toluene. This stimulus response transforms the latexes from being compatible with polar solvents to being compatible with nonpolar solvents. Further work on this system demonstrated that lengthy nanoworms of polymer were produced by micellar polymerization. The resulting polymers condensed into nanoparticles having an apparent vesicular structure, but after forming spheroids of 50 nm diameter, an adjacent spheroid was condensed, and so on, yielding “nanoworms” composed of lamellar layers arranged as stacked lamellae rather than as concentric lamellae as often seen in multilamellar vesicles [55]. Under other conditions unilamellar and multilamellar vesicles were formed, and it was found that the shapes ranged from spherical to polyhedral with flat facets, depending on the alkyl chain length of the composing vinylimidazolium monomer.

Stimuli-responsive diblocks of PIL-*b*-PMMA, PIL-*b*-PMAA, and PIL-*b*-Pam, where PMMA is poly(methyl methacrylate), PMAA is poly(methacrylic acid), PAm is polyacrylamide, and the ILs are various 1-[methacryloyl- ω -alkyl]-3-alkyl-imidazolium X^- and were prepared by RAFT polymerization and reported by the Lyon group [56, 57]. The stimuli responsiveness of these diblocks was examined by exchanging $(\text{X}^-) \text{Br}^-$ for $(\text{CF}_3\text{SO}_2)_2\text{N}^- (\text{Tf}_2\text{N}^-)$. Hydrophilic–hydrophilic diblocks (PMAA-*b*-PIL) and hydrophobic–hydrophilic diblocks (PIL-*b*-PMMA) were converted to hydrophilic–hydrophobic and hydrophobic–hydrophobic diblocks, respectively, by this anion exchange process [57]. In a following study [56] it was shown that these anion exchange transitions were accompanied by particle formation and condensation. Many of these particles were shown by TEM analyses to be vesicles in water or THF. Structural transitions were shown to be reversible by phase transfer and anion exchange back to the starting anion. This reversibility, demonstrated earlier for homopolymers of imidazolium-based PIL, is the most important property discovered for anion-responsive PIL.



Carrasco and co-workers [58] demonstrated an interesting effect of anion exchange on the lamellar packing of PS-*b*-P2VP diblocks. These diblocks were first made by anionic polymerization. Random and partial quaternization of the 2-vinylpyridine moieties was then done using bromoethane to produce PS-*b*-Poly(2VP-*r*-2VC₂P⁺Br⁻) diblocks. Phase imaging in AFM analysis of polymer thin films showed that the lamellar packing effect of quaternization of 20 % of the pyridine groups increased from 19 nm for the periodic block separation

Fig. 5.2 Two-component phase diagram of the water/**TB** system as a function of temperature and **TB** weight fraction, w . Illustrated are single-phase sol and gel domains. Filled and open circles represent data obtained in two separate series of experiments. The inset illustrates a sequence of unimer to micelle to lyotropic mesophase (hypothesized to be a liquid-crystalline phase of ordered micelles) (©2012 Wiley; reproduced by permission from Ref. [43])



distance in the starting material to 34 nm for the ethylpyridinium bromide containing “diblocks.” When Br^- was anion exchanged for Tf_2N^- , this separation increased to 48 nm, and when anion exchanged for $\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$ the separation distance was 73 nm.

Other Lyotropic Mesophases. The triblock **TB** discussed above was also found to exhibit interesting sol–gel transitions thermoreversibly [43]. Above weight fractions of 0.32, a line of LCST (lower critical solution temperature) forms that traverses from about 50 °C to about 8 °C as weight fraction increases to 0.65 as shown in Fig. 5.2. This behavior is somewhat reminiscent of similar thermoreversible sol–gel transitions exhibited by PEO-PPO-PEO Pluronic triblocks in water, although these systems also exhibit thermoreversible UCST [59, 60]. In this **TB** case, the morphology of the micelles formed is not known nor has the gel phase morphology yet been identified. In the case of the somewhat similar F127, spherical micelles form in the sol phase, and these assemble into a cubic mesophase upon gel formation [61, 62].

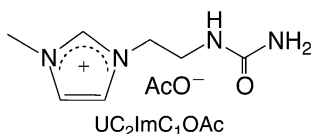
Anion Recognition and Sensing

The extremely large dynamic range of cation-anion interactions that exists in IL is best exemplified presently by imidazolium-anion pairings examined in PIL comprising imidazolium-based monomers. Developing supramolecular sensors for anion recognition is an ongoing activity, and imidazolium groups are often found in such molecules and complexes. Some anion-specific effects have been observed in studies focusing on imidazolium-based supramolecular complexes [63, 64], anion exchange resins [65], and polymers aimed at developing anion sensors [66] and quantitative analyses [36]. These studies and the examples of anion-sensitive

stimuli responsiveness of imidazolium-containing polymerized ionic liquids (PILs) discussed in this chapter show unequivocally that this responsiveness comes from interactions associated with anion-imidazolium ion pairing. The imidazolium ring provides pi-pi, pi-quadrupole, electrostatic (ring), and acidic C(2)-H protons that all interact attractively with anions [67].

Various examples of imidazole and imidazolium-containing polymeric systems have been noted to be anion responsive, but none of these cases involved direct imidazolium-anion complexation [68]. The strong imidazolium-anion interactions of the type and specificity found in PIL appear not to have become a focal point in anion recognition sensor development, in spite of aqueous sensing based on poly(imidazolium thiophene) colorimetry and in spite of its being noted that more hydrophobic anions like BF_4^- and PF_6^- are interferences for iodide [69]. It was stated that a “similar imidazolium salt does not show appreciable affinity for iodide” [69], and the basis for this allegation was a study of chloride binding by an elegant tris-imidazolium ligand in acetonitrile/DMSO solutions [70], a good solvent for imidazolium-iodide ion pairs.

Urea-functionalized imidazolium salts such as 1-ethylurea-3-methylimidazolium acetate ($\text{UC}_2\text{ImC}_1\text{OAc}$) were examined as recognition agents for anions such as halides, BF_4^- , PF_6^- , and BPh_4^- (tetraphenylborate) in $\text{DMSO}-d_6$ [71]. Conformational changes induced by C(2)-H and urea proton chemical shifts were used to determine IL-anion interaction strengths, and relative strengths for halides decreased in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$.

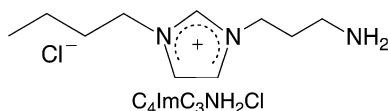


The sensitivity of various anion-imidazolium ion pairs can strongly depend on solvent, and ion pairs insoluble in water can be quite soluble in DMSO and other solvents. Numerous other studies of (non-polymeric) elegant multi-imidazolium-anion recognition agents have focused on anions such as F^- , Cl^- , and H_2PO_4^- and have used PF_6^- derivatives that are quite soluble in the nonaqueous solvents [72–74]. An imidazolium-anthracene cyclophane as an aqueous iodide sensor based upon fluorescence quenching was explained mechanistically as due to iodide binding via “hydrogen bonding” to the imidazolium ring, as monitored by proton chemical shifts [75]! Developing anion sensors for such hydrophobic anions in water has been mentioned by some of those developing the PILs discussed in this chapter [56].

Photonic crystals based on face-centered cubic and hexagonal packing of polymeric and metal-oxide microparticles and nanoparticles have been widely studied during the past 15 years [76]. Such crystals diffract light in ways analogous to diffraction of x-rays and electrons by molecular crystals and have been found to exhibit many interesting optical effects. Novel sensors have been derived from such new materials, wherein by one means or another, the analyte causes a change in the

effective d-spacing of the particle array, and the reflected or transmitted color changes can be easily quantified using UV/Vis spectrometry. The use of hydrogels as particles in such arrays or as binders gluing such arrays together has been reviewed [77]. Li and co-workers [78] composed such cubic close-packed arrays on PMMA substrate using monodisperse silica nanoparticles about 260 nm in diameter. The interstices were then filled with a methanolic chloroform solution 1 mM in each of MAA and 1-(6-acryloyloxyhexyl)-3-methyl imidazolium bromide, $\text{AC}_6\text{ImC}_1\text{Br}$, and 2 mM in EGDMA cross-linking agent. This monomer solution was then infused into the silica photonic crystal along with thermal initiator (AIBN), heated to form a cross-linked copolymer throughout the crystal. This composite material was then rinsed in aqueous HF to dissolve the silica templating particles to yield an inverse opal structure of stimuli-responsive PIL. This inverse opal obtained produced various apparent colors when soaked in different solvents. When soaked in 0.02 M solutions of Br^- , NO_3^- , BF_4^- , ClO_4^- , PF_6^- , and Tf_2N^- , the color of the sensor moved from red (in water) to orange, to yellow, to green, to darker green, to bluish green, and to blue, respectively. These color changes corresponded to gradual shrinking of the cross-linked PIL with a concomitant decrease in the d-spacings of these reverse opaline structures.

Another optically detected anion recognition phenomenon utilizes the interactions of gold nanoparticles upon aggregation that shift the isolated red or pink plasmon resonance to a blue- or purple-colored resonance in aggregates and clusters. This type of interaction has been used to detect DNA strands and segments analytically as an early nanoparticle-based diagnostic test [79]. By synthesizing gold nanoparticles surface functionalized with 1-aminopropyl-3-butyl-imidazolium chloride ($\text{C}_4\text{ImC}_3\text{NH}_2\text{Cl}$), two Spanish groups showed that simple visible spectrometric detection of gold nanoparticle aggregation could be used to measure the onset of dispersion destabilization by various anions [80]. While part of the observed destabilization may be due to charge-induced screening, some of the anions such as BF_4^- , ClO_4^- , and $(\text{CF}_3\text{CF}_2\text{SO}_2)_2\text{N}^-$ were very active, and this activity suggests these anions may interact much more strongly than some of the others.

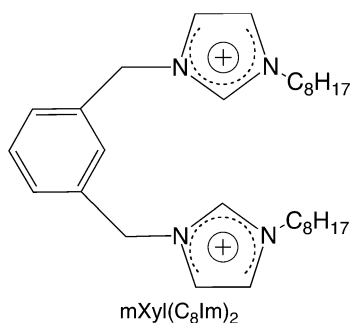


Ion-selective electrodes have been reported for PF_6^- and BF_4^- [81]. Cationic malachite green and methylene blue were complexed with $\text{C}_6\text{ImC}_1\text{PF}_6$ to form ionophores suitable for polymeric membrane anion-selective electrodes. The potential responses were essentially Nernstian over 4 (10^{-5} – 0.1 M PF_6^-) and 5 (10^{-6} – 0.1 M PF_6^-) decades, respectively, for malachite green and methylene blue. Slightly less satisfactory results were obtained for BF_4^- [81].

Ionic liquid membrane anion-selective electrodes have been formulated using tridodecylmethyl ammonium chloride, PVC (polyvinyl chloride), and IL (and/or NPOE, 2-nitrophenyl octyl ether). The ionic liquids used were chloride,

bis(trimethylpentyl)phosphinate, Tf_2N^- , PF_6^- , and tris(pentafluoroethyl)trifluorophosphate salts of trihexyltetradecylphosphonium [82]. The most Nernstian responses were obtained for salicylate, thiocyanate, and perchlorate anions. Screen-printed iodide-selective electrodes based on ILs and metalated phthalocyanine have been reported [83]. Such an electrode based upon $\text{C}_{12}\text{ImC}_1\text{PF}_6$ exhibited essentially Nernstian behavior over four decades in I concentration (10^{-5} to 0.1 M). Similar screen-printed electrodes based on phosphonium ILs were subsequently reported [84]. The ILs were diphenylbutylethylphosphonium hexafluorophosphate (DPBEPF_6) and the ditriflate imide homologue, DPBEPNTf_2 . The former gave better performance for iodide, using tetrakis(*t*-butyl)phthalocyaninatocobalt(III) iodide as an activator.

An elegant amperometric assay for heparin based upon anion recognition by a homopolymer of 1-vinyl-3-butyl-imidazolium chloride, VImC_4Cl , has been developed [85]. A glassy carbon electrode is coated with a dispersion of MWCNT stabilized by an excess of poly VImC_4Cl . The MWCNT component provides a high surface to volume matrix for heparin absorption. The chloride is then displaced by saturating with $\text{Fe}(\text{CN})_6^{3-}$ followed by rinsing. This $\text{Fe}(\text{CN})_6^{3-}$ saturated electrode provides a pronounced amperometric peak current at about 0.2 V relative to $E_{\text{Ag}/\text{AgCl}}$. Heparin is a physiologically important and highly sulfated glycosaminoglycan. Its biological function is not certain, but it is known to be an effective anticoagulant. When heparin absorbs into the electrode matrix, it anion exchanges with the ferricyanide. This absorption over a given time is linearly related to the heparin solution concentration. Amperometric measurement then exhibits a suppressed amperometric response, and this suppression provides a quantitative measurement. This amperometric response was linear over a heparin concentration range of almost 13 μM , after which the response leveled off (saturated).



The meta-xylyl-bis-imidazolium dication, $\text{mXyl}(\text{C}_8\text{Im})_2$, when associated with 1,5-naphthalene disulfonate (1,5-NDS) was shown to exhibit significant binding affinity for a variety of anions in acetonitrile [67]. Association constants were measured from NMR experiments. Binding affinities for halides increased in the order $\text{I}^- < \text{Br}^- < \text{Cl}^-$; this is opposite the trend seen in water. Binding with carboxylates is much stronger than with halides, and certain dicarboxylates induce precipitation. Bisimidazolium and bisbenzimidazolium cholapods were

synthesized from methyl deoxycholate and examined for halide, acetate, and HSO_4^- binding in chloroform using NMR proton chemical shift data [86]. The bisimidazolium moiety exhibited the greatest affinity for chloride and the bisbenzimidazolium bound acetate most strongly. Two tris-imidazolium bromide salts have been developed to complex picric acid [87]. Tris(*N*-imidazolylmethyl)mesitylene was used to alkylate three equivalents of 9-bromomethylantracene to produce one of the sensors, and tris(*p*-bromomethylphenyl)methane was used to alkylate three equivalents of 9-(*N*-imidazolylmethyl)anthracene to make the other sensor. Anthracene-based fluorescence (385–500 nm) quenching was used to measure the analyte concentration with high sensitivity (400 ppb).

Gels

The general topics of hydrogels and organogels have received wide attention and have amply been reviewed [88–94]. Ionic liquid-based gels have resulted in a broadly diverse set of new and interesting soft materials. Such stimuli-responsive materials range from new formulations for controlled release to chemomechanical actuators to supports for catalysis, among other novel applications. The roles of ILs in gels include solvation, triggering, and network formation.

Ionic liquids have excellent ionic conductivity up to their decomposition temperature. This advantage enables them to play an important role in electrolyte matrixes. However, from the viewpoint of eliminating leakage, solid or quasi-solid ion-conductive electrolytes are generally preferred over fluidic materials. Therefore, it is desirable to convert IL-based electrolyte solutions into a solid or quasi-solid form.

Polymer/IL Gels. A major motivation for forming IL-based gels is their use as semisolid electrolytes in advanced materials such as batteries, fuel cells, and solar cells. In these systems the relatively high ionic conductivity of the IL components provides important functionality. Compounds of low molecular weight [95–98], nanoparticles [99–101], and single-walled carbon nanotubes (SWCNTs) [102–105] have been used to induce network formation and gelation of ILs.

Gels composed of polymers and ILs with special emphasis on the physical properties of and physical interactions in so-called ion gels have been reviewed [106]. Proton transport is discussed in terms of two mechanisms: vehicle transport and the Grotthuss mechanism (proton hopping). Proton hopping corresponds to proton transport along hydrogen bonds and hopping from one site to another. In the vehicle mechanism, a carrier such as imidazolium or hydronium diffuses with a proton.

Gels of poly(3-lithiumsulfopropyl acrylate) (PAC3SLi) and of poly(2-acrylamido-2-methylpropane lithiumsulfonate) (PAMPSLi) with ILs C_2ImHBF_4 , $\text{C}_2\text{ImHNTf}_2$, $\text{C}_2\text{ImHSO}_4\text{M}$, and $\text{C}_1\text{PyHSO}_4\text{M}$, where M + is an alkali ion and C_1Py is *N*-methylpyrrolidine, were prepared to find highly ionically conducting compositions [107]. At polymer/IL equal weight mixtures, these gels had quite low conductivities, ranging from 3×10^{-8} S/cm to 2×10^{-6} S/cm.

Gels composed of polymers in ILs that exhibit volume phase changes have also been reviewed [106]. Examples of polymers exhibiting an UCST (upper critical solution temperature) such as PNIPAM (poly[N-isopropylacrylamide]) in $C_2\text{ImC}_1\text{NTf}_2$ (1-ethyl-3-methylimidazolium bis[trifluoromethanesulfone]imide) and LCST (lower critical solution temperature) such as PBzMA [poly(benzyl methacrylate)] in $C_2\text{ImC}_1\text{NTf}_2$ are examined. PNIPAM in water undergoes an LCST type of transition, where the polymer condenses on itself as temperature is raised through its LCST. This same polymer is insoluble at lower temperatures in $C_2\text{ImC}_1\text{NTf}_2$. However, it becomes soluble and gels as temperature is raised through its UCST [108]. Similarly, PBzMA goes from being soluble or highly solvated in hydrophobic ILs, such as $C_2\text{ImC}_1\text{NTf}_2$, to condensing upon itself as temperature exceeds its LCST [109]. The methods to prepare highly conductive IL-based polymer gels can be classified into three types: IL doping of polymers, in situ polymerization of vinyl monomers in ILs, and polymerization of polymerizable ILs.

IL Doping. The copolymer, poly(vinylidene fluoride)-hexafluoropropylene (poly(VdF-HFP)), is the most widely studied gel former by IL doping. It was reported by Gozdz et al. in 1994 [110]. Poly(VdF-HFP) is optically transparent, has good mechanical stability, and easily forms films. Carlin and co-workers [111–113] reported the preparation of IL/poly(VdF-HFP) gels containing trapped ILs, such as $C_2\text{ImC}_1$ salts of triflate (CF_3SO_3^-) and tetrafluoroborate (BF_4^-). The resulting IL-based gels formed freestanding and flexible films with room-temperature conductivities ranging from 1.1 to 5.8 mS cm^{-1} . These gels have high potential as catalytic membranes [113] (a Pt/C loaded example was effective at converting propene to propane). The IL component provides a separate phase for catalysis, and the gas phase provides reagent and product transport.

Graetzel and co-workers successfully prepared a poly(VdF-HFP) gel containing 1-methyl-3-propylimidazolium iodide, $C_3\text{ImC}_1\text{I}$ [114]. This gel was used as a solid-state electrolyte in dye-sensitized nanocrystalline TiO_2 solar cells. Salomon et al. doped P(VdF-HFP) copolymers with 1-ethyl-3-methylimidazolium bisperfluoroethyl-sulfonyl imide, $C_2\text{ImC}_1\text{N}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$, to prepare a polymer gel [115]. Similar poly(VdF-HFP)-IL gels were prepared based on ionic liquids of 1-(2-hydroxyethyl)-3-methyl imidazolium tetrafluoroborate ($\text{HOC}_2\text{ImC}_1\text{BF}_4$) and 1-(2-hydroxyethyl)-3-methyl imidazolium hexafluorophosphate ($\text{HOC}_2\text{ImC}_1\text{PF}_6$) by Lee et al. [116]. The resulting rubbery films exhibited ionic conductivities of 1–0.01 mS cm^{-1} in a temperature range of 20–70 °C. IL/poly(VdF-HFP) gels have also been used to fabricate bucky gel actuators by Aida et al. [117] based on poly(VdF-HFP)/1-butyl-3-methylimidazolium tetrafluoroborate ($C_4\text{ImC}_1\text{BF}_4$).

An IL/polymer gel based upon poly-[vinylpyrrolidone-co(vinyl acetate)] poly(VP-co-VA) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($C_4\text{ImC}_1\text{Tf}_2\text{N}$) has also been reported [118]. These $C_4\text{ImC}_1\text{Tf}_2\text{N}$ /poly(VP-co-VA) gels had a conductivity around $10^{-3} \text{ S cm}^{-1}$ at 22 °C for copolymer concentrations up to 30 wt%. Sekhon et al. recently reported that the ionic conductivity of polymer electrolytes containing poly(ethylene oxide) (PEO) and 2,3-dimethyl-1-octylimidazolium triflate ($C_8\text{Im}(\text{C}_1\text{C}_1\text{Tf})$) increases with the addition of propylene

carbonate [119]. Lewandowski et al. prepared a series of thin-film polymer electrolytes based on a polymer mixture (PEO, poly(acrylonitrile), and poly(vinylalcohol)) and ILs (1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, and 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethane sulfonyl)imide) by a casting technique. The resulting polymer electrolytes showed a rubber-like elasticity and the maximum conductivity of 15 mS cm^{-1} at room temperature [120].

A highly efficient stereocomplex formation between stereoregular isotactic poly(methyl methacrylate) (*it*-PMMA) and syndiotactic poly(methyl methacrylate) (*st*-PMMA) with a narrow molecular weight distribution in an IL, 1-butyl-3-methylimidazolium hexafluorophosphate ($\text{C}_4\text{ImC}_1\text{PF}_6$) has been prepared. Stereocomplex formation produced thermoreversible gels with melting points as high as 175°C [121]. Li et al. reported the preparation of polystyrene- $\text{C}_4\text{ImC}_1\text{PF}_6$ (PS- $\text{C}_4\text{ImC}_1\text{PF}_6$) composite nanofiber by an electrospinning method. The results showed that the average diameter of these nanofibers increased with increased IL content in the original PS-IL solution. The resultant electrospun composite film displayed both superhydrophobicity and conductivity, which may be due to the micro- and nanoscale hierarchical structures of the electrospun PS- $\text{C}_4\text{ImC}_1\text{PF}_6$ composite film and the intrinsic hydrophobicity and conductivity of $\text{C}_4\text{ImC}_1\text{PF}_6$. Entrapment of IL within polymer by electrospinning provides a facile way to create IL-based nanofibers and composite films and may find wide applications in the fabrication of controllable and functional surfaces [122].

Lodge and co-workers reported a new way to prepare IL gels through the self-assembly of a triblock copolymer, poly(styrene-*block*-ethylene oxide-*block*-styrene), in $\text{C}_4\text{ImC}_1\text{PF}_6$ [123]. Transparent ionic gels can be formed with as low as 5 wt% of triblock copolymer. The ionic conductivity of the resulting ionic gels at $1.2\text{--}1.6 \text{ mS cm}^{-1}$ is comparable to or higher than most conventional polymer electrolytes. Similarly, thermoreversible ionic gels were recently prepared through the self-assembly of poly(*N*-isopropylacrylamide-*b*-ethylene oxide-*b*-*N*-isopropylacrylamide) (PNIPAM-PEO-PNIPAM) triblock copolymers in a room-temperature ionic liquid, $\text{C}_2\text{ImC}_1\text{NTf}_2$ [124]. The gelation temperature (T_{gel}) of such ionic gels was 17°C , and this T_{gel} could be increased by incorporating solvophobic blocks of polystyrene (PS) into the PNIPAM-PEO-PNIPAM triblock copolymers to produce well-defined PNIPAM-PS-PEO-PS-PNIPAM pentablock copolymers. This T_{gel} could also be tuned over $17\text{--}48^\circ\text{C}$ by varying the molecular weight of the PS blocks.

A lower critical solution temperature (LCST)-type phase separation for polymers and polymer gels in a hydrophobic ionic liquid has been reported by Noda and Watanabe [125]. Poly(benzyl methacrylate) (PBzMA) and its copolymers exhibit LCST-type phase separation in $\text{C}_2\text{ImC}_1\text{NTf}_2$. The phase-separation temperature T_c increases with alkyl chain length of the imidazolium substituent of ionic liquids [109]. In addition, cross-linked PBzMA ion gels show reversible and discontinuous volume phase transition in $\text{C}_2\text{ImC}_1\text{NTf}_2$ with changing temperature. LCST-type phase separation of polymers in an ionic liquid is greatly affected by the distribution of the solvophilic and solvophobic groups on the polymer chains.

In the case of poly(styrene-*co*-methyl methacrylate) (poly(*S-co*-MMA)) in $C_2ImC_1NTf_2$, the LCST-type phase-separation temperature for poly(*St-co*-MMA)s decreases with increasing *S* (styrene) [126]. Lodge reported the lyotropic phase behavior of poly(1,2-butadiene-*b*-ethylene oxide) diblock copolymers (PB-PEO) in two ionic liquids, $C_2ImC_1NTf_2$ and $C_4ImC_1PF_6$. PB-PEO/ionic liquid systems show body-centered cubic lattices of spheres, hexagonally ordered cylinders, and lamellae phases similar to that seen for the same PB-PEO block copolymers in water and in other molecular solvents [127]. Being able to form similar mesophases and assemblies of block copolymers in various solvents including ILs was recognized [127] as a seminal step in the use of block copolymer ionic liquid composites for diverse applications.

Ionic liquid confinement by epoxy resins has been examined [128] for $C_2ImC_1NTf_2$, $C_4ImC_1NTf_2$, and $C_6ImC_1NTf_2$ in resins based on bisphenol A diglycidyl ether (BADGE), *N,N,N',N'*-tetraglycidyl-diaminodiphenylmethane (MY-721), and *N,N,N',N'*-tetraglycidyl-*m*-xylenediamine (Tetrad-X). The glycidyl ether groups were cross-linked using tetraethylenepentamine (TEPA). Resins prepared without either of the tetraglycidyl moieties severely phase separated from the ILs. At $C_2ImC_1NTf_2$ contents up to 40 % (w/w), the incorporated IL was confined, and the plasticized resin exhibited a very high Young's modulus (800–650 MPa) and low ionic conductivity. At higher IL loadings there was microphase separation and the material properties degraded with increasing IL loading. With $C_2ImC_1NTf_2$ this degradation was gradual over 40–50 % (w/w) with the Young's modulus decreasing from 650 to 50 MPa, the ionic conductivity increasing over a wide frequency range by 1–2 orders of magnitude, and the morphology transitioning from homogeneous-appearing fracture surfaces to spheroidal agglomerates.

An application of IL-containing gels as gate dielectrics in polymer thin-film transistors has been reported [129, 130]. PS-PEO-PS triblock copolymers were used to support the ILs $C_2ImC_1NTf_2$, $C_4ImC_1PF_6$, and $C_2ImC_1OctOSO_3$ ($OctOSO_3 \sim$ octylsulfate). The best performance was obtained with $C_2ImC_1NTf_2$; the ion gel conductivity of 7.6 mS cm^{-1} was nearly as high as the room-temperature conductivity of the neat IL. The on/off current ratio was of the order of 10^5 , the maximum capacitance obtained was $10\text{--}40 \text{ }\mu\text{F cm}^{-2}$ over the $10\text{--}10,000 \text{ Hz}$ range, respectively, and an operating frequency of 1 kHz was demonstrated. The switching times of the order of 1 ms show improvement over solid-state dielectrics and offer the promise of higher frequency operation of organic thin-film transistors.

In Situ Polymerization in ILs. Mixing ionic liquids with polymers is a direct way to prepare physically gelled ionogels. This approach is limited by the choice of polymers and ILs and does not allow intrinsic “tuning” of interactions between the polymer and IL phases. Due to a large number of vinyl monomers having large solubility in ILs, the formation of ionic gels by in situ chemical reactions, such as polymerization (cross-linking) of various monomers in the presence of ILs, should allow enhanced chemical control over the physical and chemical nature of such IL-based gels. It was reported that 2-hydroxyethyl methacrylate can be polymerized in an ionic liquid, 1-butylpyridinium tetrafluoroborate ($BPBF_4$), by in situ radical polymerization [125]. Polymerization gives transparent, mechanically strong, and highly conductive polymer electrolytes. Poly(methyl methacrylate) (PMMA)/ $C_2ImC_1NTf_2$

gels were prepared by in situ polymerization of MMA in the IL. In the presence of a cross-linking agent, the resulting PMMA/IL electrolytes displayed elastomeric properties and high conductivity (ca. 10^{-3} S/cm $^{-1}$) at room temperature [128–130]. Rogers's group reported the first cross-linking reaction of disuccinimidylpropyl poly(ethylene glycol) (PEG) monomers with four-arm tetraamine PEG cross-linkers in the hydrophobic ionic liquid, C₆ImC₁NTf₂ [131]. The general behavior and physical properties (e.g., shrink–swell upon hydration) of the resultant IL-PEG gels are generally comparable to those of analogous PEG hydrogels.

To realize polymer electrolytes with high ionic conductivity, a series of polymer composites comprising a room-temperature ionic liquid, C₂ImC₁NTf₂, by in situ polymerization of vinyl monomers (such as MMA, acrylonitrile, vinyl acetate, styrene, 2-hydroxyethyl methacrylate, methyl acrylate, and acrylamide) was prepared [132]. However, only methyl acrylate and MMA can be polymerized in C₂ImC₁NTf₂ without macrophase separation. The glass transition temperatures of the PMMA/C₂ImC₁NTf₂ gels decrease with increasing mole fraction of C₂ImC₁NTf₂, and the ionic conductivity reaches a value close to 10 mS cm $^{-1}$ at ambient temperature. These highly conductive IL-based ion gels yielded flexible and transparent films. The most striking result obtained [132] was that the total carrier number in the ion gel at certain compositions exceeded the value obtained for the IL itself. This surprising finding highlights the importance of developing a detailed understanding of the specific physical interactions between ILs and the supporting polymer matrices in which the ILs are compatible.

Polymerizable ILs. Polymerization of monomers that are ILs to produce polymerized ionic liquids, PILs, is another route to ionic gels. Ohno's group synthesized a series of polymer electrolytes by polymerization of ionic liquid-based monomers [133–139]. In general, a polymerizable vinyl group was covalently introduced on the cation or (and) anion moiety of an ionic liquid. Polymerization at suitable temperature yielded polymerized (or cross-linked) ionic gels [139, 140]. A variety of polymerizable IL systems such as polycation-type ILs [1373], polyanion-type ILs [135], copolymer [135], and poly(zwitterion) [136] have been reported. However, the ionic conductivity of the polymerized ILs was generally lowered due to considerable elevation of glass transition temperature (T_g) and to reduced numbers of mobile ions after covalent bonding of the component ions. Initial work in this area has been reviewed by Ohno [139].

Templating on liquid crystal structures is a promising approach for the preparation of anisotropic functional materials. Kato and co-workers reported the synthesis of one-dimensional ion-conductive polymer films based on polymerizable columnar liquid-crystalline ionic liquids [141]. The ionic moieties self-assemble into the inner part of columnar structures through nanosegregation and electrostatic interactions and form a hexagonal columnar LC phase between 20 °C and 50 °C. The aligned IL-based nanostructures were preserved via polymerization of liquid crystals resulting in polymer films containing anisotropically oriented nanochannels. The resulting polymer films had anisotropic ionic conductivities where conductivities parallel to the columnar axis were higher than those perpendicular to the columnar axis.

Firestone and co-workers reported preparation of a nanostructured liquid-crystalline hydrogel through self-assembly and photopolymerization of an ionic liquid acrylate monomeric amphiphile, 1-(8-(acryloyloxy)octyl)-3-methylimidazolium chloride, $\text{AcrC}_8\text{ImC}_1\text{Cl}$ [142]. The resultant poly($\text{AcrC}_8\text{ImC}_1\text{Cl}$) hydrogel adopts an ordered lamellar structure and is sufficiently physically cross-linked to undergo reversible swelling in water to more than 200 times its original volume. Upon increasing water content, the photopolymerizable 1-(10-(acryloyloxy)decyl)-3-methylimidazolium chloride produces a rod-coil IL cation that yields self-assembled mesophases. Covalent linking of the IL cations by UV-induced polymerization converts the lyotropic mesophase into three-dimensional biocontinuous chemical gels [143]. Reducing the alkyl chain length, as in the polymerizable IL $\text{AcrC}_8\text{ImC}_1\text{Cl}$, severely reduces the self-assembled mesophase order and triggers the formation of only weakly ordered lamellar structures. In a similar system, a novel polymeric gel that serves as a soft dynamic nanostructure permitting tuning of encapsulated metal particle–particle interactions has been reported by Firestone’s group. Gold nanoparticle-containing PIL composites were synthesized in a single step by UV irradiation of a metal-ion-precursor-doped, self-assembled polymerizable ionic liquid gel, 1-decyl-3-vinylimidazolium chloride. One of the interesting properties of these gold–polymer composites is that the composite undergoes a structural conversion to a disordered structure by swelling in alcohol, which is accompanied by a color change from purple to pale pink. These results demonstrate the far-field tuning of the plasmonic spectrum of gold nanoparticles by solvent-mediated changes in its encapsulating matrix [144]. This swelling decouples the plasmon interactions between nanoparticles to yield the pink color, characteristic of isolated gold nanoparticles.

Gels composed of $\text{C}_4\text{ImC}_1\text{BF}_4$ (continuous phase) and $\text{tBAm}_x\text{EO}_y\text{tBAm}_x$ ($\text{tBAm} \sim$ t-butylacrylamide; $\text{EO} \sim$ ethylene oxide) triblock copolymers (network forming solute) that are transparent were synthesized by Sharma et al. [145] using a RAFT process. The endblock homopolymers of poly(tBAm) are insoluble in the continuous phase, so we would expect micellization of such triblocks to form, with the EO segments being solvated by the $\text{C}_4\text{ImC}_1\text{BF}_4$. Extremely long middle blocks of EO were used (592 units) to achieve solubility, and the endblocks were 24, 41, and 51 units long with M_n (from NMR), respectively, of 6, 10.5, and 13 kDa. Micellization was not reported, but gelation at room temperature occurred reversibly at decreasing triblock concentrations of 12 %, 8 %, and 5 %, respectively, for endblock lengths of 24, 41, and 51. Gelation occurred on cooling (e.g., at 46 °C in 6 % with 51 unit endblocks) with some hysteresis on warming (e.g., 50 °C). Electrical (ionic) conductivity was only slightly lower than that of the IL itself (4 mS/cm).

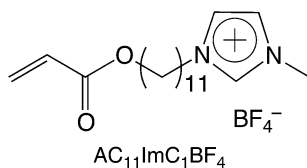
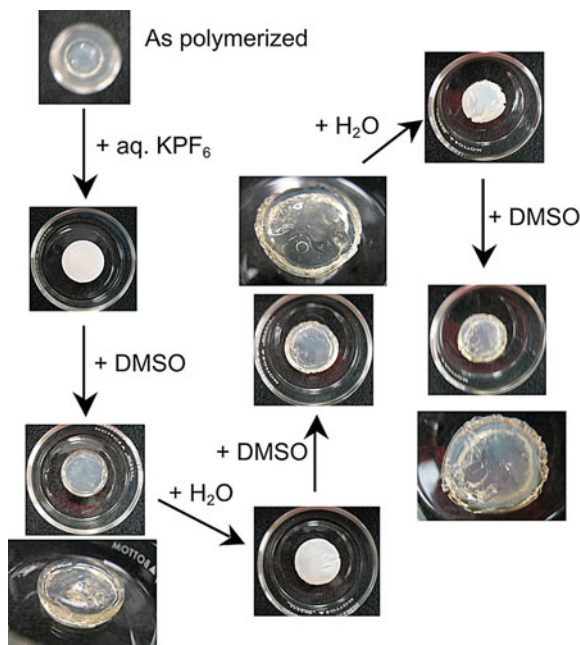


Fig. 5.3 Thick film of aqueous propanol copolymer ($AC_{11}ImC_1BF_4/MMA$) gel prepared by microemulsion polymerization and subsequent transformations induced by ion exchange with PF_6^- and solvent shifting by immersion cyclically in DMSO and water. Chemomechanical dissipation is evident from the roughness exhibited around the wafer periphery after each immersion in water



Stimuli-responsive hydrogels prepared by microemulsion polymerization of methyl methacrylate (MMA) and the polymerizable surfactant acrylates, $AC_{11}ImC_1Br$ and $AC_{11}ImC_1BF_4$, form gels that are both anion and solvent responsive [15, 16, 146–148]. Such gels have been shown to be bicontinuous and to retain the morphology of the microemulsion precursor to a greater extent than reported for any other biocontinuous microemulsion system by two orders of magnitude when considering thermally initiated systems [148]. These hydrogels transform into open cell and opaque monoliths upon exposure to anions more hydrophobic than Br^- in the case of the $AC_{11}ImC_1Br$ system and more solvophobic than BF_4^- in the case of the $AC_{11}ImC_1BF_4$ system. When this latter system was transformed into a porous material with PF_6^- , the resulting porous material was reversibly transformed back into a solvogel upon soaking in DMSO, as shown in Fig. 5.3, where DMSO and water were cyclically interchanged.

Other Applications

Dispersion Phase Transfer. A key problem in practical nanotechnology is that the solvent system in which nanoparticles and nanoobjects are made or most easily dispersed is often antagonistic to the environment in which the materials ultimately are used. The Mecerreyes group [14, 149, 150] introduced the concept of anion control of polymer solubility and the anion stimuli responsiveness of imidazolium polymers. In their third paper on this topic, they provided insight into a very useful

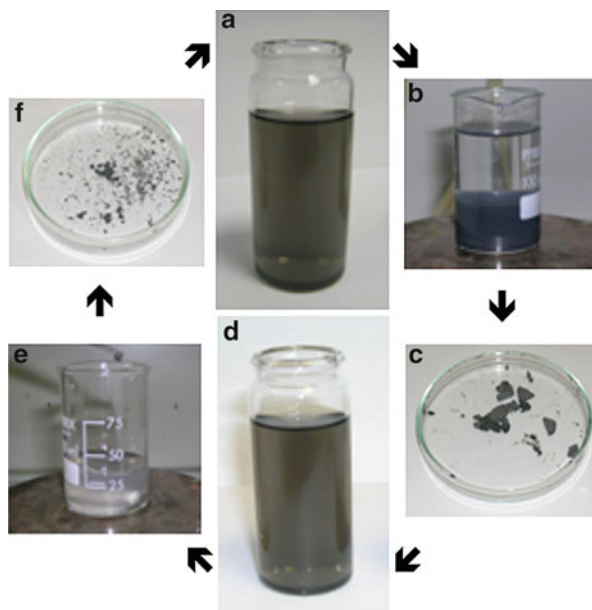


Fig. 5.4 Cyclical procedure for reversibly transferring dispersed nanoobjects between aqueous and organic phases. (a) Aqueous dispersion of SWCNT stabilized by adsorbed poly(VC₂ImBr) and solution of excess poly(VC₂ImBr); (b) destabilization of aqueous SWCNT dispersion (stabilized by adsorbed poly(VC₂ImBr)) by addition of molar excess of Pf₂NLi resulting in precipitation of poly(VC₂ImNPf₂)-stabilized SWCNT into agglomerated mass; (c) filtration, isolation, and drying of agglomerated poly(VC₂ImNPf₂)-SWCNT; (d) stable acetone dispersion of poly(VC₂ImNPf₂) stabilized SWCNT obtained from (c); (e) addition of an acetone-TBABr (tetrabutylammonium bromide) solution to the acetone dispersion (d) of poly(VC₂ImNPf₂)-SWCNT transforms the poly(VC₂ImNPf₂) to poly(VC₂ImBr) and induces precipitation and agglomeration of the SWCNT; (f) filtration, isolation, and drying of poly(VC₂ImNPf₂)-SWCNT; (a) the isolated poly(VC₂ImNPf₂)-SWCNT is readily redispersed in water forming a stable aqueous dispersion. Adopted with permission from R. Marcilla, M. L. Curri, P. D. Cozzoli, M. T. Martínez, I. Loinaz, H. Grande, J. A. Pomposo, D. Mecerreyes, *Small* **2006**, 2, 507–512

phase transfer application [150] system. A sequence of steps for reversibly transferring materials from water to nonaqueous solvent and back to water is illustrated in Fig. 5.4. The homopolymer poly(VC₂ImX) (V is vinyl) was used to stabilize SWCNT cyclically in water and acetone. The anion-sensitive solubility of this stabilizing polymer was used to promote both water (X = Br[−]) and acetone (X = Pf₂N[−]) dispersibility. Similar cyclical processes were demonstrated for gold nanorods and for silver nanoparticles [150]. The seminal feature demonstrated was the control of solubility by selecting appropriate anions that are ion exchanged for one another. Anion-based solubility control is the fundamental basis of imidazolium-anion stimuli responsiveness. Similar phase transfer phenomena were demonstrated by Texter and Ager for concentrated (1 % w/w) graphene dispersions in water [151]. In these dispersions nanolatexes of a copolymer of AC₁₁ImC₁Br and MMA were used to stabilize the graphene. Destabilization was

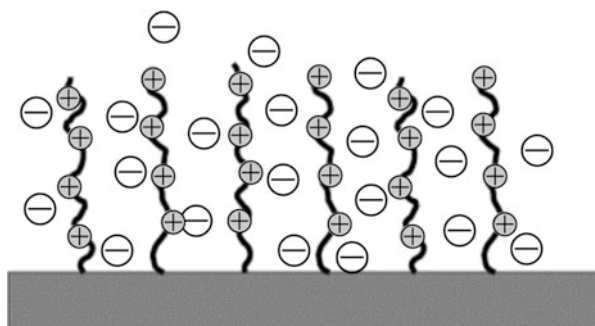
obtained by adding an equivalent amount of $\text{NaN}(\text{CN})_2$. The resulting destabilized and aggregated graphene was collected by filtration and easily redispersed by mild sonication in acetone. This stable dispersion was then destabilized by adding an excess of tetrabutylammonium bromide, and the solids were again collected by filtration. These solids were then easily redispersed in water, illustrating a phase transfer cycle analogous to that illustrated in Fig. 5.3 for dilute SWCNT. In a related work [152], a copolymer of PNIPAM and of VImC_2Br was used to prepare dilute dispersions of MWCNT in water. High KBr caused the dispersion to salt out, and raising the temperature above the volume phase transition at 38°C also caused the dispersion to destabilize, coagulate, and sediment. Such destabilization makes isolation by filtration efficient, and these transitions are fully reversible.

Reversible Nanoparticle Formation. Doubly stimuli-responsive dihydrophilic diblock copolymers of poly(*N*-isopropylacrylamide-*b*-ionic liquid), PNIPAM-*b*-PIL, have been synthesized by Tauer and co-workers [153–155] and by Yuan and co-workers [152, 156]. Doubly hydrophilic block copolymers of PMAA and ILs were discussed earlier in the discussion of vesicle formation [56, 57]. Diblock copolymers of PNIPAM and $\text{AC}_{11}\text{ImC}_1\text{Br}$ and triblock copolymers of MMA, PNIPAM, and $\text{AC}_{11}\text{ImC}_1\text{Br}$ and of styrene (S), PNIPAM, and $\text{AC}_{11}\text{ImC}_1\text{Br}$ were found to be doubly stimuli responsive. A key observation in the diblock PNIPAM and $\text{AC}_{11}\text{ImC}_1\text{Br}$ aqueous system was that transparent micellar solutions could be reversibly condensed to extremely stable core/shell particles by raising temperature above the volume phase transition temperature (of PNIPAM) at 32°C . In this case the PNIPAM condensed to form cores of PNIPAM stabilized by a surrounding corona or shell of poly $\text{AC}_{11}\text{ImC}_1\text{X}$ blocks. Such reversible nanoparticle formation is peculiar but colloiddally significant, since the first-order phase transition did not result in macroscopic phase separation. Addition of BF_4^- and PF_6^- produced dispersions having cores of destabilized poly $\text{AC}_{11}\text{ImC}_1\text{X}$ ($\text{X} = \text{BF}_4$ or PF_6) stabilized by a corona of PNIPAM blocks. In the triblock studies it was demonstrated that the operational volume phase transition temperature could be tuned by selection of hydrophobic monomer and poly $\text{AC}_{11}\text{ImC}_1\text{Br}$ block length.

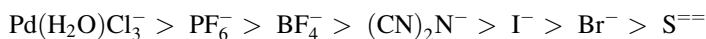
Yuan and co-workers made diblocks of PNIPAM and VImC_2Br using RAFT polymerization and observed similar phenomena. They found that adding high bromide sufficed to cause core formation by poly VImC_2Br blocks [156]. These core/shell particles remained colloiddally stable because of the stabilizing influence of the corona of PNIPAM blocks. When such dispersions of core/shell particles were subjected to temperature above the PNIPAM volume phase transition at 32°C , these blocks collapsed and the dispersion exhibited macrophase separation. As described earlier, a copolymer of PNIPAM and of VImC_2Br that stabilized MWCNT in water could also be destabilized by high KBr and by warming above the volume phase transition temperature.

Osmotic Spheres and Brushes. A collection of studies has shown that block copolymers and nanolatexes of $\text{AC}_{11}\text{ImC}_1\text{Br}$ provide outstanding dispersion stability for various forms of nanocarbon, latex beads, and organic pigments [151, 157–162]. A variety of destabilization studies have shown that such nanolatexes

Fig. 5.5 Osmotic brush cartoon. In an osmotic brush the counter ions are “trapped” within the brush



can be destabilized by stimuli responsiveness to certain anions that interact strongly with the imidazolium ring [33, 163]. These effects can be summarized in a Hofmeister series ranking of relative destabilizing power:



that showed lower anion concentrations destabilized more slowly than higher concentrations and that certain anions destabilized more slowly than others at the same concentration. When one considers that such nanolatexes are destabilized by 0.35 mM KPF₆ (I = 0.35 mM) but are stable in 1.5 M Na₂S (I = 4.5 M), destabilization by Debye-Hückel charge screening can be ruled out. It should be noted that this range of ionic strengths covers a dynamic range >10⁴. We therefore must conclude that these nanolatexes behave as osmotic spheres. They appear to be the first experimental realization of osmotic spheres, wherein the counter anions are effectively trapped within the particles. A schematic of an osmotic brush is illustrated in Fig. 5.5. The attraction between the imidazolium ring and various anions provides for these anions being “trapped” within the nanolatexes or within the pendant blocks when considering the brush formed by adsorption from solution for the triblock discussed next.

It was found that an early triblock stabilizer, poly(AC₁₁C₁ImBr-*b*-PO-*b*-AC₁₁C₁ImBr), was an excellent stabilizer for a yellow azo-based pigment (pigment PY138) in water [159]. Dispersions of this pigment appeared stable for many months. A series of equal aliquots of this dispersion was prepared and inoculated with increasing doses of aqueous KPF₆. The samples were mixed and set aside to observe the onset of possible sedimentation. Such sedimentation (following dispersion destabilization) was observed in the three most concentrated (in KPF₆) samples, wherein the stabilization afforded by the AC₁₁C₁ImBr blocks was inactivated by the conversion of these blocks from hydrophilic to hydrophobic [159].

It subsequently was found that the nanolatexes, poly(AC₁₁C₁ImBr-*co*-MMA), and the triblock, (AC₁₁C₁ImBr)_{6.5}-*b*-PO₆₀-*b*-(AC₁₁C₁ImBr)_{6.5}, were excellent stabilizers for graphene in water, although the triblock was not quite as effective as the nanolatexes [162].

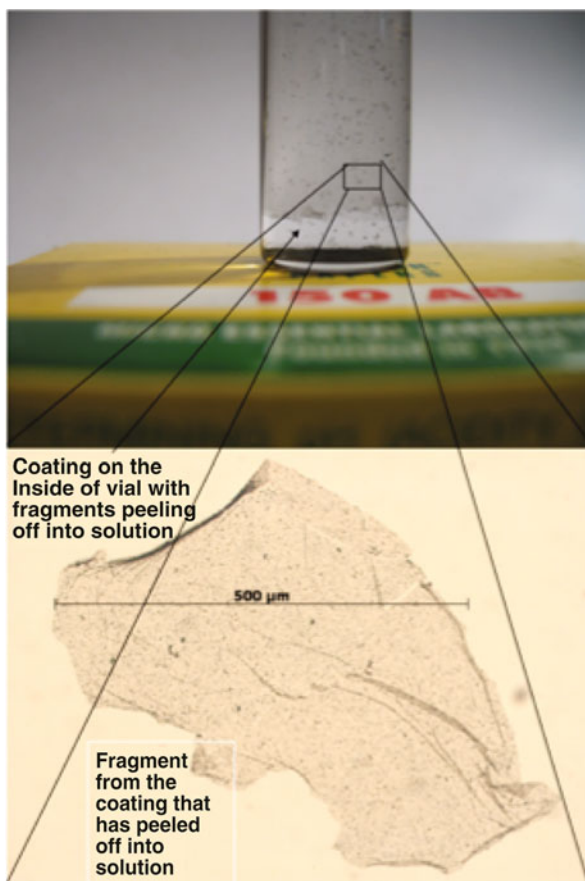
The high stability exhibited by poly($\text{AC}_{11}\text{C}_1\text{ImBr-co-MMA}$) nanolatexes in high salt is an example of immunity to coagulation by Debye-Hückel charge screening. This immunity derives from the osmotic sphere structure of the adsorbed latexes wherein the anion counter ions are trapped (due to imidazolium-anion attraction). Diffusion of counter ions in and out of osmotic spheres is osmotically retarded [33]. A triblock, poly($\text{AC}_{11}\text{C}_1\text{ImBr-}b\text{-PO-}b\text{-AC}_{11}\text{C}_1\text{ImBr}$), as discussed in the last section was shown to be an excellent stabilizer for an aqueous yellow pigment dispersion. It was also shown that this same triblock immunizes model latex colloids against coagulation by Debye-Hückel charge screening [159].

Highly sulfate-group (negatively) charged model latexes (100 and 500 nm in diameter) were evaluated for their stability to coagulation by adsorbed triblock poly($\text{AC}_{11}\text{C}_1\text{ImBr-}b\text{-PO-}b\text{-AC}_{11}\text{C}_1\text{ImBr}$). Since these negatively charged polystyrene latexes would be destabilized by partial or full neutralization of the electrokinetic negative charge by the adsorbed cationic polymer, an excess of triblock was added, and after sonication, the latexes were very well restabilized. After addition of a swamping amount of electrolyte (1 meq KBr), the control suspensions immediately coagulated, and the latexes restabilized with triblock remained colloidally stable with no sign of coagulation or sedimentation after 16 h [159]. This Debye-Hückel “immunity” shows that such stimuli-responsive triblocks adsorbed from solution form *de facto* osmotic brushes with excellent stabilizing properties.

Controlled Destabilization and Coating. The PF_6^- anion causes dilute graphene dispersions stabilized by the nanolatex discussed above to destabilize and sediment [162]. It also was discovered that the more weakly interacting iodide could be tuned over a couple of orders of magnitude in concentration to produce very rapid to very slow aggregation and sedimentation. The graphene concentration is also an important formulation variable. It was found that such controlled destabilization could be used to produce very slow deposition by sedimentation on various substrates. The mechanism was assigned as one that transforms the adsorbed osmotic spheres (nanolatexes) into hydrophobic surface domes exhibiting hard-wall repulsion and attractive van der Waals forces upon collision with other graphene sheets [162]. This destabilization offers a new approach to producing nanocarbon self-assembly, nanocarbon electrodes, and nanocarbon coatings [162] and a new approach to supramolecular layer deposition. An example using a dilute graphene in water dispersion is illustrated in Fig. 5.6. Such novel coating procedures are expected to ultimately yield macroscopic and thin graphene electrodes suitable for display applications in competition with ITO technology.

Wetting and Wettability. Homopolymers of ILBr synthesized by a two-phase ATRP process that produced very broad molecular weight distributions (by essentially imparting continuous initiation throughout the reaction period) have been found to exhibit interesting properties [164, 165]. Such homopolymers can be precipitated into nanoparticles by addition of a suitably stimulus-inducing anion, such as PF_6^- [164]. Although it was expected that thin films of such homopolymers might exhibit poration in response to bromide ion exchange with hexafluorophosphate, a dewetting phenomenon was observed instead [164, 165]. Extensive examination of

Fig. 5.6 Iodide destabilization of aqueous graphene dispersion. (*top*) Vial of destabilized dispersion showing thin graphene film on interior walls and much thicker sediment on bottom of vial; (*bottom*) film fragment photomicrograph showing edges of composing graphene flakes



the conditions and available surface energy data yielded the conclusion that this dewetting was not driven by surface energy decreases, but rather by mechanical stress relaxation. This is an exciting new application area, and there is considerable interest in new polymeric materials that change dimension on exposure to suitable stimuli.

Magnetic ILs. Hamaguchi and co-workers appear the first to report the synthesis of magnetic liquids by transforming IL chlorides, $C_4\text{ImC}_1\text{Cl}$ and $\text{NCC}_3\text{ImC}_1\text{Cl}$ (1-butyronitrile-3-methylimidazolium chloride), into IL FeCl_4^- salts [166]. Mecerreyes and co-workers reported PIL with FeCl_4^- and FeBr_4^- counter anions, including microgel PIL particles that could be recovered in a magnetic field [167]. Gradzieski and co-workers showed that microemulsions of water and a magnetic room-temperature ionic liquid stabilized by an ionic surfactant and decanol as cosurfactant exhibited normal structural properties [168].

The Eastoe group reported [169] the conversion of an IL surfactant, 1-methyl-3-decyl imidazolium chloride ($C_{10}\text{ImC}_1\text{Cl}$), to the corresponding FeCl_4^- salt. Such large and paramagnetic anions cause pronounced decreases in the melting points of the corresponding solid materials. The cmc values increased slightly for the imidazolium

moiety on conversion to the paramagnetic form. An applied magnetic field influences the surface tension at the air–water interface for all species, whether only diamagnetic or paramagnetic. This imidazolium chloride moiety increased its surface tension by about 5 % in an applied field, while the imidazolium FeCl_4^- moiety decreased its surface tension by about 9 % in the same magnetic field [169]. Similar results were reported for GdCl_4^- , HoCl_4^- , and CeCl_4^- salts of 1-methyl-3-decyl imidazolium ($\text{C}_{10}\text{ImC}_1+$) [170]. Polarized microscopy was used to show effects on mesophase behavior and SANS was used to show detailed effects on micellization [170]. An interesting dicationic surfactant based on the IL dimer cation, $[\text{C}_4\text{mim}_2]$ (1,2-ethyl bis [1'-yl,3'-butyl imidazolium]), the AOT anion, and FeCl_3Br^- exhibited melting below -25°C has also been reported [171]. This kind of exotic room-temperature IL surfactant is multi-responsive to magnetic fields, to anions that bind strongly to the imidazolium ring, and to solvent shifting.

An interesting application of this technology has been demonstrated by a new millifluidic synthesis of large beads based on 2-methylimidazole (MeIm) being alkylated by 5-bromo-1-pentene to produce the bifunctional monomer, 1,3-bis (1-pentenyl)-2-methylimidazolium bromide, $\text{VC}_3(\text{Me})\text{ImC}_3\text{VBr}$ [172]. Highly cross-linked beads a little less than 1 mm were produced. Anion exchange was investigated for an extensive series: Cl^- , I^- , $(\text{NH}_4)_2\text{S}_2\text{O}_8^{2-}$, ClO_4^- , PF_6^- , and NTf_2^- . Beads anion exchanged into the chloride form were then incubated with methanolic FeCl_3 and methanolic DyCl_3 to produce magnetic beads containing FeCl_4^- and DyCl_4^- anions. These beads responded to an applied magnetic field, making them separable by a simple magnetic field, important in assay and concentration applications.

Outlook

When one considers the number of interesting anion-responsive and temperature-responsive effects that have been observed for imidazolium-based molecules, ligands, monomers, and polymers for a collection of less than a dozen anions to date, it seems likely that we will see many, many new phenomena reported in the forthcoming years involving imidazolium rings and other anions, in addition to other IL ring systems and their interactions with various sets of anions.

Magnetic effects are clearly in their infancy, but manipulating mesophases, polymerization systems, and microemulsion association structures are expected to lead to interesting new materials. Effects of electric fields on a macroscale have yet to be significantly examined, but dielectric spectroscopy studies suggest IL and PIL may provide simple and effective routes to supercapacitors and intermittent high energy storage.

Preliminary studies of ionic liquid polymers of ionic liquids suggest that such new liquid polymers may revolutionize PEM (polyelectrolyte membrane) technology in batteries, fuel cells, and solar cells and supported IL membranes for diverse separation processes. When such liquid PILs are appropriately tethered, these technology advances will begin to be realizable.

Perhaps one of the most important practical application areas of such PIL systems is in the area of dispersion stabilization. Growing osmotic brushes by surface-initiated polymerization offers the ultimate in dispersion stabilization. However, such stabilization is extremely expensive in any high-volume manufacturing scenario. We have already seen, though, that nanolatexes and block copolymers can provide osmotic sphere and osmotic brush stabilization by adsorption from solution. Such convenience makes high-volume applications to diverse materials feasible.

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Ionic Liquid and Cellulose Technologies: Dissolution, Modification and Composite Preparation

6

Mehmet Işık, Haritz Sardon, and David Mecerreyes

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Abstract

This chapter summarizes the recent advances in the development of new cellulose technologies using ionic liquids. Dissolution of cellulose in ionic liquids has been used to produce new processing technologies, cellulose functionalization, and new cellulose materials including blends, composites, fibers, and ion gels.

Keywords

Cellulose • Ionic liquid • Polymerized ionic liquid • Composite • Ion gel

M. Işık • H. Sardon

POLYMAT, University of the Basque Country UPV/EHU, San Sebastian, Spain

D. Mecerreyes (✉)

Institute for Polymer Materials, POLYMAT, University of the Basque Country UPV/EHU, Donostia-San Sebastian, Spain

Ikerbasque, Basque Foundation for Science, Bilbao, Spain

e-mail: david.mecerreyes@ehu.es

Cellulose and Conventional Processing Technologies

Cellulose is the most abundant natural polysaccharide on earth being the main structural component of plant cell walls and some seaweed. Cellulose is formed from repetitive D-glucose units, which condense through $\beta(1 \rightarrow 4)$ -glycosidic bonds as shown in Fig. 6.1 [1]. This natural polysaccharide has become one of the most used biomaterial due to its fascinating structural and physical properties and biocompatibility. These properties arise from the multiple hydrogen bonding interactions that are presented on cellulose, which forms materials with high tensile strength and crystallinity.

Although cellulose was discovered in 1838 by Anselme Payen, the first cellulose-based thermoplastic material was not produced until 1870 by Hyatt Manufacturing Company. This material was produced by treating cellulose with nitric acid to form cellulose nitrate and commercialized under the trade name “celluloid” [2, 3]. A few years later, a new process named viscose was developed to regenerate cellulose fibers in a larger scale. This process rendered possible the utilization of cellulose in different fields such as textile, construction, ceramics, paints, cosmetics, or alimentary industry [4, 5].

The four main resources to obtain cellulose are forestry, agricultural crops, industrial and animal residues. The biomass that is obtained from all those sources contains three major components; cellulose, lignin and hemicellulose with percentages ranging from 40 % to 50 %, 18 % to 35 %, and 25 % to 35 %, respectively, each component being strongly dependent on the employed source [6]. Thus, the extracted biomass has to be processed in order to separate the different components and isolate the cellulose.

There are three major industrially employed processing or pulping technologies called sulfite, organosolv, and Kraft processes. Although the Kraft process is the most widely used pulping method, there are important drawbacks related to the use of this process such as the degradation of lignin and hemicellulose, the utilization of high temperature and pH, the release of organic sulfur compounds, or the water contamination. On account of these, the major challenge is the separation and purification of the biomass without destroying the lignin and hemicellulose using more benign strategies [7].

As previously mentioned, the strong inter- and intramolecular hydrogen bond interactions make cellulose insoluble in water and in most of the conventional organic solvent systems, making its processing challenging. Aside from conventional solvents, some other solvents such as *N,N*-dimethylacetamide-lithium chloride, *N*-methylmorpholine-*N*-oxide, dimethyl sulfoxide-tetrabutylammonium fluoride or

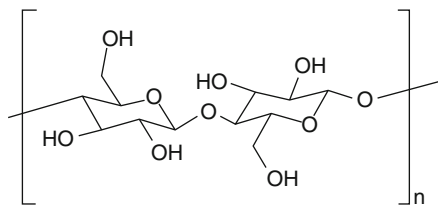
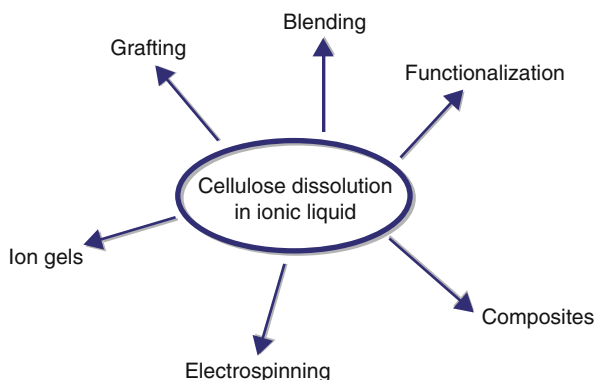


Fig. 6.1 Chemical structure of cellulose

Fig. 6.2 Ionic liquid and cellulose materials and technologies generated by the ability of some ionic liquids to dissolve cellulose



molten salt hydrates (lithium perchlorate trihydrate) have been used to solubilize cellulose [8, 9]. Among the different solvents that are able to solubilize cellulose, *N*-methylmorpholine-*N*-oxide (Lyocell process) and a mixture of alkali and carbon disulfide solution (viscose process) are the most utilized to process cellulose. In the case of viscose process, cellulose is first alkalized, and afterwards it is derivatized to cellulose xanthate with the subsequent addition of CS₂. This is one of the major methods used to manufacture cellophane in spite of the toxicity of the reagents and by-products [10]. Cellulose regeneration in Lyocell process is achieved by using *N*-methylmorpholine-*N*-oxide (NMMO) to dissolve cellulose rather than functionalization of cellulose as shown in viscose process. The process involves the dissolution of cellulose in NMMO and regeneration in water to form the cellulose fiber known as Lyocell [10]. The dissolution process requires high temperatures which creates the risk to decompose NMMO leading to an undesired explosion.

All in all, due to the drawbacks associated with the current methodologies used to dissolve and process cellulose, environmentally friendly and more efficient solvents are required. In the last decade, ionic liquids have emerged as effective and green solvents, mainly due to their high thermal and chemical stability, nonflammable nature, and miscibility with many other solvent systems. In the early 2000s, Rogers et al. discovered the ability of some ionic liquids to dissolve cellulose. This chapter summarizes the most actual ionic liquid and cellulose materials and technologies developed after this discovery, focusing in the dissolution, modification and composite preparation (Fig. 6.2).

Ionic Liquids and Cellulose Dissolution

Cellulose Dissolution in Ionic Liquids

The first report on cellulose dissolution in ionic liquids was published in 2002 [11]. In this study, ionic liquids combining imidazolium cation with different anions were investigated. It was found out that chloride, as a small hydrogen bond

acceptor, was the most effective anion in comparison to large, non-coordinating anions like hexafluorophosphate, also including bromide, thiocyanate, and tetrafluoroborate. Along the same lines, many ionic liquids have been reported in literature with the ability to efficiently dissolve cellulose such as the ones with halides like 1-butyl-3-methylimidazolium chloride (BMIMCl), phosphate, formate, and acetate. In many studies with ionic liquids, it was foreseen that the anion is of great importance and responsible for the dissolution of cellulose and the role of cation was not entirely demonstrated. However, some recent studies have shown that not only the structure of the anion is important but also the structure of the cation is significant in the solvation process. Thus, acidic protons on the heterocyclic rings increase substantially the solubility by forming hydrogen bonds with hydroxyl and ether oxygen of cellulose [12]. While 1-butyl-3-methylimidazolium acetate displayed 23 g/mol solubility at 40 °C, changing the cationic structure to 1-methoxyethyl-3-methylimidazolium resulted in a dramatic decrease to 8 g/mol solubility at the same temperature. In summary, the maximum solubility of cellulose was found to be 14.5 wt% for 1-allyl-3-methylimidazolium chloride at 80 °C [13] and 16 wt% for 1-ethyl-3-methylimidazolium acetate at 90 °C [14], which can be increased up to 25 wt% with microwave heating.

Since the first report showing the power of ionic liquids to dissolve cellulose, they have been largely investigated either to dissolve or to create an appropriate media for the functionalization of cellulose [11]. Representative ionic liquids reported for cellulose dissolution are given in Table 6.1.

Dissolution of Other Polysaccharides in Ionic Liquids

Although it is not the topic of this chapter, it is worth to remark that besides cellulose, ionic liquids have shown ability to dissolve other polysaccharides. They have been used to dissolve many biopolymers that are linked together by strong intermolecular hydrogen bonds such as chitin, chitosan, galactomannan, or starch. For instance, chitosan is the second most abundant biopolymer and is the *N*-deacetylated product of chitin. Xie et al. reported that 1-butyl-3-methylimidazolium chloride can dissolve up to 10 wt% chitin or chitosan in 5 h [22]. The materials were easily regenerated in a nonsolvent media such as water or methanol, and the materials were used as reversible sorbents of CO₂. In a similar study, Wu et al. used a room temperature ionic liquid 1-butyl-3-methylimidazolium acetate to dissolve native chitin which has a more complex inter- and intramolecular hydrogen bond network than cellulose due to presence of acetamide groups in the repeat units [23]. Polarized optical microscopy was used to follow the dissolution of chitin. Modifications on the structure of native chitin during the dissolution process were investigated by means of WAXD, SEM, and FTIR. The weakening of hydrogen bond interactions for the regenerated chitin was detected by FTIR, and WAXD studies revealed the decrease in crystallinity as a result of dissolution process in the ionic liquid. Another polysaccharide that can be dissolved in ionic liquids is galactomannan. Lacroix et al. used imidazolium-based ionic liquids to dissolve guar gums of high molecular weights, which were then

Table 6.1 Solubility of cellulose in different ionic liquids

Ionic liquid	Temperature (°C)	Solubility (wt%)	Ref.
1-Allyl-3-methylimidazolium chloride	80	8–14.5	[13]
	90	5	[15]
	100	10	[16]
	100–130	5–14.5	[13]
	90	5	[15]
1-Allyl-2,3-dimethylimidazolium bromide	80	4–12	[17]
1-Butyl-3-methylimidazolium chloride	90	<5	[15]
	100	10	[11]
	110	10	[18]
	83	18	[19]
	100	20	[16]
	100	20	[20]
	85	13.6	[21]
1-Butyl-3-methylimidazolium formate	110	8	[18]
1-Butyl-3-methylimidazolium dicyanamide	110	1	[18]
1-Butyl-3-methylimidazolium bis [trifluoromethyl]sulphonyl]imide	110	0.5	[18]
1-Ethyl-3-methylimidazolium chloride	90	5	[15]
1-Ethyl-3-methylimidazolium acetate	90	16	[15]
	85	13.5	[21]
	110	15	[18]
	110	12	[18]
3-Methyl- <i>N</i> -butylpyridinium chloride	105	12	[19]
Triethyl-2-(2-methoxyethoxy) ethan ammonium acetate	110	10	[18]

modified for the first time through esterification reactions with acid chlorides in varying ionic liquids. The chain integrity of the biopolymer was preserved since mild conditions were applied for the dissolution process [24]. In another study, three different galactomannans with different degree of branchings were processed with imidazolium ionic liquids to obtain composite materials [25]. The mechanical properties of the final composites were easily tuned by changing the ratio between the ionic liquids and the biopolymers. Starch, being the major component in many food plants, can also be dissolved and processed with ionic liquids to give materials with tunable properties. Liu et al. utilized 1-ethyl-3-methylimidazolium acetate ionic liquid to dissolve waxy cornstarch. The rheological properties of solutions with varying solid contents were examined. It was found out that the intrinsic viscosity was much less temperature sensitive than cellulose [26]. Fort et al. used 1-butyl-3-methylimidazolium chloride ionic liquid to screen fruit ripening [27]. Banana pulps at any stage of ripening were dissolved in the ionic liquid, and the compositions were analyzed by high-resolution ^{13}C NMR spectroscopy. The composition of the pulp during the initial stages of ripening mostly composed of starch which is gradually converted to sucrose, glucose, and fructose through enzymatic degradation process.

Chemical Modification of Cellulose in Ionic Liquids

One direct application of the ability of ionic liquids to dissolve cellulose is their use as solvent media for the chemical modification of cellulose. Some of the conventional solvent systems that are industrially used to process cellulose have been successfully utilized as a reaction media for homogeneous cellulose derivatizations [28–34]. However, the high toxicity and cost together with the difficulty for their recovery have limited their use. For this reason, ionic liquids emerged as greener and more effective solvents to conduct chemical modifications of cellulose. Ever since the effective utilization of ionic liquids for the dissolution of cellulose, many studies have been carried out to use ionic liquids as reaction media for the functionalization of cellulose [19]. Hence, versatile properties of ionic liquids have come forward as efficient media for functionalization. General reaction scheme for cellulose modifications is shown in Fig. 6.3. Even though particular interest has been given to the acetylation of cellulose due to its many applications, other functionalizations to produce cellulose butyrate, cellulose phthalate, and cellulose benzoate have been carried

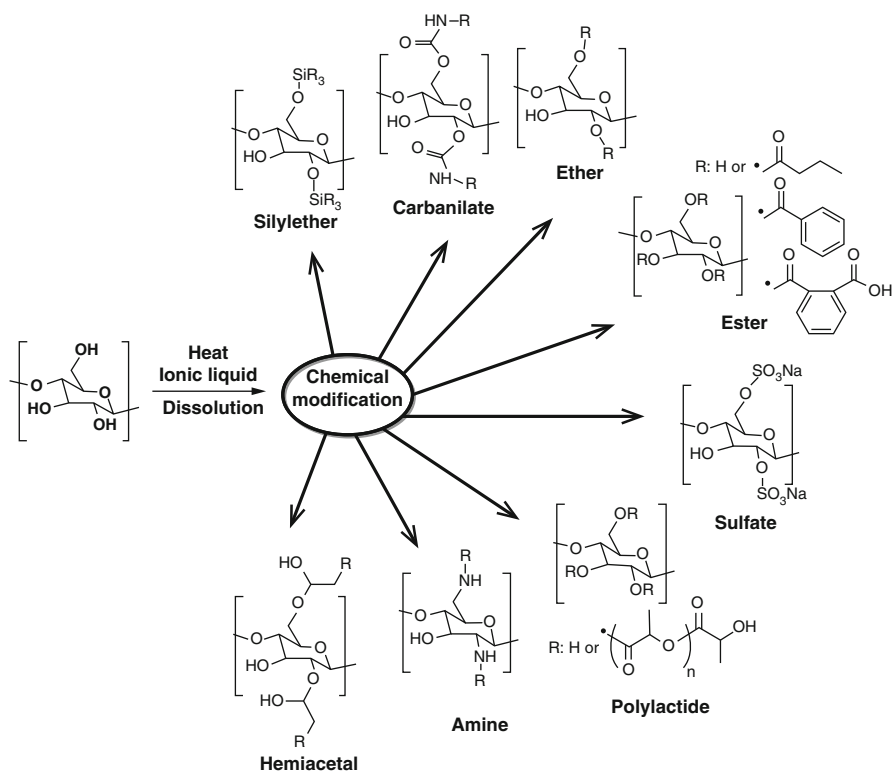


Fig. 6.3 Schematic representation of chemical modification of cellulose in ionic liquids

out. As an example, Cao et al. reported the catalyst-free acetylation of cellulose with acetic anhydride in 1-allyl-3-methylimidazolium chloride (AMIMCl) as solvent [35]. Five percent cellulose solution was prepared in the aforementioned ionic liquid at 100 °C, followed by the addition of acetic anhydride for acetylation of cellulose. Different degrees of substitutions were obtained depending on the treatment time.

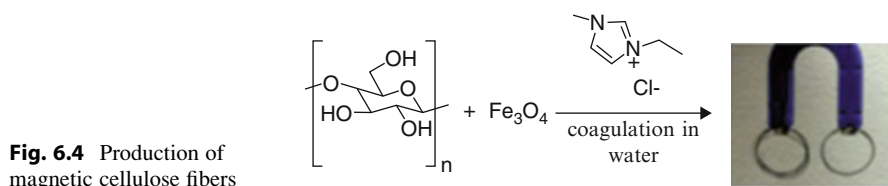
These compounds find applications in different fields such as medicine, agriculture, or textile [36, 37]. Aside from etherification and esterification reactions, cellulose derivatization with different functional groups such as silylates, sulfates, sulfonates, amines, hemiacetals, azides, carbanilates, etc. [38–41] has been also successfully achieved by modifying the hydroxyl groups of cellulose. Finally, it is remarkable to mention the work carried out by Tome et al. In this case they used tetradecyltriethylphosphonium bis(trifluoromethylsulfonyl) imide [TDTHP][NTF₂] ionic liquid to solubilize cellulose and functionalize with various anhydrides. This particular ionic liquid can catalyze the esterification reaction. Thus, Tome et al. were able to modify bacterial and vegetal cellulose with various anhydrides utilizing ionic liquid [TDTHP][NTF₂] [42]. They found that the grafted fibers displayed higher surface hydrophobicity depending on the anhydride used for modification. Further characterization of the grafted fibers showed that the esterification only took place at the fibers' outmost layers indicating that the ultrastructure was not affected.

Another interesting approach to modify cellulose is the grafting of polymer branches to cellulose to impart new properties without destroying its intrinsic characteristics [43, 44]. Recently, ring-opening polymerization was used to modify cellulose. Generally, cyclic monomers such as epoxides, lactones, and anhydrides are used together with cellulose both dissolved in an appropriate ionic liquid [19, 45]. Wang et al. grafted cellulose with poly(*p*-dioxanone): first cellulose was dissolved in BMIMCl followed by the ring-opening polymerization of *p*-dioxanone. Differential scanning calorimetry (DSC) analysis of the grafted cellulose demonstrated a clear glass transition temperature indicating that the crystallinity of cellulose was destroyed [46]. Similarly, Meng et al. produced cellulose-based ATRP macroinitiators via direct acylation in 1-allyl-3-methylimidazolium chloride. Similarly, cellulose 2-bromoisobutyrylate has been used to conduct atom transfer radical polymerization (ATRP) [47]. Analogously, Lindqvist et al. successfully functionalized the hydroxyl groups with 2-bromoisobutyryl bromide; subsequently they grew methylmethacrylate or styrene chains through ATRP [48]. In a more recent study, cellulose was grafted with maleic anhydride/glycidyl methacrylate-*g*-ethylene octane copolymer, and the resulting material was used to perform melt spinning to produce composite fibers. Grafting cellulose with long and flexible macromolecules resulted in a decrease in the crystallinity of cellulose, which induced a melt-spinnable composite material. The degree of modification determined the melt flowability of the cellulose composite. For instance, having 15 wt% of graft polymer led to the formation of cross-linked structure which increased the dynamic melt viscosity, eventually decreasing the spinnability of the material [49].

Cellulose Composites

As discussed along this chapter, ionic liquids are ideal to dissolve cellulose, hence they have been extensively employed for the preparation of cellulose-polymer blends. First of all, the cellulose together with the polymer are dissolved and blended in the ionic liquid. Afterwards, the resulting homogeneous solution is precipitated to recover the blended polymeric mixture and to remove the ionic liquid. Along this line, Kadokawa et al. used 1-butyl-3-methylimidazolium chloride as solvent to mix cellulose with starch. Mixtures containing different cellulose-starch ratios were prepared and films were obtained by casting the homogeneous solution in between two glass plate followed by the removal of the solvent with acetone or ethanol [50]. Similarly, polyamines were incorporated into cellulose with a similar preparation method in which cellulose solutions were let to mix with different amounts of polyamines to form the corresponding composite materials [51]. The primary amines on the surface enabled to employ these materials as solid support matrices for biocatalyst immobilization. Another interesting approach is the one described by Sun et al. where magnetically active cellulose composites were manufactured through blending cellulose with magnetites using 1-ethyl-3-methylimidazolium chloride as solvent [52] (see Fig. 6.4).

Briefly, cellulose was treated with the ionic liquid to give a homogeneous mixture and the desired amount of magnetite was added and mixed thoroughly. Afterwards, the resulting mixture was coagulated in a water bath yielding composite cellulose fibers. It was found out that the addition of magnetites lowered the mechanical properties due to the poor compatibility between the magnetites and cellulose. Another natural polymeric material, wool, has also been blended with cellulose by dissolving both materials in a mutual solvent such as 1-butyl-3-methylimidazolium chloride [53]. The solution containing both materials was precipitated in water giving a composite material with better thermal stability than the individual components. Moreover, the mechanical strength of the composite was improved with increasing cellulose content, and the elongation at break values was considerably enhanced with respect to individual components. This fact was attributed to the strong hydrogen bonding interactions between the hydroxyl groups of wool and cellulose within the composite observed by Fourier transform infrared spectroscopy (FTIR). It is also worth mentioning that the ionic liquid solvent was recycled with high yield and purity after composite preparation.



Polymerized Ionic Liquid-Cellulose Composites

Aside from the utilization of ionic liquids as solvent, cellulose composites can also be prepared by directly polymerizing ionic liquid monomers in the presence of cellulose. In this context two different strategies are mainly employed, (a) to combine directly cellulose with ionic liquid monomers or (b) with a mixture of ionic liquid/monomer. Regarding this methodology, one strategy to prepare cellulose composites with ionic liquid monomers is the in situ polymerization of monomeric ionic liquid to form an interpenetrating polymer networks (IPN). IPNs are considered a class of multicomponent polymer composites in which at least one constituent network is formed in the presence of the other polymer. Concerning the chemical structure, there are two types of IPNs, full- and semi-IPN. In the first, all the components are cross-linked, whereas in the latter, one of the components is immobilized in the network of the other component [54–56].

As far as the cellulose solubility is concerned, imidazolium-type ionic liquids have shown the best performance [11]. Therefore, imidazolium-based materials are ideal candidates to combine with cellulose due to their high affinity and compatibility. Along these lines, M. Murakami et al. prepared imidazolium-type ionic liquid monomer, 1-(3-acryloyloxybutyl)-3-methylimidazolium bromide (AcMIMBr). Eventually, the monomer and cellulose were dissolved in the ionic liquid 1-butyl-3-methylimidazolium chloride (BMIMCl), and the in situ polymerization was carried out at elevated temperatures in the presence of an initiator [54]. The scheme for the experimental procedure is given below (see Fig. 6.5).

The composite material was purified by treating the final product with acetone followed by a methanol Soxhlet extraction. Differential scanning calorimetry (DSC) profile of the composite showed a sharp melting peak together with a clear glass transition temperature (T_g), whereas polymerized ionic liquid displayed a single T_g . The thermal degradation profile of the composite was similar to the polymerized ionic liquid homopolymer. Thermal findings of the composite material indicate that the cellulose was properly compatibilized with the polymerized ionic liquid system [54]. In order to compare the IPN with physical blending, Murakami et al. prepared the same polymerized ionic liquid and blended with cellulose in the same ionic liquid. They found that the polymerized ionic liquid was almost entirely removed during the isolation period indicating that blending was not sufficient to obtain efficient compatibilization between the polymerized ionic liquid and cellulose. The main

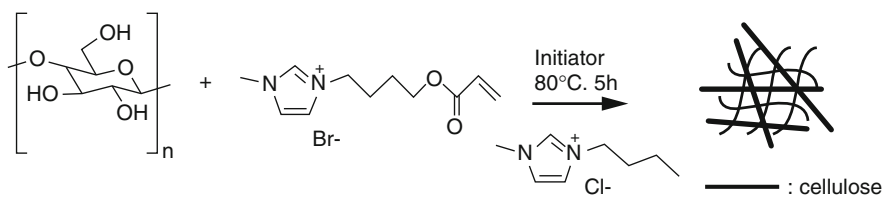


Fig. 6.5 Schematic representation for the preparation of cellulose-polymerized ionic liquid composites [54]

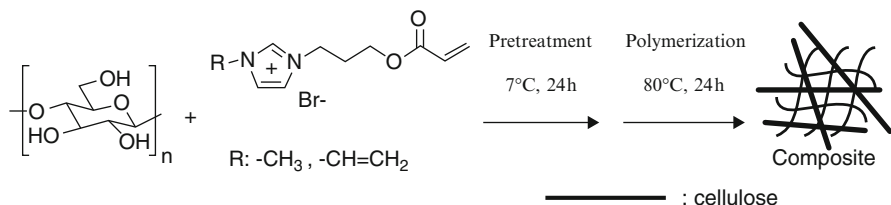


Fig. 6.6 Schematic representation of the composite preparation process

limitation of this approach was the necessity to use an ionic liquid solvent in order to dissolve both components. Takegawa et al. overcame this problem by first treating the cellulose with a mixture of mono- and difunctional ionic liquid monomers followed by the polymerization in the presence of an initiator [57] (see Fig. 6.6).

Briefly, they first treated cellulose with the monomer mixture for 24 h at 7°C using different monomer ratios. They characterized the crystalline structure of the modified cellulose using X-ray diffractometry (XRD), and they found that most of the crystallinity was loosen. Thus, the necessity to use an ionic liquid solvent was overcome. Another point worth mentioning is that the physical properties of the final composite could be adjusted by altering the feed ratio of the ionic liquid monomers. Finally, the stability of the polymerized ionic liquid in the composites was evaluated by quantifying the weight loss after washing with methanol. They did not observe any significant change in the cross-linked samples upon the treatment with methanol, whereas the samples without difunctional ionic liquid monomer exhibited a substantial weight loss. These results confirmed that the cross-linking provided further stability to the composite, while linear system was completely soluble and it was washed out with methanol. Analogously, Kadokawa et al. applied a similar approach to produce cellulose-polymerized ionic liquid composites. In this particular case, the ionic liquid monomer contained a vinylbenzyl and vinyl functional groups that can produce an IPN. First of all, the composite was treated with the monomer for 24 h at 7°C , and afterwards it was polymerized at elevated temperature to produce the IPN. XRD analysis showed that in this case the crystalline structure of cellulose was only partially destroyed [55].

Similarly, in situ polymerization of ionic liquid monomers can also be utilized to produce cellulose-based ionic porous materials. Hence, Prasad et al. obtained a porous cellulose polymeric ionic liquid-based material using templating technique with oil/ionic liquid emulsion system [58]. In the first step, the cellulose was dissolved in BMIMCl and AcMIMBr and 1-(3-acryloyloxypropyl)-3-vinylimidazolium bromide (AcVIMBr) monomer mixture. After, the mixture was in situ polymerized at elevated temperature. Then, the synthesized system was mixed with corn oil and sorbitan monooleate prior to the sonication process. The sonicated sample was treated with methanol, acetone, and hexane solvent system to produce the porous composite material. Scanning electron microscopy (SEM) analysis (see Fig. 6.7) showed that the pore sizes were around $0.15\text{--}1.3\text{ }\mu\text{m}$ coexisting with smaller sizes of $30\text{--}70\text{ nm}$.

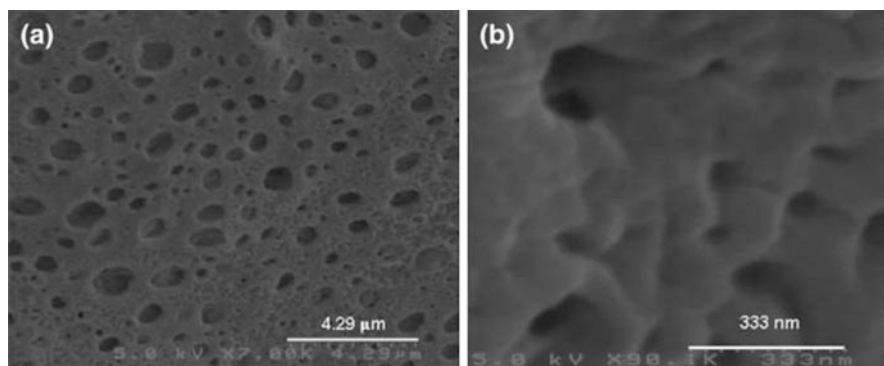


Fig. 6.7 SEM images of the porous cellulose based composite. (a) low and (b) high magnification [58]

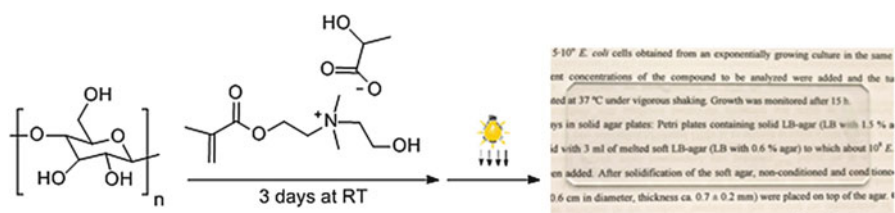


Fig. 6.8 Cellulose – polymerized ionic liquid composite coating prepared through photopolymerization [59]

Recently, our group developed a benign and facile in-situ polymerization method to produce cellulose – polymerized ionic liquid composite coatings [59]. In this work, cellulose, treated with a methacrylic based quaternary ammonium ionic liquid monomer at room temperature, was applied onto a surface and photopolymerized in the presence of a photoinitiator (see Fig. 6.8). The resulting coating with 5 wt% of cellulose displayed good transparency indicating a good compatibility between the ionic liquid monomer and cellulose.

Cellulose Based Ion Gels

1-Butyl-3-methylimidazolium chloride (BMIMCl) is one of the most effective ionic liquid solvent in order to break down the strong intra- and inter-molecular interactions that are present in cellulose. Interestingly, when cellulose is dissolved in this ionic liquid an unexpected gel formation could be observed (see Fig. 6.10). Thus, Kadokawa et al. found out that when cellulose was dissolved in the aforementioned ionic liquid and kept at room temperature for 7 days, a gel was gradually forming with the segregation of excess BMIMCl from the gel [60]. The solvent excess was removed by washing the sample with ethanol and drying it under

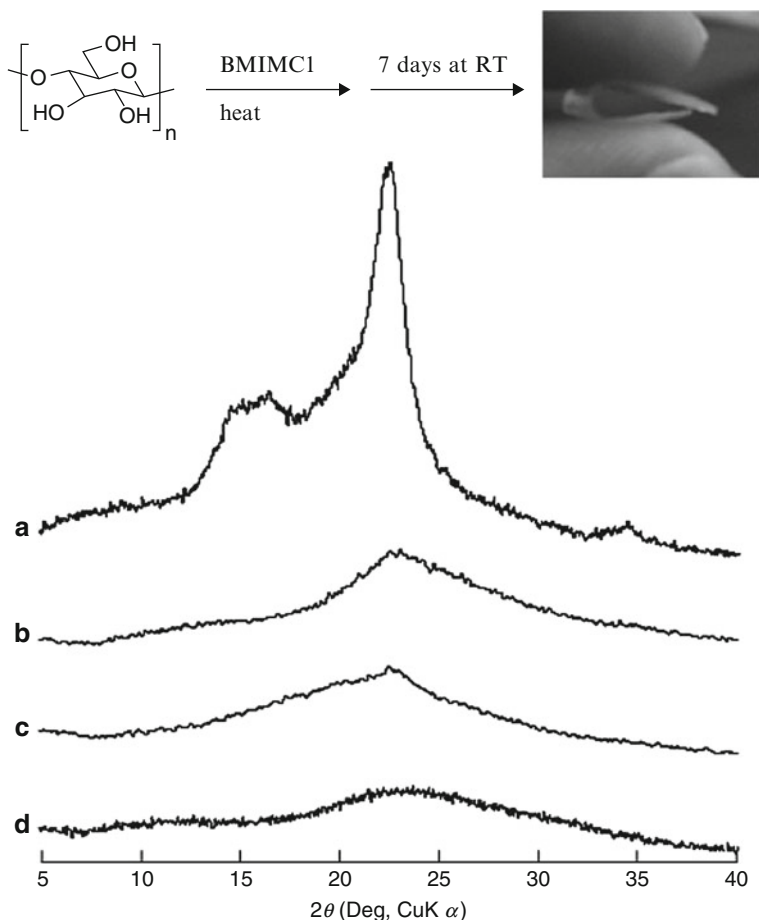


Fig. 6.9 Cellulose based ion gel preparation and XRD signals of (a) cellulose, (b) cellulose solution in BMIMCl, (c) cellulose ion gel and (d) BMIMCl [60]

vacuum. The gel was analyzed with elemental analysis, XRD and thermogravimetric analyzer (TGA). XRD showed that the crystalline nature of cellulose was destroyed (see Fig. 6.9) after the treatment with BMIMCl and amorphousity was preserved after gelation.

Moreover, TGA signals demonstrated that the gel was composed of BMIMCl, cellulose and water. In the light of this information, the formation of the gel network was attributed to the development of noncrystalline cellulose aggregates in the solution upon the gradual absorption of water due to strong hygroscopic nature of BMIMCl. They found that when the gel was heated up to 120 °C, it became soft and gradually turned into a fluid at 150 °C. The soft material that was formed at 120 °C could be transformed into a gel by standing it at room temperature for 2 days. The regenerated gel displayed better transparency in spite of maintaining

the flexibility. They suggested that after the heat treatment the noncrystalline cellulose aggregates were better dispersed obtaining more homogeneous system and resulting in a more transparent gel. Similarly, the same group reported the preparation of cellulose-starch based ion gels prepared from BMIMCl solutions [50]. A mixture of cellulose (10 %) and starch (5 %) was dissolved in BMIMCl. The mixture was kept at room temperature for 4–6 days until gelation took place. Then, the excess BMIMCl was removed by methanol washing to give a flexible cellulose-starch based ion gel. In this case, XRD studies also demonstrated that the crystalline nature of both cellulose and starch was mostly destroyed after the treatment. The thermal analysis revealed the presence of water in the gel indicating a similar gelation mechanism as the previous cellulose based ion gel.

Interestingly, cellulosic ion gels are having many applications in the fields of electrolytic membranes, lithium-ion batteries, fuel cells, electrochemical- and bio-sensors, actuators and separation membranes. Due to its technological and industrial interest, It is expected that these materials are much more developed in the near future.

Cellulosic Electrospun Fibers from Ionic Liquids

Electrospinning of cellulose fibers from conventional solvent systems was complicated due to their toxicity and harsh conditions required for dissolution. Hence, solubility of cellulose in ionic liquids facilitated the electrospinning process of this material to obtain fibers with tunable properties. Electrospun fibers of cellulose and cellulose derivatives find uses in the fields where other polymeric electrospun fibers are used such as filtration and biomedical applications [61]. One important aspect of electrospinning from ionic liquid systems is their nonvolatile nature; consequently they do not evaporate during the flight from the spinneret to the collector. Therefore, the process requires a custom designed spinning procedure, in which the cellulose fibers are deposited into a coagulant media such as alcohol or water in order to recover the fibers and remove the ionic liquid. The fiber production process can be achieved through two main techniques; (a) dry-wet or (b) wet-wet electrospinning. In the first system, the solution is spun from the spinneret through an air-gap between nozzle and the coagulation bath. The formed fibers are immediately drawn out with a collector. In the latter system, the electrospun jet directly enters into the coagulation bath to form the fibers which are drawn out with a collector in the same way. The ionic liquid used to dissolve cellulose is removed from the fiber by passing through a coagulation bath in both two processes. For instance, Han et al. used 1-allyl-3-methylimidazolium chloride (AMIMCl) and dimethylsulfoxide (DMSO) solvent system in order to produce electrospun cellulose fibers. The fibers were collected onto a rotating copper-wire drum under a high humidity and the remaining ionic liquid was eliminated resulting in a self-standing solid electrospun network (see Fig. 6.5). X-ray diffraction (XRD) analysis revealed (see Fig. 6.10) that the cellulose fibers were almost entirely amorphous after the electrospinning process [62].

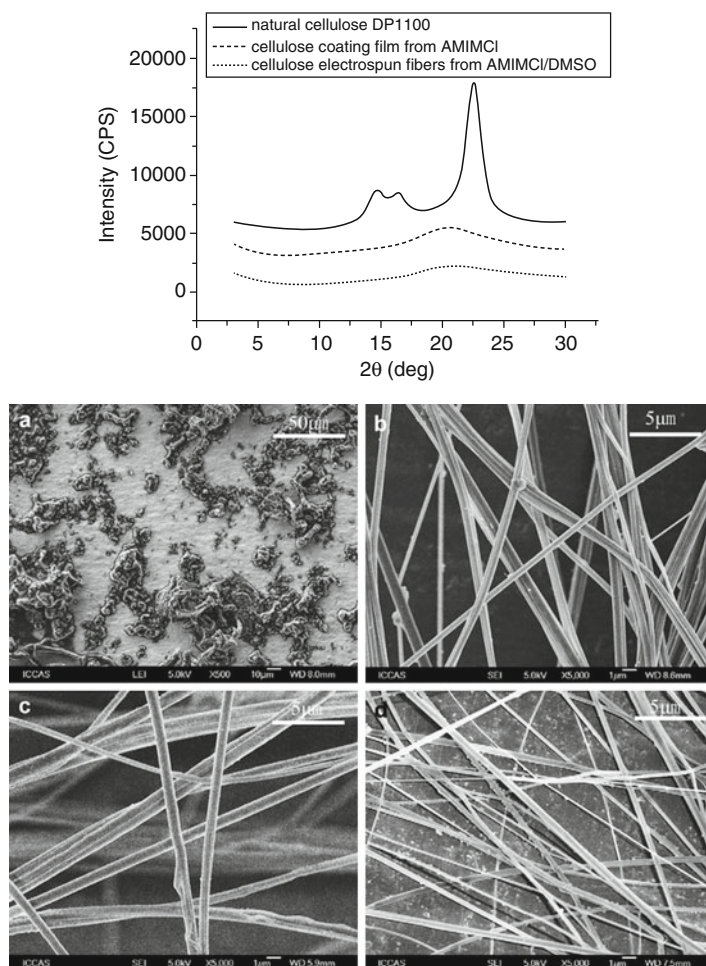


Fig. 6.10 XRD patterns of natural cellulose and electrospun fibers from AMIMCl, (a–d) SEM images of fibers produced at different IL/DMSO concentrations [62]

Similarly Chin et al., deposited cellulose fibers directly into aqueous media in order to coagulate the fibers and remove the ionic liquid. They demonstrated that in this case cellulose preserved the crystallinity up to a certain extent even after the electrospinning process [63]. In addition, they found that thermal stability of the fibers was also lower compared to neat cellulose. They suggested that the thermal stability was reduced because of partial degradation of cellulose during electrospinning process.

Besides using only cellulose, it can be combined with other polymeric structures as described prior to the electrospinning process to modify its properties. For instance, Viswanathan et al. prepared cellulose-heparin composites using ionic liquids [64]. They combined the blending process with the electrospinning process.

Thus, two different solutions were prepared, on the one hand the cellulose was dissolved in BMIMCl and on the other hand heparin was dissolved in 1-ethyl-3-methylimidazolium benzoate. Prior to the electrospinning the two solutions were mixed and the blended fibers were collected in ethanol through precipitation of electrospun fibers. They found that the composite fibers displayed anticoagulant activity indicating that bioactivity of heparin remained unaffected. Analogously, multiwall carbon nanotubes (MWCN) were successfully blended with cellulose using 1-ethyl-3-methylimidazolium chloride ionic liquid prior to the electrospinning process. Firstly, MWCN were dissolved into the ionic liquid to give a solid paste. Secondly, one fifth of the desired amount of cellulose was dissolved in the ionic liquid at 80 °C and this solution was mixed with the previously prepared paste. Subsequently, remaining cellulose was added in small portions and mixed at 80 °C until a homogeneous mixture is obtained. Finally the mixture was spun into a coagulation bath containing ethanol as the coagulant (wet spinning) [65]. The materials displayed lower thermal shrinkage, enhanced mechanical strength and good electrical conductivity with the incorporation of carbon nanotubes.

Outlook

Use of ionic liquids in new cellulose processing and materials technologies is still expanding. The use of ionic liquids for cellulose dissolution stems from the unique properties of ionic liquids to interact with the strong hydrogen bonds of polysaccharides. Pioneering works on the dissolution of cellulose in ionic liquids has been used to develop new processing technologies, cellulose functionalization methods and new cellulose materials including blends, composites, fibers and ion gels. However, due to its potential interest and versatility of both cellulose and ionic liquids more developments are expected in the near future. Taking into account that current industrial biomass processing technologies produce many hazardous waste products that cannot be recycled, ionic liquid-based technologies offer great opportunities for the development of a new sustainable cellulose industry.

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Ionic Liquids and Polymeric Ionic Liquids in Analytical Environmental Applications

7

Honglian Yu, Cheng Zhang, and Jared L. Anderson

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Abstract

Ionic liquids (ILs) are a class of organic salts with unique properties and have been shown to be particularly useful for the development and improvement of sample preparation and detection methodologies. ILs and polymeric ionic liquids (PILs) have played an important role in the analysis of environmental samples. These compounds have been widely applied in various microextraction techniques due to their tunable analyte selectivity, low volatility, good thermal stability, as well as variable viscosity and solvent miscibility. The unique

H. Yu • C. Zhang • J.L. Anderson (✉)

Department of Chemistry and School of Green Chemistry and Engineering, The University of Toledo, Toledo, OH, USA

e-mail: honglian.yu@rockets.utoledo.edu; zhang.cheng@rockets.utoledo.edu;

Jared.Anderson@UToledo.edu

properties also make ILs and PILs an emerging class of stationary phases in gas chromatography (GC). IL/PIL-based stationary phases exhibit excellent applicability in multidimensional GC separations. This chapter will highlight the applications of ILs and PILs in a number of microextraction techniques in addition to their utilization in separation science with a particular emphasis on their use in environmental analysis.

Keywords

Ionic liquids • Polymeric ionic liquids • Microextraction • Gas chromatography • Environmental analysis

Introduction

The monitoring of environmental hazardous materials using cost-effective, highly sensitive, and environmentally friendly methodologies has always been a major topic in the analytical chemistry community [1, 2]. Overall, sample preparation is the most critical step for the quantitative analysis of environmental samples. Considerable effort has been focused on the engineering of novel sample preparation methods in the last several decades, including the development of microextraction techniques. By definition, microextraction techniques are non-exhaustive sample preparation methods that use small quantities of the extraction phase (microliter or less) compared to the total sample volume [3]. Techniques such as single-drop microextraction (SDME), hollow fiber membrane liquid-phase microextraction (HF-LPME), dispersive liquid–liquid microextraction (DLLME), and solid-phase microextraction (SPME) have minimized the use of large quantities of toxic and volatile organic solvents [4]. The development of novel extraction phases in various techniques has contributed to enhancing analyte extraction efficiency and selectivity. Meanwhile, these extraction techniques have been continually engineered to improve their simplicity, throughput, automation capability, and cost-effectiveness.

Ionic liquids (ILs) have attracted intense interest in sample preparation due to their unique characteristics [5]. The physicochemical properties of ILs can be modified by altering the cation/anion combinations and/or functionalizing their chemical structures with different substituents. In addition to being excellent extraction solvents in sample preparation, ILs have also been utilized as porogens, solvents/cosolvents, catalysts, and additives in various chemical systems [6, 7]. Analogously, polymeric ionic liquids (PILs) have been gaining momentum as SPME sorbent coatings due to their superior thermal stability and robustness [8]. Employing PILs as SPME sorbent coatings enables the thermal desorption of analytes at elevated temperature without compromising fiber integrity.

ILs and PILs are also playing important roles in various separation and detection techniques. For example, ILs have been successfully applied as GC stationary phases, high-performance liquid chromatography (HPLC) mobile phase additives,

matrices in matrix-assisted laser desorption ionization (MALDI), and capillary wall modifiers in capillary electrophoresis (CE) [6]. With regard to IL-based GC stationary phases, the unique characteristics of these compounds allow them to provide good separation power [9]. Moreover, the structural modification of ILs provides an additional dimension of selectivity which makes them amenable for the separation of multiple classes of analytes. Similarly, PIL-based GC stationary phases can provide enhanced thermal stability and low column bleed without sacrificing chromatographic selectivity [10].

This chapter provides an overview of the applications of ILs and PILs in environmental analyses and is divided into two primary sections. The first section explores the exploitation of ILs and PILs for various microextraction techniques including SDME, HF-LPME, DLLME, and SPME. Representative contributions will be categorized based on the different target analyte classes investigated. The second section will focus on the development of ILs and PILs as stationary phases in both single- and multidimensional GC separations. The engineering of novel IL/PIL-based GC stationary phases and their separation of various environmental samples will be discussed.

Application of ILs and PILs in Microextraction Techniques for Environmental Analysis

Single-Drop Microextraction (SDME)

Single-drop microextraction (SDME), introduced by Liu and Dasgupta in the 1990s, is an extraction technique that employs a solvent microdroplet as an extraction phase [11, 12]. Jeannot and Cantwell firstly performed analytical quantification by coupling this technique with a chromatographic system [13]. In their study, a Teflon rod was used to hang and immerse an 8 μL microdroplet of *n*-octane into an aqueous sample solution for extraction. Analysis of the sample was performed by withdrawing the extraction solvent into a microsyringe and subjecting it to GC separation [13]. The same group improved upon this technique by replacing the Teflon rod with a microsyringe as a support, which allowed extraction and sampling to be combined into one step [14]. Theis et al. further developed this technique by exposing the microdroplet in the headspace of the sample vial during the extraction step, further broadening the range of sample matrices and analytes that could be analyzed [15, 16].

The extraction solvent plays an important role in SDME. In direct immersion SDME (DI-SDME), the extraction solvent is usually water immiscible, since water is the most common sample matrix. On the other hand, low volatility and high viscosity are desirable properties for an extraction phase in headspace SDME (HS-SDME) to ensure minimal loss of the solvent. Hydrophobic organic solvents were commonly chosen as extraction solvents in the early stages of SDME method development [14–16]. However, there are only a small number

of organic solvents that can fulfill the physicochemical properties required in SDME. Contrarily, due to their tunable structures, ILs can be excellent extraction solvents for SDME, as demonstrated by Liu and coworkers in 2003 [17]. A summary of applications in which ILs have been employed in SDME is shown in Table 7.1.

Extraction of Volatile Organic Compounds (VOCs)

The 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$) IL was applied by Aguilera-Herrador et al. as a solvent in the analysis of three VOCs (dichloromethane, *p*-xylene, and *n*-undecane), which are commonly known to be environmental water pollutants [18]. The extracted analytes were thermally desorbed by using a newly designed interface for the GC/MS inlet at 140 °C, as shown in Fig. 7.1 [18]. The interface consisted of three components, namely, the microsyringe injection zone, a removable perfluoroalkoxy (PFA) tubing unit, and a transfer line to the GC inlet. This interface not only allowed the direct coupling of IL-HS-SDME with GC/MS but also prevented contamination of the GC injector. The feasibility of the proposed interface was demonstrated by a low limit of detection (LOD, 5.6–15.6 $\mu\text{g L}^{-1}$) and low relative standard deviation (%RSD, 3.3–4.4 %) obtained when determining the concentration of target analytes. The same technique was also applied for the analysis of BTEX (benzene, toluene, ethylbenzene, and xylene isomers) and trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) using the 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$) IL as an extraction solvent [18–20].

A method utilizing IL-DI-SDME coupled to high-performance liquid chromatography/ultraviolet detection (HPLC/UV) was employed to analyze carbonyls in environmental water samples [21]. The selected analytes were derivatized using 2,4-dinitrophenylhydrazine (DNPH) prior to extraction in order to improve the sensitivity. In the extraction system, an LC syringe with a polytetrafluoroethylene (PTFE) sleeve fixed on the tip was applied to control the exposure of the $[C_8MIM][PF_6]$ IL extractant. Good analytical performance and recovery were obtained using this technique [21].

Extraction of Chlorobenzenes

HS-SDME coupled with HPLC analysis was adopted for the determination of chlorobenzenes in water using the $[C_4MIM][PF_6]$ IL as an extraction solvent [22]. The Plackett–Burman design was applied to optimize experimental parameters during the extraction step. The design of experiment (DOE) via ANOVA initially revealed that the extraction time, temperature, and sample ionic strength were the most influential variables for improving the extraction efficiency. Further, DOE optimization demonstrated that high extraction temperatures in HS-SDME can increase the analyte matrix-to-headspace diffusion coefficients while also decreasing its headspace-to-extractant partition coefficient [22]. In other studies, modifications of the GC inlet were performed in order to avoid contamination of the GC inlet (by the IL extraction phase) during the thermal desorption of chlorobenzene and their derivatives [23, 24].

Table 7.1 Summary of applications involving the use of ILs in SDME for environmental analysis

Analytes	Matrix	Applied ILs	IL volume (μL)	Extraction mode	Separation and detection method	LOD (μg L ⁻¹)	Recovery (%)	Reference
Dichloromethane, <i>p</i> -xylene, and <i>n</i> -undecane	Water	[C ₄ MIM][PF ₆]	2	HS	GC/MS	5.6–15.6	–	[18]
BTEX	River, drinking, tap, and well water	[C ₈ MIM][PF ₆]	2	HS	GC/MS	0.022–0.091	88.9–103.1	[19]
Trihalomethanes	River, drinking, tap, well, swimming-pool water	[C ₈ MIM][PF ₆]	2	HS	GC/MS	0.5–0.9	91.6–101.7	[20]
Carbonyl compounds derivatized by DNPH	River water, snow water, seawater	[C ₈ MIM][PF ₆]	10	DI	HPLC/UV	0.04–2.03	84.3–106.8	[21]
Chlorobenzenes	Tap, river, effluent water	[C ₄ MIM][PF ₆]	5	HS	HPLC/PDA	0.102–0.203	94.1–100.9	[22]
Chlorobenzenes	Tap, river, effluent water	[C ₆ MIM][PF ₆]	5	HS	GC/MS	0.001–0.004	90–115	[23]
Chlorobenzenes	Dye wastewater	[C ₈ MIM][PF ₆]	1	HS	GC/FID	0.1–0.5	88.9–110.9	[24]
Aromatic amines	Tap, well, rainwater	[C ₄ MIM][PF ₆]	15	HS	HPLC/UV-vis	0.09–0.38	81.9–99.1	[25]
Aromatic amines	Tap, rainwater	[C ₆ MIM][PF ₆]	15	DI	HPLC/UV-vis	1–2.5	81.7–97.9	[26]
Sulfonamides	Ground, lake, and pool water	[C ₈ MIM][PF ₆]	10	HS	HPLC/VW	0.5–2	63.5–115.8	[27]
Phenols	Lake water and dye wastewater	[C ₈ MIM][PF ₆]	1	HS	GC/FID	0.1–0.4	81–111	[28]

(continued)

Table 7.1 (continued)

Analytes	Matrix	Applied ILs	IL volume (μL)	Extraction mode	Separation and detection method	LOD (μg L ⁻¹)	Recovery (%)	Reference
Phenols	River and tap water	[C ₄ MIM][PF ₆]	0.00240	DI	CE	5–50	93.5–110.1	[29]
PAHs	Water	[C ₄ MIM][PF ₆], [C ₆ MIM][PF ₆], [C ₈ MIM][PF ₆], 1-octanol	3	DI/HS	HPLC/VW-FL	–	–	[17]
PAHs and other aromatic compounds	Tap, creek, river water	[C ₆ MIM][FAP], [C ₄ MPL][FAP], [PH ₃ T] [FAP], [HNH ₂ MPL][FAP]	10	DI	HPLC/UV-vis	0.03–1.2	79–114	[30]
PAHs and other aromatic compounds	Water	micellar ILs: [C ₄ MIM][C ₁₁ –[C ₁₀ MIM][Br] and [C ₄ MIM][C ₁₁ –SDS	6.5, 10	HS	HPLC/UV-vis	0.1–260.3	–	[31]
Hg species	Seawater, fish tissues, human hair, and wine	CYPHOS IL 101	6	HS	ETAAS	0.01	95–105	[32]
MeHg ⁺ , EtHg ⁺ , PhHg ⁺ , and Hg ²⁺	Tap and river water and wastewater	[C ₆ MIM][PF ₆]	4	DI	HPLC/PDA	1.0–22.8	83–123	[33]

Pb	Water, food samples, NIST SRM 1643e trace elements in water, NIST SRM 1549 nonfat milk powder	[C ₄ MIM][PF ₆]	7	DI	ETAAS	0.015	–	[34]
Pb	Tap, mineral, well, and river water	CYPHOS IL 101	4	DI	ETAAS	0.0032	97–105	[35]
Organotin	Deionized water, wastewater, and water from trading port and industrial and agricultural areas	[C ₄ MIM][PF ₆]	10	HS	HPLC/FL	0.62–0.95	86.9–92.1	[36]
Co	Tap, subterranean canal, river, underground water	[C ₆ MIM][PF ₆]	9	DI	ETAAS	0.04	–	[37]
Mn	Tap, subterranean canal, river, underground, spring water, NIST SRM 1643e trace elements in water	[C ₄ MIM][PF ₆]	4	DI	ETAAS	0.024	95–105	[38]
MMT	Tap water, gasoline sample	[C ₄ MIM][PF ₆]	2.5	HS	ETAAS	0.010	81.2–101.0	[39]
Cu	Tap water, lake water, SRM (tea and defatted powder)	[C ₄ MIM][PF ₆]	20	DI	UV–vis ICP-MS	0.15	98.3–105	[40]

(continued)

Table 7.1 (continued)

Analytes	Matrix	Applied ILs	IL volume (μL)	Extraction mode	Separation and detection method	LOD (μg L ⁻¹)	Recovery (%)	Reference
Cd	Tap water, lake water, river water, SRM of rice (GBW08512, GBW08511)	[C ₄ MIM][PF ₆]	20	DI	ETAAS	0.015	96.5–106	[41]
Co, Hg, Pb	Lake water, river water, human hair and serum	[C ₄ MIM][PF ₆]	2.5	Cycle flow	ETV-ICP-MS	0.0015–0.0098	92.8–108.7	[42]
UV filters	River water, seawater, channel water	[C ₆ MIM][PF ₆]	10	DI	HPLC-DAD	0.06–3.00	92–115	[43]
NMs, PCMs	Wastewater	[C ₈ MIM][PF ₆]	1	HS	GC-IT-MS/MS	0.010–0.030	–	[44]
NMs, PCMs, and PCM degradation compounds	Sewage sludge	[C ₈ MIM][PF ₆]	1	HS	GC-IT-MS/MS	0.5–1.5 ^a	–	[45]
Pathogenic bacteria	Water	[C ₄ MIM][PF ₆]-Pt nanoparticles	1	DI	MALDI-TOF MS	–	–	[46]

Abbreviation: *BTEX* benzene, toluene, ethylbenzene, and xylenes, *DNPH* 2,4-dinitrophenylhydrazine, *MMT* methylcyclopentadienyl-manganese tricarbonyl, *NMs* nitro musks, *PCMs* polycyclic musks

^a0.5–1.5 ng/g

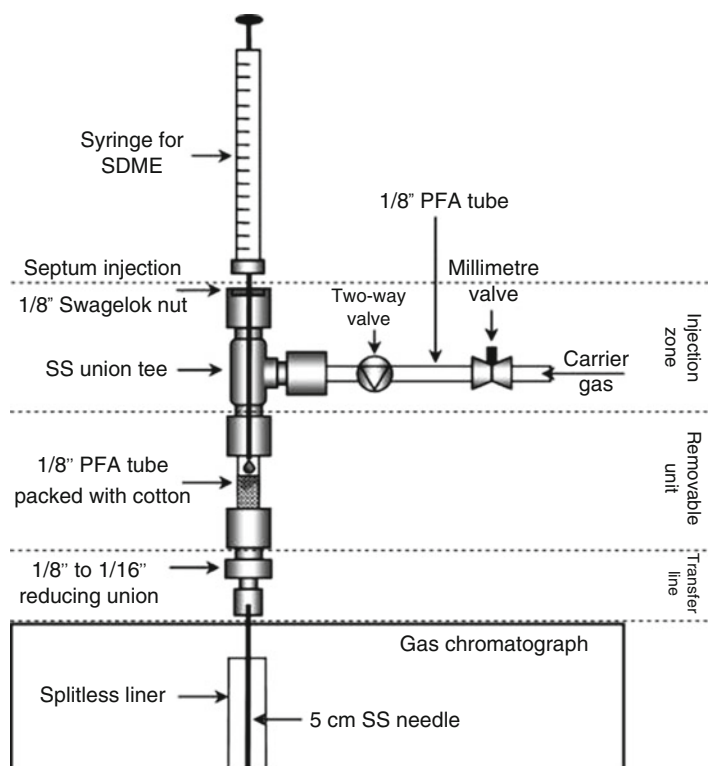


Fig. 7.1 Schematic of the interface developed for thermal desorption of extracted analytes from an IL drop in the GC inlet after SDME. PFA perfluoroalkoxy, SS stainless steel (Reprinted with permission from [18])

Extraction of Amines and Sulfonamides

The $[C_4MIM][PF_6]$ IL was applied as an extraction solvent to preconcentrate aromatic amines in water samples followed by analysis using HPLC [25]. An alternative method to study aromatic amines in water with IL as an extractant was presented by Sarafray-Yazdi and coworkers [26]. In this work, the $[C_6MIM][PF_6]$ IL microdroplet was injected into the aqueous sample solution and submerged in the solution during extraction under an ultrasonic bath. Afterwards, the IL microdroplet was withdrawn into an LC microsyringe with a PTFE sheath and introduced into an HPLC for analysis [26]. Both routes were simple, sensitive, and highly applicable for analyzing aromatic amines in water samples.

More recently, sulfonamides were determined in water samples by applying IL-HS-SDME coupled to HPLC [27]. The extraction solvent was optimized by investigating the enrichment factor, defined as a ratio between the final concentration of analyte in the extractant and the initial concentration in the sample matrix, for $[C_8MIM][PF_6]$, $[C_4MIM][PF_6]$, and octanol. The $[C_8MIM][PF_6]$ IL was selected as the optimal extraction solvent that exhibited the highest enrichment

factors for most analytes. Additionally, relatively higher enrichment factors were obtained for more hydrophobic analytes [27].

Extraction of Phenols

The on-line coupling of IL-DI-SDME with capillary electrophoresis (CE) in the determination of phenols in water samples was demonstrated [28]. The $[C_4MIM][PF_6]$ IL was transferred from a reservoir to a CE capillary and subsequently exposed to form a microdroplet in the sample solution. After the extraction step, the IL was retracted back into the capillary for CE analysis. The rate of transport and exposure of the IL was controlled through the optimization of system pressures with respect to time. The IL-SDME-CE method was validated by recovery studies in environmental water wherein excellent recovery and high reproducibility were obtained [28]. Phenols in various water samples were also studied by IL-HS-SDME coupled to GC using the $[C_8MIM][PF_6]$ IL as an extraction phase [29].

Extraction of Polycyclic Aromatic Hydrocarbons (PAHs)

A side-by-side comparison of different extraction solvents was performed in the IL-DI/HS-SDME analysis of a variety of PAHs [17]. The $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$ ILs exhibited better extraction efficiencies compared to 1-octanol. This was due, in part, to the high stability of the IL microdroplet which allowed larger extractant volumes and longer extraction times to be used. The highest enrichment factors were obtained for the $[C_8MIM][PF_6]$ IL which exhibited the lowest solubility in water. Conversely, the $[C_4MIM][PF_6]$ IL exhibited the lowest enrichment factors for the target PAHs due to its relatively higher solubility in water. Additionally, PAHs that are more volatile (i.e., naphthalene) showed higher enrichment factors when operated in HS-SDME rather than DI-SDME mode [17].

The applicability of a new class of hydrophobic ILs comprised of the tris (pentafluoroethyl)trifluorophosphate ([FAP]) anion in the DI-SDME extraction of PAHs and other aromatic compounds was demonstrated [30]. The $[C_6MIM][FAP]$ IL was compared with other hydrophobic ILs, namely, $[C_4MIM][PF_6]$, $[C_8MIM][PF_6]$, and 1,3-dibutylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($[C_4BIM][NTf_2]$) wherein superior enrichment factors were obtained using the new IL. This was attributed to the excellent hydrophobicity of the [FAP] anion and the high stability of the IL microdroplet. The effects of IL viscosity on extraction performance was also compared using four [FAP]-based ILs, namely, $[C_6MIM][FAP]$, 1-butyl-1-methylpyrrolidinium [FAP] ($[C_4MPL][FAP]$), trihexyl(tetradecyl)phosphonium [FAP] ($[PH_3T][FAP]$), and 1-(6-amino-hexyl)-1-methylpyrrolidinium [FAP] ($[HNH_2MPL][FAP]$). The $[PH_3T][FAP]$ IL exhibited the most desirable hydrophobicity, selectivity, and viscosity which contributed to the formation of a stable microdroplet and resulted in the highest enrichment factors for most analytes [30].

In order to improve the extraction efficiency of the IL-SDME method, micellar ILs were used to extract various PAHs and aromatic compounds from water [31]. Two types of micellar IL mixtures were investigated, namely, a cationic IL surfactant [1-decyl-3-methylimidazolium bromide ($[C_{10}MIM][Br]$)] in $[C_4MIM][Cl]$ and an anionic surfactant [sodium dodecyl sulfate (SDS)] in $[C_4MIM][Cl]$.

Both $[\text{C}_4\text{MIM}][\text{Cl}]-[\text{C}_{10}\text{MIM}][\text{Br}]$ and $[\text{C}_4\text{MIM}][\text{Cl}]\text{-SDS}$ mixtures exhibited higher enrichment factors for most analytes compared to the neat $[\text{C}_4\text{MIM}][\text{Cl}]$ and $[\text{C}_4\text{MIM}][\text{PF}_6]$ ILs presumably due to enhanced dispersive interactions and/or $\pi\text{-}\pi$ interactions [31].

Extraction of Metal Ions and Organometallic Compounds

A phosphonium-based IL, tetradecyl(trihexyl)phosphonium chloride (CYPHOS IL 101), was mixed with an oxidizing reagent, potassium permanganate (KMnO_4), to extract inorganic and organic mercury (InHg , OrHg) by HS-SDME coupled to electrothermal atomic absorption spectrometry (ETAAS) [32]. The InHg species were determined by adding a reducing reagent, SnCl_2 , to reduce the Hg^{2+} in the sample solution to volatile Hg^0 , allowing for the headspace extraction of the analytes. The total Hg concentration, including InHg and OrHg , was obtained by photooxidizing all mercury species in solution followed by IL-HS-SDME. Trace-level LODs (part-per-billion level) and excellent precision were obtained [32].

Different mercury species, namely, methylmercury (MeHg^+), ethylmercury (EtHg^+), phenylmercury (PhHg^+), and Hg^{2+} , in water samples were extracted using the $[\text{C}_6\text{MIM}][\text{PF}_6]$ IL via DI-SDME coupled to HPLC/photodiode array detection (HPLC/PDA) [33]. The target analytes were originally derivatized by dithizone to form neutral dithizonates which enhanced the extraction efficiency. During separation, ethylenediaminetetraacetic acid (EDTA) was used as an additive in the mobile phase to avoid interference from other metal ions.

The IL-SDME of lead (Pb) in water samples, with the assistance of chelating reagents, was studied by Manzoori and coworkers [34]. In their study, the $[\text{C}_4\text{MIM}][\text{PF}_6]$ IL was used to extract Pb(II) in sample solutions, while ammonium pyrrolidinedithiocarbamate (APDC) was employed as a chelating reagent. A similar technique was also applied for the determination of Pb in a number of water samples using CYPHOS 101 as the extraction phase and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) as a chelating reagent [35]. Trace-level LODs in the part-per-billion range with decent precision was achieved with both of the aforementioned analytical methods.

Tributyltin (TBT) and triphenyltin (TPhT) were analyzed by Sheikhloie and coworkers by IL-HS-SDME [36]. The target analytes were derivatized by sodium tetraethylborate (NaBEt_4) in solution in order to enhance their volatility, leading to an increase of the overall extraction efficiency. The derivatives were also concentrated in a microdroplet of $[\text{C}_4\text{MIM}][\text{PF}_6]$ IL and further analyzed by HPLC coupled to fluorescence detection.

A variety of metal ions and organometallic compounds were analyzed by IL-SDME-ETAAS. A microdroplet of $[\text{C}_6\text{MIM}][\text{PF}_6]$ and APDC chelating reagent was used to preconcentrate cobalt (Co) in the form of a $\text{Co(II)}\text{-APDC}$ complex [37]. The $[\text{C}_4\text{MIM}][\text{PF}_6]$ IL combined with the 1-(2-thiazolylazo)-2-naphthol (TAN) chelating reagent was applied in the extraction of Mn(II) in the natural water samples [38]. The same IL was also applied for the analysis of methylcyclopentadienyl-manganese tricarbonyl (MMT) in water and gasoline samples [39]. A similar method was adopted for the extraction of copper (Cu) by

chelating with diethyldithiocarbamate (DDTC) and the extraction of cadmium (Cd) in the form of Cd-APDC [40, 41].

IL-based cycle flow SDME, in conjunction with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS), was used to determine Co, Hg, and Pb in environmental waters and human serum [42]. The [C₄MIM][PF₆] IL was combined with a chelating reagent, 1-(2-pyridylazo)-2-naphthol (PAN), to form the extraction solvent in this study. After extraction, the IL-PAN phase was retracted from the extraction chamber and directly injected into a graphite furnace for quantitative analysis. Interference signals stemming from common coexisting metal ions, such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Fe³⁺, and Cu²⁺, were studied by recovery experiments wherein no significant interferences were observed. Higher extraction efficiencies were obtained for Co and similar extraction efficiencies were obtained for Hg and Pb compared to a traditional route employing CCl₄-PAN as an extraction solvent [42].

Extraction of Other Types of Analytes

The analysis of UV filters as an emerging class of pollutants in surface water samples was performed by using IL-DI-SDME coupled to HPLC/UV [43]. An acidic pH was used during sampling to ensure the stability of the [C₆MIM][PF₆] IL extraction phase and enhance the extraction efficiency of the target compounds. It was observed that the ionic strength and extraction time were the most important optimization variables [43].

Musk fragrances, which are commonly used in personal care products (PCPs), are another class of emerging organic contaminants [44]. A fully automated IL-HS-SDME method was developed using the [C₈MIM][PF₆] IL as an extraction phase for the analysis of nitro, polycyclic musks and polycyclic musk degradants [44]. Musk fragrances were also extracted from other environmental samples by coupling pressurized liquid extraction (PLE) to automated IL-HS-SDME [45]. The same group determined ten musk fragrances in sewage sludge from various wastewater treatment plants. It was found that the polycyclic musks appeared in these samples at concentrations above the limits of quantification (LOQs ~ 2.5–5 ng/g), while nitro musk concentrations were below LOQs and xylene was not detected [45].

Bacterial contamination is another area of interest in environmental analysis. The extraction of pathogenic bacteria by DI-SDME coupled to MALDI time-of-flight MS (MALDI-TOF MS) was performed wherein [C₄MIM][PF₆]-platinum nanoparticles (Pt NPs) were applied as an extraction phase [46]. The Pt NPs acted as a trapping layer which allowed more analytes to partition to the IL phase, thereby enhancing the overall extraction efficiency.

Hollow Fiber Membrane Liquid-Phase Microextraction (HF-LPME)

Hollow fiber membrane liquid-phase microextraction (HF-LPME) was introduced by Pedersen-Bjergaard and Rasmussen in 1999 [47]. As shown in Fig. 7.2, there are two HF-LPME extraction modes, namely, the two-phase and three-phase extraction modes [48]. In the two-phase mode, both the hollow fiber

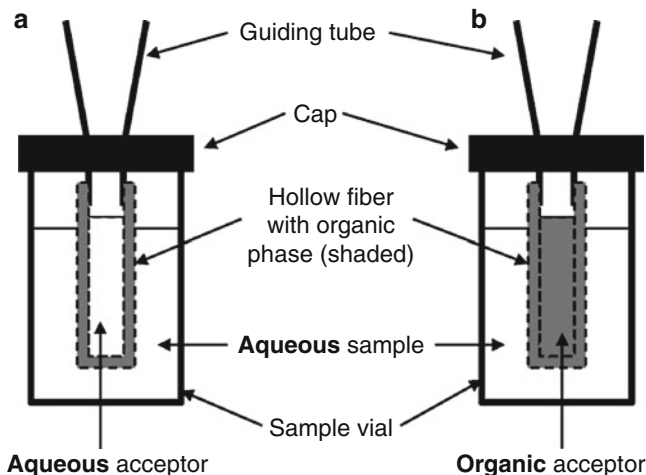


Fig. 7.2 Schematic of the basic operating principles in three-phase (a) and two-phase (b) LPME (Reprinted with permission from [48])

wall pore and lumen are filled with an extraction solvent (acceptor phase). In the three-phase mode, an organic solvent is immobilized within the pore of the membrane to function as a physical barrier, while an aqueous acceptor phase is filled within the lumen. As a result, analytes are initially extracted by the organic phase and subsequently back-extracted by the aqueous acceptor phase. Conventional organic solvents such as toluene, undecane, and octanol have been successfully applied in both extraction modes. However, there are multiple drawbacks to employing organic solvents in HF-LPME, including the introduction of toxic and volatile organic solvents to the environment as well as the limited method sensitivity and analyte selectivity. Similar to other extraction techniques, ILs have a number of unique properties that make them interesting alternatives to traditional organic acceptor phases.

The first report to use ILs in HF-LPME was by Peng and coworkers [49]. The $[C_8MIM][PF_6]$ IL was immobilized in the pores of a polypropylene hollow fiber for the extraction of chlorophenols in environmental water samples. Subsequently, a back extraction was applied by using a sodium hydroxide solution in the acceptor solution. Due to the high stability of the hollow fiber-supported IL membrane, good reproducibility with RSD values lower than 6 % was obtained. The proposed method was successfully applied for the determination of chlorophenols in real water samples with recoveries ranging from 70.0 % to 95.7 % [49].

A similar approach was also applied for the determination of sulfonamides in environmental water samples [50]. The $[C_8MIM][PF_6]$ IL demonstrated superior enrichment factors compared with organic solvents such as *n*-undecane and dihexyl ether. Due to the high solubility of the sulfonamides in the aqueous phase, tri-*n*-octylphosphine oxide (TOPO) was added into the IL phase to alter the behavior of the membrane liquid, resulting in much higher extraction efficiencies.

In addition, the IL-based membrane was observed to form an efficient barrier to large molecules in complicated sample matrices [50].

A water-miscible IL was introduced as the acceptor phase additive in HF-LPME [51]. Different analyte classes, including alkaline compounds, acidic compounds, and neutral compounds, were selected to evaluate the extraction performance of the method. By adding the [C₄MIM][Cl] IL as an acceptor phase, higher extraction efficiencies were obtained compared to conventional three-phase HF-LPME. After the optimization of the extraction conditions, the proposed method was also applied for the analysis of PAHs in river water samples wherein acceptable recoveries and LODs in the sub-ppb ranges were achieved.

Two-phase HF-LPME using a number of ILs as acceptor phases was applied for the determination of four UV filters in water samples [52]. Four ILs, including [C₆MIM][FAP], [C₄PL][FAP], [C₄MIM][PO₄], and [C₄MIM][PF₄], were evaluated in this study. The [C₆MIM][FAP] IL showed the highest selectivity for the analytes from the sample matrix. The LODs obtained using this method ranged from 0.3 to 0.5 ng mL⁻¹ with reported enrichment factors up to 216.

IL-based HF-LPME has also been coupled with flame atomic absorption spectrometry (FAAS) for the analysis of Cr(VI) and Cr(III) ions in aqueous solutions [53]. In this approach, the [C₄MIM][BF₄], [C₆MIM][PF₆], and [C₈MIM][PF₆] ILs and diethyldithiocarbamate (DDTC) were used as enhancement and chelating reagents, respectively. The addition of [C₄MIM][BF₄] increased the enrichment factors of Cr(VI) by nearly 3.5-fold. The method was also applied to certified reference environmental water samples and different real water samples with satisfactory results. The Cr(VI) ion was also chosen as an analyte of interest in an automated on-line IL-based HF-LPME method using a 10 % (v/v) methyltriocetyl ammonium chloride acceptor phase [54].

In order to further increase the mass transfer of the analytes between the aqueous sample and extraction solvent, a modified HF-LPME technique called solvent bar microextraction (SBME) was developed [55]. A three-phase liquid–liquid–liquid solvent bar microextraction (LLL-SBME) procedure was firstly applied for the analysis of phenols in seawater samples using the [C₄MIM][PF₆] IL as an intermediary solvent. To prepare the solvent bar, a 2.8-cm hollow fiber segment was filled with acceptor solution and two ends heat sealed. After immersing the solvent bar into the selected IL for 5 s, the IL-impregnated solvent bar was applied for extraction. Subsequent to the extraction step, one end of the solvent bar was cut and the acceptor solution subjected for HPLC-UV analysis. Compared with the conventional three-phase LLL-SBME and IL-supported hollow fiber-protected three-phase LLL-SBME, the proposed method demonstrated higher extraction efficiency for the extraction of phenols.

Dispersive Liquid–Liquid Microextraction (DLLME)

Dispersive liquid–liquid microextraction (DLLME) has become a very popular sample preparation technique since its introduction by Rezaee et al. in 2006 [56].

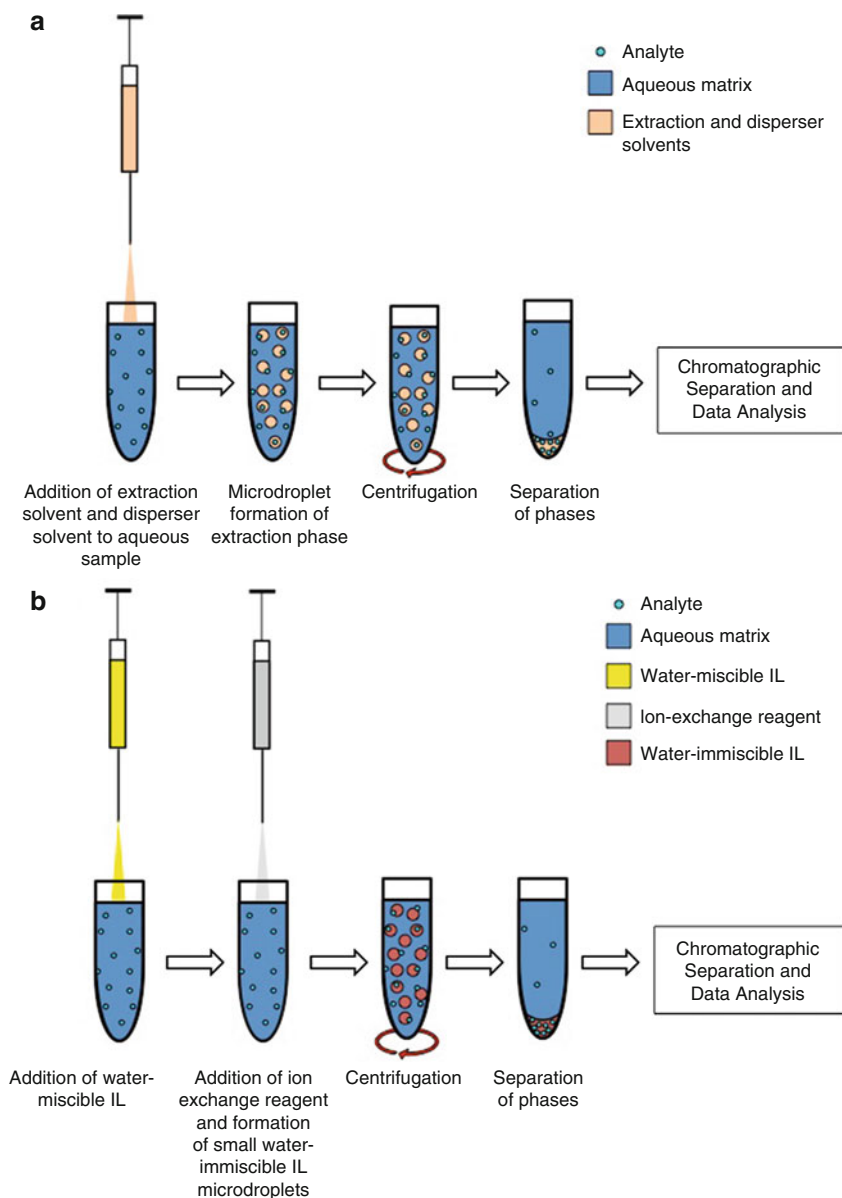


Fig. 7.3 Schematic of the basic operating principles in DLLME (a) and in situ IL-based DLLME (b) (Reprinted with permission from [4])

This method involves the use of three liquid phases, namely, the aqueous sample, a hydrophobic extraction solvent, and a disperser solvent which is miscible in both phases. The basic operating procedure of DLLME is illustrated in Fig. 7.3a [4]. During extraction, micro-volume amounts of the extraction and disperser solvents are

injected into the aqueous phase. Equilibrium is quickly achieved due to the formation of small microdroplets possessing high surface area within the sample solution. Subsequently, the extraction and aqueous phase can be separated by centrifugation to form a biphasic system where the sedimented phase is collected for chromatographic analysis. Because of its simplicity, high throughput, excellent preconcentration capabilities, and low organic solvent consumption, DLLME coupled to GC or HPLC has been extensively applied for the analysis of various organic compounds [57]. Additionally, DLLME can also be combined with FAAS or electrothermal atomic absorption spectrometry (ETAAS) for the determination of inorganic compounds in the environment [58].

The extraction efficiency in DLLME can be influenced by several experimental parameters including the chemical structure and volumes of the extraction and disperser solvent, the extraction time, sample volume, sample pH, and ionic strength [57, 58]. In most cases, the extraction solvent should possess higher density than water to allow phase separation during centrifugation. Chlorinated solvents, such as dichlorobenzene, chloroform, and carbon tetrachloride, have been widely used as extraction solvents in DLLME. Unfortunately, chlorinated solvents can be highly toxic and possess high vapor pressure which can significantly contribute to environmental pollution. Due to the unique properties of ILs, such as low vapor pressure and tunable viscosity, miscibility, and selectivity, there has been growing interest in the analytical community to exploit these solvents as viable alternatives in DLLME. This section will introduce the application of ILs in DLLME for environmental analysis. A summary of these studies is presented in Table 7.2.

Extraction of Pesticides

The first application of ILs as extraction solvents in DLLME was demonstrated by Zhou and coworkers [59]. The $[\text{C}_6\text{MIM}][\text{PF}_6]$ IL was selected as an extraction solvent since this IL exhibited low solubility and higher density than water. To allow complete homogenization of the IL in the aqueous solution, temperature-controlled (TC) IL-DLLME was applied by heating the sample solution to 70 °C. Subsequently, the sample solution was cooled in an ice bath and the IL phase separated by centrifugation followed by HPLC analysis. The TC IL-DLLME method was demonstrated to be inexpensive and highly convenient for the determination of pesticides in water samples. The TC IL-DLLME technique was also applicable in the determination of trace organophosphorus pesticides [60], chlorotoluron, diethofencarb and chlorbenzuron [61], dichlorodiphenyltrichloroethane (DDT) and its metabolites, and hexabromocyclododecane diastereomers in environmental samples [62, 63].

Methanol was applied as an IL disperser solvent in the IL-DLLME of four heterocyclic insecticides in water samples [64]. The $[\text{C}_6\text{MIM}][\text{PF}_6]$ IL was dissolved in methanol and rapidly injected into the sample containing the analytes. Analysis was performed by HPLC coupled to diode array detection (HPLC-DAD). Under optimized conditions, enrichment factors in the range of 209–276 were obtained for fipronil, chlorfenapyr, buprofezin, and hexythiazox. A similar

Table 7.2 Summary of applications utilizing ILs as an extraction solvent in DLLME for environmental analysis

Analytes	Matrix	Applied ILs	Method applied for phase separation	Separation and detection method	LOD ($\mu\text{g L}^{-1}$)	Recovery (%)	Reference
Pyrethroid pesticides	Tap, ground, river, and reservoir water	$[\text{C}_6\text{MIM}][\text{PF}_6]$	Temperature-controlled method followed by centrifugation	HPLC-UV	0.28–0.60	76.7–135.6	[59]
Organophosphorus pesticides	Tap, well, rain, and river water	$[\text{C}_6\text{MIM}][\text{PF}_6]$	Temperature-controlled method followed by centrifugation	HPLC-UV	0.17–0.29	88.2–103.6	[60]
Chlorotoluron, diethofencarb, and chlorbenzuron	Melted snow, tap and lake water	$[\text{C}_6\text{MIM}][\text{PF}_6]$	Temperature-controlled method followed by centrifugation	HPLC-UV	0.04–0.43	86.3–106.5	[61]
DDT and its metabolites	Everglade, river, reservoir, and snow samples	$[\text{C}_6\text{MIM}][\text{PF}_6]$	Temperature-controlled method followed by centrifugation	HPLC-UV	0.24–0.45	87.4–110.0	[62]
Hexabromocyclododecane diastereomers	River water	$[\text{C}_6\text{MIM}][\text{PF}_6]$	Temperature-controlled method followed by centrifugation	RRLC-ESI-MS-MS	0.1	77.2–99.3	[63]
Heterocyclic insecticides	Tap, lake, and fountain water	$[\text{C}_6\text{MIM}][\text{PF}_6]$	Centrifugation	HPLC-DAD	0.53–1.28	79–106 %	[64]
Organophosphorus pesticides	Tap, well, rain, and river water	$[\text{C}_6\text{MIM}][\text{PF}_6]$	Centrifugation	HPLC-UV	0.1–5	87.3–117.6	[65]
Phenylurea pesticides	River and lake water	$[\text{C}_6\text{MIM}][\text{NTf}_2]$	In situ metathesis reaction followed by centrifugation	VWD	0.06–0.08	92.1–104.8	[68]
Benzoylurea insecticides	Lake water	$[\text{C}_6\text{MIM}][\text{PF}_6]$	Magnetic retrieval of the IL using magnetic nanoparticles	HPLC-VWD	0.05–0.15	79.7–91.7	[69]
Triclosan and triclocarban	Tap and wastewater	$[\text{C}_6\text{MIM}][\text{PF}_6]$	Centrifugation	HPLC-MS/MS	0.04–0.58	70–103.5	[66]

(continued)

Table 7.2 (continued)

Analytes	Matrix	Applied ILs	Method applied for phase separation	Separation and detection method	LOD ($\mu\text{g L}^{-1}$)	Recovery (%)	Reference
Bisphenol A and 2-naphthol	Tap, lake, and river water	[C ₆ MIM][PF ₆]	Temperature-controlled method followed by centrifugation	HPLC-VWD	0.58–0.86	99.4–108.1	[71]
Aromatic compounds	Tap, well, river, and creek water	[C ₄ MIM][NTf ₂]	In situ metathesis reaction followed by centrifugation	HPLC-UV	0.02–0.3	84–115	[67]
PAHs	Tap, bottled, fountain, well, contaminated rivers, rainwater, treated and raw wastewater	[C ₈ MIM][PF ₆]	Centrifugation	HPLC-fluorescence	0.00003–0.002	90.3–103.8	[72]
Aromatic amines	Melted snow, river and brook water	[C ₆ MIM][PF ₆]	Centrifugation	HPLC-UV	0.17–0.49	92.2–119.3	[73]
Antidepressant drugs	Canal water	[C ₆ MIM][FAP]	Applied a μ -SPE device to extract analytes from the IL phase	HPLC-UV	0.3–1	94.3–117.4	[76]
Pharmaceuticals	Wastewater	[C ₈ MIM][PF ₆]	Centrifugation	HPLC-MS/MS	0.0002–0.06	88–111	[74]
Lovastatin and simvastatin	Lake and river water	[C ₆ MIM][PF ₆]	Temperature-controlled method followed by centrifugation	HPLC-UV	0.17–0.29	80.5–112	[75]
Hg	Saline solution	[C ₆ MIM][PF ₆]	Chelate with TMK/temperature-controlled	UV	0.7	97.3–104	[79]

			method followed by centrifugation				
Pd	Food additive, seawater, tea and biological samples	[C ₆ Py][PF ₆]	Chelate with TMK/temperature-controlled method followed by centrifugation	UV	0.2	100.5–104.5	[80]
Co	Mineral, river, and seawater	[C ₆ MIM][PF ₆]	Chelate with 1-(2-Pyridylazo)-2-naphthol (PAN)/temperature-controlled method followed by centrifugation	FO-LADS	0.14	96–103	[78]
Pb, Cd	Tap water	[C ₆ MIM][PF ₆]	Chelate with sodium diethyldithiocarbamate trihydrate (NaDDTC · 3H ₂ O)/Centrifugation	FAAS	0.6 (Pd) 0.03 (Cd)	–	[81]
				FAAS	1.5	100	[82]
Pb	Tap and mineral water	[C ₆ MIM][PF ₆]	Chelate with APDC/centrifugation	FAAS			
V	Tap and river water	[C ₄ MIM][PF ₆]	Chelate with 5-Br-PADAP/centrifugation	ETAAS	0.0049	97.7–101.9	[84]
Co	Tap and river water, urine, and saliva	[C ₆ MIM][PF ₆]	Chelate with 1-nitroso-2-naphthol/centrifugation	ETAAS	0.0038	98–103	[85]
Zn	Tap, spring, and underground water	[C ₆ Py][PF ₆]	Chelate with 8-hydroxyquinoline (oxine)/centrifugation	FAAS	0.22	97–102.5	[87]
Al	Mineral water and rainwater	[C ₆ Py][PF ₆]	Chelate with 8-hydroxyquinoline (oxine)/centrifugation	SFS	0.05	92.7–101.5	[88]

(continued)

Table 7.2 (continued)

Analytes	Matrix	Applied ILs	Method applied for phase separation	Separation and detection method	LOD ($\mu\text{g L}^{-1}$)	Recovery (%)	Reference
Arsenite and arsenate	Tap and river water	$[\text{C}_4\text{MIM}][\text{NTf}_2]$	Chelate with APDC/cooling followed by centrifugation	ETAAS	0.013	98.7–103	[90]
Lanthanoids	Uranium dioxide powders	$[\text{C}_6\text{MIM}][\text{PF}_6]$	Chelate with 1-hydroxy-2,5-pyrrolidinedione/centrifugation	ICP-OES	0.34–1.29	–	[89]
Boron species	Synthetic seawater	<i>N</i> -methyl- <i>d</i> -glucaminium-based ILs	IL was applied as chelating reagent/centrifugation	HPLC-UV	–	–	[91]

Abbreviation: *TMK* Michler thioketone, *APDC* ammonium pyrrolidinedithiocarbamate, *RRLC-ESI-MS-MS* rapid resolution liquid chromatography–electrospray ionization tandem mass spectrometry, *VWD* HPLC-variable-wavelength detection, *FO-LADS* fiber optic-linear array detection spectrophotometry, *FAAS* flame atomic absorption spectrometer, *ETAAS* electrothermal atomic absorption spectrometer, *SFS* stopped-flow spectrofluorometry, *ICP-OES* inductively coupled plasma optical emission spectrometer

approach was employed for the determination of organophosphorus pesticides, triclosan, and triclocarban in water samples [65, 66].

A novel microextraction technique called in situ metathesis reaction, combined with IL-DLLME, was firstly developed by Yao and coworkers [67]. Figure 7.3b illustrates this method. A hydrophilic IL (i.e., [C₄MIM][Cl]) was added as a starting extraction solvent and fully dissolved in the aqueous sample solution. The extraction phase was then exchanged to a water-immiscible IL by adding an ion-exchange reagent (LiNTf₂) into the sample solution. Due to the formation of fine microdroplets, the contact area between the IL extraction phase and aqueous sample can be significantly increased. The approach was compared with the traditional IL-DLLME method using hydrophobic IL and disperser solvent. The IL-DLLME method involving in situ metathesis reaction can significantly decrease the extraction time while also increasing the enrichment factors.

The same method was applied for the determination of five phenylurea pesticides in environmental water samples [68]. Parameters including the amount of [C₆MIM][Cl] IL, the molar ratio of [C₆MIM][Cl] and LiNTf₂, ionic strength, ultrasonic time, and centrifugation time were optimized using a Plackett–Burman design. Under optimized conditions, good repeatability (RSD 2.4–3.5 %), linearity (0.5 µg L⁻¹–500 µg L⁻¹), low LODs (0.06 µg L⁻¹–0.08 µg L⁻¹), and enrichment factors (244–268) were obtained [68].

In order to achieve better phase separation after the extraction step, a magnetic retrieval IL-DLLME procedure was introduced for the analysis of five benzoylurea insecticides in environmental water samples [69]. After the extraction process was complete, Fe₃O₄ magnetic nanoparticles were added into the sample solution as a carrier to retrieve and separate the IL containing the analytes. After removing the sample solution, the IL phase was desorbed to an HPLC using acetonitrile. Compared to the conventional IL-DLLME, this method can drastically decrease the time required for sample preparation as the entire extraction process can be completed within 5 min [69].

The IL-DLLME method was also coupled to a pretreatment procedure for the determination of pesticides in fruit samples [70]. Banana samples were homogenized and extracted with acetonitrile. After suitable evaporation, the sample was dissolved in water and TC IL-DLLME was applied using the [C₆MIM][PF₆] IL as extraction solvent.

Extraction of Aromatic Compounds

A cold-induced aggregation (CIA) IL-DLLME method for the determination of bisphenol A and 2-naphthol in water samples was reported by Jiang and coworkers [71]. Results including extraction time, linear range, and LODs were compared with other methods such as LLE-HPLC, SPME-HPLC, and IL-DLLME. Shorter extraction times and smaller volumes of IL were required for the CIA IL-DLLME, and higher precision was obtained for this method.

The traditional IL-DLLME method was applied by Pena et al. for the preconcentration of 18 PAHs in water samples [72]. The extraction efficiency of the IL-DLLME procedure was compared with the previously reported liquid–liquid

extraction (LLE) procedure, and a slightly higher matrix effect was observed for IL-DLLME. However, the IL-DLLME procedure appeared to be an effective alternative, boasting a faster and simpler methodology while also consuming smaller volumes of organic solvent.

An ultrasound-assisted IL-DLLME method was developed by Zhou and coworkers for the analysis of aromatic amines in water samples [73]. In this study, $[\text{C}_6\text{MIM}][\text{PF}_6]$ was finely dispersed in aqueous samples by ultrasonication. An in situ metathesis reaction combined with the ultrasound-assisted IL-DLLME method was later developed by Yao et al. for the determination of aromatic compounds in water samples [67].

Extraction of Pharmaceutical Compounds

Ultrasound-assisted IL-DLLME has also been coupled with LC-MS/MS for the analysis of pharmaceuticals including paracetamol, metoprolol, bisoprolol, betaxolol, ketoprofen, naproxen, ibuprofen, flufenamic acid, and tolafenamic acid in wastewaters [74]. In this approach, the $[\text{C}_8\text{MIM}][\text{PF}_6]$ IL and acetonitrile were used as extraction and disperser solvents, respectively. In order to increase the interface between the viscous IL extraction phase and the sample solution, sonication was applied to assist the formation of a cloudy solution in this procedure. Moreover, sonication assisted in reducing the consumption of acetonitrile from 1.0 to 0.5 mL. The optimized method was applied for the determination of flufenamic acid and metoprolol in water samples from a wastewater treatment plant. A similar approach was also applied for the determination of lovastatin and simvastatin in aqueous samples [75].

Ge and coworkers combined IL-DLLME with micro-solid-phase extraction (μ -SPE) for the determination of tricyclic antidepressants (TCAs) in water samples [76]. After sonication-assisted DLLME, a μ -SPE device containing zeolite imidazolate framework 4 (ZIF-4) was added into the sample solution and a vortex-assisted extraction was performed. The analytes were then extracted by the μ -SPE device and analyzed via HPLC. This method avoided tedious heating or cooling and centrifugation steps in the conventional DLLME procedures. Compared with a conventional μ -SPE method which may require more than 50 min, the total sample preparation time for the IL-DLLME- μ -SPE method was less than 10 min.

Extraction of Metal Ions

A cold-induced aggregation microextraction (CIAME) technique was employed by Baghdadi and coworkers for the extraction and preconcentration of metal ions in water samples [77]. Hg was selected as a test analyte to evaluate the performance of the method. The $[\text{C}_6\text{MIM}][\text{PF}_6]$ IL was used as an extraction solvent and Michler thioketone (TMK) was used as chelating reagent. After the extraction and centrifugation steps, Triton X-114 was chosen as an anti-sticking agent to prevent the IL from sticking on the wall of the centrifuge tube. Compared with other extraction methods such as cloud point extraction (CPE), the use of large amounts of water-miscible organic solvents in CIAME does not affect the absorbance of the

Hg-TMK complex. The analytical performance of CIAME was compared with other approaches wherein the LOD for CIAME-spectrophotometry is superior to those obtained by SPE-spectrophotometry and mesoporous sorbent micro-column-ICP-OES. The preconcentration of cobalt (II) ions from water samples using CIAME as a prior step to its determination by fiber optic-linear array detection spectrophotometry (FO-LADS) has also been reported [78].

It was observed that high ionic strength in aqueous solution could decrease the affinity of polar compounds to the extraction phase as well as alter the volume of the extraction phase due to the salting-in or salting-out effect. Moreover, high salt content can also increase the density of the sample solution which can affect the formation of the fine extraction phase droplets. In order to circumvent these drawbacks, an in situ solvent formation microextraction (ISFME) method was employed for the determination of mercury in saline solutions [79]. In this method, the hydrophobic IL extraction phase was formed by mixing sodium hexafluorophosphate (NaPF_6) and a hydrophilic IL ($[\text{C}_6\text{MIM}][\text{BF}_4]$) in the sample solution. The anti-sticking agent Triton X-114 was eliminated to increase the density of the extraction phase. This method can be applied for sample solutions containing relatively high salt concentrations (40 % w/v NaNO_3). More recently, the determination of palladium in food additives, seawater, tea, and biological samples was also studied using the same method [80].

Yousefi and coworkers introduced an IL-DLLME method for the preconcentration of Pb and Cd in saline samples [81]. After the extraction, the separated IL phase was dissolved in 100 μL ethanol and coupled with FAAS using a homemade microsample introduction system. This IL-DLLME method provided good accuracy and precision. A similar approach was also applied for the determination of trace Pb in real water samples [82, 83].

Berton et al. reported a TC IL-DLLME method coupled to electrothermal atomic absorption spectrometry ETAAS for the analysis of vanadium in water samples. Compared to the previously reported methods, the TC IL-DLLME method exhibited comparable or better LODs and larger linear ranges [84]. The determination of cobalt in environmental samples was also studied using this approach [85]. Subsequently, a fully on-line temperature-controlled DLLME procedure combined with ETAAS for the determination of vanadium in environmental samples was developed [86].

The 1-hexylpyridinium hexafluorophosphate $[\text{C}_6\text{Py}][\text{PF}_6]$ IL was applied for the preconcentration of zinc in water samples. A standard reference material NIST SRM 1549 nonfat milk powder was used to validate the accuracy of the developed method. The experimental zinc content was in good agreement with the certified values [87]. The same IL-based DLLME method was also combined with stopped-flow spectrofluorometry (SFS) to evaluate the concentration of aluminum in different real water samples [88].

Extraction of Other Types of Analytes

An IL-DLLME method was applied for the determination of analytes in nonaqueous samples. Mallah et al. developed an IL-DLLME method coupled

with inductively coupled plasma optical emission spectrometry (ICP-OES) for the determination of lanthanoids in uranium dioxide powders [89]. After extraction and phase separation, the precipitated phase was dried in a furnace and introduced to the ICP-OES. This IL-DLLME method was suitable for the preconcentration of lanthanoids including Sm, Eu, Gd, and Dy in environmental samples. Rabieh et al. used IL-DLLME-AAS for the determination of arsenite and arsenate in natural water samples [90]. The As (III) ion was complexed with ammonium pyrrolidinedithiocarbamate (APDC) and extracted by the $[C_4MIM][NTf_2]$ IL; high enrichment factors and good LODs were obtained. Method validation showed that interfering ions, such as alkali and alkaline earth cations, as well as chloride and sulfate anions did not affect the recovery of the experiment.

A new type of glucaminium-based IL was synthesized and applied for the extraction of boron species from water using in situ DLLME [91]. The glucaminium-based IL was capable of forming complex with boron species, thereby functioning as both a chelator and an extraction phase. The formation of two different complexes, namely, monochelate and bischelate complexes, was observed during extraction [91]. After the extraction step, the IL phase was demonstrated to be easily regenerated using 0.1 M hydrochloric acid with no significant loss of extraction efficiency observed after three generation cycles [92].

Solid-Phase Microextraction (SPME)

Solid-phase microextraction (SPME) is a sampling and preconcentration technique that has generated a large amount of interest since its introduction by Pawliszyn and coworkers in the early 1990s [93]. This technique mainly involves two steps, namely, sorption of analytes from a sample matrix to a sorbent coating and desorption of the extracted analytes to the chromatographic or electrophoretic system. During extraction, equilibrium is established between analytes in the sample matrix or headspace and the sorbent coating.

The popularity of SPME is constantly increasing due to its high sensitivity, simplicity, and cost-effectiveness. A number of commercial coatings covering a wide range of polarity have been employed as SPME sorbent phases for extracting different classes of analytes. However, novel coatings are in high demand due to the ever-increasing need for better method sensitivity and analyte selectivity. The use of ILs in SPME was initially investigated by Liu and coworkers in 2005 [94]. Due to their tunable selectivity, ILs can easily be applied as SPME sorbent phases. Unfortunately, most ILs suffer from a significant reduction in viscosity at high desorption temperatures, resulting in them flowing from the fiber to the GC injector. The introduction of polymeric ionic liquids (PILs) as SPME sorbent coatings can overcome this limitation since PILs exhibit higher thermal stability and better resistance to reduction in viscosity at elevated temperatures [95].

This section will focus on the application of IL/PILs as SPME sorbent coatings for environmental analysis. A summary of these IL/PIL SPME studies for environmental samples is shown in Table 7.3. Different sorbent-to-support loading strategies, which

Table 7.3 Summary of applications which employ ILs and PILs as sorbent materials in SPME for environmental analysis

Analytes	Sample matrix	Coating	Coating method	Fiber lifetime	Desorption temperature (°C)	LOD ($\mu\text{g L}^{-1}$)	Recovery (%)	Reference
Alcohols, acetone, ethyl acetate, and acetonitrile	Water	[(C ₂ OHIM) ₂ T] 2[NTf ₂] [(C ₂ OHIM) ₂ T] 2[TfO]	Covalent bonding	–	120	0.047–0.086	97.4–104.7	[96]
Alcohols, aldehydes, and esters	Well and river water	[VC ₆ IM][Cl] copolymerized with [(VIM) ₂ C ₈] 2[Br] and [(VIM) ₂ C ₁₂] 2[Br]	On-fiber UV-initiated polymerization	>90	175	0.01–2.5	58–135.8	[97]
Benzene, toluene, ethylbenzene, and xylenes	Water	PDMS, PDMS-IL-HT, PDMS-IL-LT	Sol-gel chemistry	180	250	0.0001–0.5	91.2–103.3	[98]
Diazinon, fenitrothion, malathion, fenvalerate, phosalone, and tridemorph	Human hair and water samples	[C ₄ MIM][OH]-mediated sol-gel sorbent	Sol-gel chemistry	1	N/A	0.004–0.095 (in water) 0.003–0.08 (in hair)	86.2–98.8 (in water)	[99]
Organophosphorus pesticides	Human hair samples	Butyl sultone pyridinium cation- and Keggin anion-based IL as porogen for sol-gel sorbent	Sol-gel chemistry	1	N/A	0.00034–0.84	83–92	[7]
Organochlorine pesticides	Lake water	Nanostructured polyaniline-IL [C ₄ MIM][PF ₆] composite	Electrochemical polymerization	250	250	0.00012–0.00031	88.9–112.9	[100]

(continued)

Table 7.3 (continued)

Analytes	Sample matrix	Coating	Coating method	Fiber lifetime	Desorption temperature (°C)	LOD ($\mu\text{g L}^{-1}$)	Recovery (%)	Reference
Pyrethroids	Vegetables	Copolymerized [VC ₆ IM][PF ₆]	On-fiber thermal-initiated polymerization	–	260	0.21–0.49	67.4–94.01	[102]
PAHs	Water	[C ₈ MIM][TfO], [BeMIM][TfO], and [PhproMIM][TfO]	Dip coating on a Nafion membrane-supported fiber	50	240	0.004–0.005	80–110	[103]
PAHs	Water and mosquito coil smoke	[C ₃ MIM][PF ₆]	Dip coating on bare fused silica fiber, Nafion membrane-supported fiber, etched fiber	–	220	–	–	[104]
PAHs	Water	[VC ₄ IM][Cl] copolymerized with 1-vinyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride	On-fiber thermal-initiated copolymerization	40	280	0.05–0.25	49.6–105	[105]
Anilines, phenols, and phthalate esters	Water	Poly[VC ₈ IM][SS]	Surface radical chain-transfer reaction on derivatized surface	90	250	0.01–10	73.4–113	[106]
Phenols and PAHs	River water samples	Poly[VC ₈ IM][PF ₆]	In situ surface radical chain-transfer polymerization	55	250	0.01–0.06	83.35–119.24	[107]

PAHs	Water	Poly[VBC ₁₆ IM][NTf ₂] and poly[VC ₁₆ IM][NTf ₂]	Dip coating	70	250	0.003–0.07	–	[108]
PAHs and substituted phenols	Water	Poly[VC ₁₆ IM][NTf ₂]	Dip coating	50	250	0.005–4.4	75.8–119	[109]
PAHs, parabens, and alkylphenols	Water	Poly[VBC ₁₆ IM][NTf ₂]	Dip coating	70	250	0.009–7	78.3–109	[110]
PAHs	Hair spray and nail polish	Poly[VC ₈ IM][NapSO ₃]	In situ surface radical chain-transfer polymerization	100	250	0.005–0.05	–	[111]
PCBs	Seawater and bovine milk	[VBC ₁₆ IM][NTf ₂] copolymerized with [(VIM) ₂ C ₁₂] 2[NTf ₂] and [(VBIM) ₂ C ₁₂] 2[NTf ₂]	On-fiber UV-initiated polymerization	–	280	0.001–0.0025 (GC/ECD)	61.2–135.7 (seawater)	[112]
						0.0025–0.025 (GC/MS)	89.3–132.5 (bovine milk)	
PEEs and aromatic amines	Lake and sewage water	[AMIM][PF ₆]-OH-TSO, [AMIM][NTf ₂]-OH-TSO	Sol-gel chemistry	–	280	0.003–0.1248	83.1–104.1	[113]
Phthalate esters	Agricultural plastic films	[AMIM][NTf ₂]-OH-TSO	Sol-gel chemistry	> 122	360	0.003–0.063	90.2–111.4	[114]
Organophosphate	Lake, waste-, and tap water, sewage treatment plant effluent	[AMIM][BF ₄]	Sol-gel chemistry	200	250	0.0007–0.012	75.2–101.8	[115]

(continued)

Table 7.3 (continued)

Analytes	Sample matrix	Coating	Coating method	Fiber lifetime	Desorption temperature (°C)	LOD (µg L ⁻¹)	Recovery (%)	Reference
Alcohols, phthalate esters, PEEs, fatty acids, and aromatic amines	Water	[A(Benzo ₁₅ C ₅)HIM][PF ₆]	Sol-gel chemistry	–	250–300	–	–	[116]
PEEs, fatty acids, aromatic amines, alcohols, phthalate esters, and PAHs	Water	[TESPMIM][PF ₆]-, [TESPMIM][BF ₄]-, and [TESPMIM][NTf ₂]-based sol-gel sorbent	Sol-gel chemistry	–	280	–	–	[117]
VFAs and alcohols	Water	Poly[VC ₆ IM][Cl], poly[VC ₆ IM][NTf ₂]	Dip coating	30–40	200	0.02–7.5	–	[118]

Abbreviation: PEEs phenolic environmental estrogens, VFAs volatile fatty acids, PCBs polychlorinated biphenyls

can improve the chemical and mechanical stability of extraction system, are also discussed. Additionally, special emphasis on the selectivity of various IL/PIL sorbent coatings for select analytes will be given.

Extraction of VOCs

Two ILs with the same cation (bis-hydroxyethyl imidazolium trioxoethylene) and different anions, $[\text{NTf}_2]$ and trifluoromethylsulfate $[\text{TfO}]$, were chemically bonded to silica particles and glued to a SPME support to extract several less-volatile alcohols, acetone, ethyl acetate, and acetonitrile in water [96]. The bonded IL-Si coatings exhibited superior extraction efficiencies compared to IL coatings that were directly loaded to a support. The chemically bonded IL-Si coating achieved lower extraction efficiencies compared to a 100- μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) and 85- μm polyacrylate (PA) coatings due to its smaller film thickness (40 μm) [96].

The mechanical stability, robustness, and lifetime of PIL-based coatings were introduced by covalently bonding UV-photoinitiated cross-linked PILs on etched and derivatized fused silica fibers as shown Fig. 7.4 [97]. The IL monomer, 1-vinyl-3-hexylimidazolium chloride $[\text{VC}_6\text{IM}][\text{Cl}]$, was copolymerized with one of two different IL cross-linkers, namely, 1,8-di(3-vinylimidazolium)octane dibromide $[(\text{VIM})_2\text{C}_8] 2[\text{Br}]$ and 1,12-di(3-vinylimidazolium)dodecane dibromide $[(\text{VIM})_2\text{C}_{12}] 2[\text{Br}]$. Higher mechanical stability of the IL coatings was achieved by the immobilization and cross-linking of the PIL coatings compared to the analogous linear PIL coatings produced via thermal-initiated polymerization. The polar cross-linked PIL coatings were applied in both headspace and direct immersion SPME and were employed to efficiently extract polar analytes (e.g., alcohols, aldehydes, and esters) from real water samples. Moreover, low sorbent coating bleed was observed, making the fibers highly useful for GC/MS analysis [97].

ILs were also applied as a cosolvent in the preparation of three PDMS sorbent coatings by high temperature (PDMS-IL-HT), low temperature (PDMS-IL-LT), and

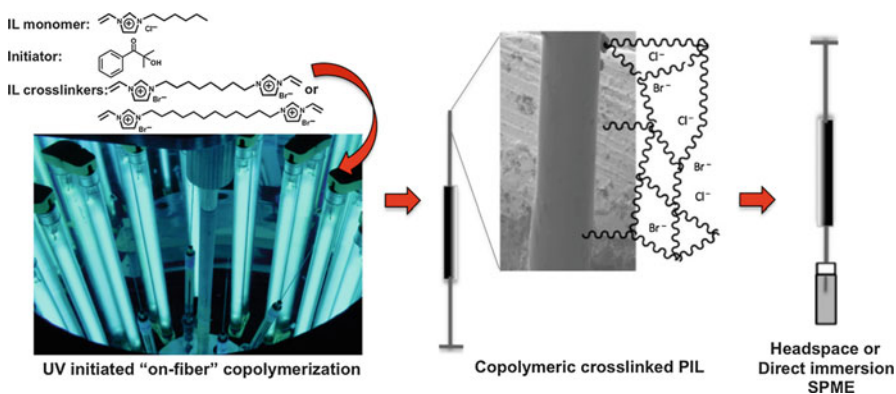


Fig. 7.4 Schematic of UV-initiated "on-fiber" copolymerization of IL-based sorbent coatings for headspace or direct immersion SPME (Reprinted with permission from [97])

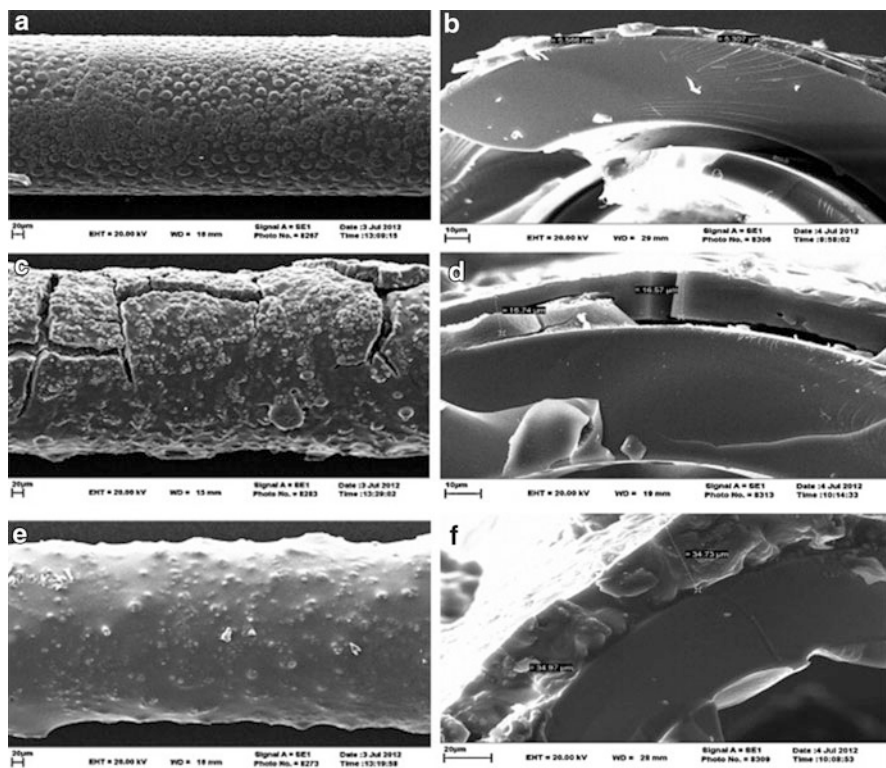


Fig. 7.5 SEM images of three different PDMS-based SPME fibers. (a), (c), and (e): surface of PDMS, PDMS-IL-HT, and PDMS-IL-LT fibers at a magnification of 500-fold, respectively; (b), (d), and (f): cross sections of PDMS (2,000-fold), PDMS-IL-HT (3,000-fold), and PDMS-IL-LT (2,000-fold), respectively (Reprinted with permission from [98])

traditional (PDMS) sol-gel chemistry [98]. The extraction efficiency of the coatings was compared with the extraction of BTEX compounds from water samples. The PDMS-IL-HT fiber exhibited more than a 100-fold higher extraction efficiency compared to the traditional PDMS fiber and a 300-fold higher extraction efficiency compared to the PDMS-IL-LT fiber. The PDMS-IL-HT coating was observed to possess a porous morphology compared to the other coatings, as shown in Fig. 7.5, resulting in a significant enhancement in the sorption efficiency [98].

Extraction of Pesticides

Ebrahimi et al. loaded a sol-gel extraction phase into hollow fibers in the presence of IL and nanomaterials [99]. The fabricated fibers were used for the extraction of different pesticides, including diazinon, fenitrothion, malathion, fenvalerate, phosalone, and tridemorph, from water samples and human hair. The 1-methyl-3-butyl imidazolium hydroxide IL, $[C_4MIM][OH]$, functioned as a porogenous agent during gel growth. A sorbent structure possessing high porosity was obtained by optimizing the

amount of IL in solution. This also provided better extraction efficiency due to larger analyte-to-sorbent contact areas. Different nanomaterials, such as carboxylic acid-derivatized multi-walled carbon nanotubes (COOH-MWCNTs), amino-derivatized multi-walled carbon nanotubes (NH₂-MWCNTs), nano-SiO₂, nano-TiO₂, and nano-MgO, were also doped in the sol solution, and their extraction performance was compared. Overall, the nano-MgO-doped extraction phase provided the best extraction efficiency due to the high surface areas of the nano-MgO material [99]. The same group also applied a butyl sultone pyridinium cation and Keggin anion IL, (PYBS)₃PW₁₂O₄₀, as a porogen for the fabrication of sol-gel hollow fibers. The IL was homogeneously dispersed into the extraction phase, thereby creating more active adsorption sites. The extraction efficiency of organophosphorus pesticides using the (PYBS)₃PW₁₂O₄₀-doped sol-gel coating was superior compared to the IL-free sol-gel coating [7].

A polyaniline-[C₄MIM][PF₆] IL composite (BPAN) was prepared through electrochemical deposition on a steel wire and applied for the analysis of organochlorine pesticides [100]. The novel BPAN fiber (15 μm) showed higher extraction efficiency compared to a simple polyaniline (PANI) fiber and a commercial PDMS fiber (30 μm). The BPAN fiber exhibited an increased specific surface area (by SEM imaging), which provided more active sites for analytes to adsorb to the coating. Additionally, the incorporated [C₄MIM][PF₆] IL provided preferred interaction between analytes and the coating. The BPAN fiber also exhibited better fiber lifetime (250 times) compared to the PANI and PDMS fibers, which was in agreement with another study using the IL-PANI fiber [101].

Zhang et al. developed a chemically bonded polymeric coating for the extraction of pyrethroids [102]. A treated fiber was firstly derivatized by γ-methacryloxypropyltrimethoxysilane and subsequently copolymerized with 1-vinyl-3-hexadecylimidazolium hexafluorophosphate ([VC₁₆IM][PF₆]) in the presence of a thermal initiator, 2,2-azobisisobutyronitrile (AIBN). Compared to a commercial PDMS fiber (100 μm), the fabricated fiber (15–20 μm) showed approximately 20 % higher extraction efficiency which may be due to the enhanced π–π interaction and dispersive interactions established between the IL coating and the target analyte [102].

Extraction of PAHs and Other Aromatic Compounds

Nafion-supported IL coatings with increased loading and stability of the extraction phase were applied for the analysis of PAHs in water [103]. Nafion, a cation exchange polymer, was preloaded before coating the IL onto the silica fiber acting to stabilize the IL film through electrostatic interactions. The introduction of the Nafion membrane also reduced the formation of IL droplets on the silica support. Three different ILs (1-octyl-3-methylimidazolium trifluoromethanesulfonate ([C₈MIM][TfO]), 1-benzyl-3-methylimidazolium trifluoromethanesulfonate ([BeMIM][TfO]), 1-phenylpropyl-3-methylimidazolium trifluoromethanesulfonate ([PhproMIM][TfO])) were compared. The Nafion/[C₈MIM][TfO] coating possessed the highest extraction efficiency compared to the other ILs. The proposed method was validated by analyzing rainwater samples from an industrial park and groundwater collected on

campus. Naphthalene, fluorene, and anthracene were detected in rainwater in quantities above the LOD [103].

PAHs in water were also extracted by using etched fused silica fibers wherein the bare fibers were treated by ammonium hydrogen difluoride prior to loading the IL [104]. This pretreatment increased the surface area of the fiber, facilitating a more homogenous and higher IL loading on the fiber. Three different fibers, including bare fused silica, Nafion membrane-supported, and etched fused silica were coated with the $[C_4MIM][PF_6]$ IL to extract a number of PAHs. The extraction efficiency obtained by the Nafion membrane-supported fiber was three to five times higher than the bare fused silica fiber but inferior to the etched fiber. The etched/IL-coated fiber (30 μm) also provided higher extraction efficiency compared to a commercial PDMS fiber (7 μm) [104].

A PIL coating covalently bonded to stainless steel fiber supports by a series of modification steps was exploited for the extraction of PAHs from water samples [105]. Initially, a gold film was coated on a stainless steel fiber followed by the immobilization of 3-(mercaptopropyl) triethoxysilane to the support via Au-S bond. Afterwards, a silica layer was formed by hydrolysis and polycondensation reaction. The silica layer of the support was then chemically bonded to the 1-vinyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride IL. This IL layer was subsequently copolymerized with an IL monomer, 1-vinyl-3-butylimidazolium chloride ($[VC_4IM][Cl]$), using AIBN-initiated free radical polymerization. The fabricated PIL coating was observed to possess a highly porous morphology. Compared to a commercial PDMS fiber (7 μm), the PIL fiber showed higher extraction efficiency for smaller PAHs [105].

A double-confined PIL coating was developed for the extraction of three types of aromatic compounds, namely, anilines, phenols, and phthalate esters in high ionic strength aqueous solutions [106]. A stainless steel fiber was initially coated with a silver layer by the silver mirror reaction followed by functionalization with a monolayer of dithiol. The IL monomer, 1-vinyl-3-octylimidazolium *p*-styrenesulfonate ($[VC_8IM][SS]$), was chemically bonded to the derivatized fiber through surface radical chain-transfer reaction. Due to its structure, both the cation and anion comprised in the IL monomer can be subjected to copolymerization to generate poly $[VC_8IM][SS]$ on the fiber surface. Higher chemical stability of poly $[VC_8IM][SS]$ -coated SPME fiber in high ionic strength solution was observed compared to a poly $[VC_8IM][BS]$ fiber, which contained a polymerizable cation. In terms of extraction capability, the poly $[VC_8IM][SS]$ fiber exhibited comparable extraction efficiency for phenols and superior extraction efficiency for anilines and phthalate esters [106].

Xu and coworkers developed an alternative route for loading PIL coatings to a stainless steel substrate for the extraction of PAHs and phenols [107]. The bare fiber was initially coated with a layer of silica via medium-frequency unbalanced magnetron sputtering, followed by the hydroxylation of silica. Subsequently, a sol-gel process was carried out by co-condensation of 3-mercaptopropyltrimethoxysilane and tetramethoxysilane to further derivatize the fiber with mercaptopropyl groups. Afterwards, the IL monomer ($[VC_8IM][PF_6]$) was linked to the derivatized fiber and polymerized by surface radical chain-transfer polymerization. The fabricated PIL

fiber was applied to extract the model analytes, exhibiting good extraction efficiency and high thermal stability [107].

Aside from improving the chemical and physical stability of a sorbent coating in SPME for environmental study, tuning the IL/PIL structure to enhance sorbent-to-analyte selectivity was also studied. Meng and coworkers synthesized a novel PIL comprised of benzyl moieties, poly{1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide} (poly[VBC₁₆IM][NTf₂]), as a selective SPME sorbent coating [108]. Compared to an analogous nonfunctionalized PIL, poly{1-vinyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide} (poly[VC₁₆IM][NTf₂]), and a commercial PDMS fiber, the benzyl-functionalized PIL coating exhibited superior extraction efficiency for select PAHs due to enhanced π - π interactions [108]. López-Darias et al. also applied the poly[VC₁₆IM][NTf₂] PIL as SPME coating for the extraction of PAHs and substituted phenols in water [109]. Similarly, the poly(1-vinyl-3-octylimidazolium 2-naphthalene-sulfonate) (poly[VC₈IM][NapSO₃]) PIL, possessing aromatic functionality, was also synthesized and exploited as an aromatic-selective SPME sorbent coating [110, 111].

More recently, two types of benzyl-functionalized and cross-linked PIL SPME coatings were used for extracting polychlorinated biphenyls (PCBs) from seawater and bovine milk samples [112]. The coatings were prepared by the copolymerization of the [VBC₁₆IM][NTf₂] IL monomer with two IL cross-linkers ([(VIM)₂C₁₂] 2[NTf₂] and [(VBIM)₂C₁₂] 2[NTf₂]), respectively, using “on-fiber” UV-initiated polymerization on a surface-modified silica fiber, as previously mentioned [97, 112]. The newly fabricated fibers exhibited higher sensitivities than the commercial PDMS fiber (7 μ m) when they were applied in the extraction of the target analytes. Additionally, the PIL sorbent coating comprised of the benzyl-functionalized cross-linker possessed higher sensitivities compared to its non-benzyl-functionalized counterpart [112].

Extraction of Other Types of Analytes

Novel IL-based sol-gel SPME extraction phases were investigated [113]. Two allyl-functionalized ILs, 1-allyl-3-methylimidazolium hexafluorophosphate ([AMIM][PF₆]) and 1-allyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([AMIM][NTf₂]), were applied, generating two types of coatings, [AMIM][PF₆]-OH-TSO and [AMIM][NTf₂]-OH-TSO. The sol-gel fibers possessed a porous surface morphology, high thermal stability, and excellent chemical stability in different pH and solvents. Superior extraction efficiency of polar phenolic environmental estrogens (PEEs) and aromatic amines was obtained using the novel coatings, compared to commercial PDMS (100 μ m) and PDMS/DVB (65 μ m) fibers [113]. Zhou et al. employed the same sol-gel coating, [AMIM][NTf₂]-OH-TSO, for determining phthalate esters in agricultural films [114]. Compared to the PDMS, PDMS/DVB, and PA fibers, similar or superior extraction efficiencies were obtained from the sol-gel coating [114]. Another IL, [AMIM][BF₄], was adopted by Gao et al. for fabricating IL-based sol-gel coating to extract organophosphate [115]. Compared to the [AMIM][PF₆], the [AMIM][NTf₂]-based sol-gel fibers, and three commercial fibers (PDMS, PDMS/DVB, PA fibers), the [AMIM][BF₄]-based

sol-gel fiber showed superior extraction efficiency due to its highly porous morphology [115].

Using similar sol-gel chemistry, a crown ether-functionalized IL, 1-allyl-3-(6'-oxo-benzo-15-crown-5 hexyl)imidazolium hexafluorophosphate {[A(Benzo 15C5)HIM][PF₆]}, was fabricated and applied as a SPME sorbent coating in the extraction of alcohols, phthalate esters, PEEs, fatty acids, and aromatic amines [116]. Compared to the commercial PDMS, PDMS/DVB, and PA fibers, the crown ether-functionalized IL coating possessed superior extraction efficiency for most of the model analytes due to enhanced hydrogen bonding interaction and/or π - π interaction between the coating and target analytes [116].

The role of counteranions in sol-gel coatings was explored by Shu and coworkers [117]. Three alkoxy-functionalized ILs with different anions, 1-(3-triethoxysilyl propyl)-3-methylimidazolium hexafluorophosphate ([TESPMIM][PF₆]), 1-(3-triethoxysilyl propyl)-3-methylimidazolium tetrafluoroborate ([TESPMIM][BF₄]), and 1-(3-triethoxysilyl propyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([TESPMIM][NTf₂]), were applied as SPME sorbent coatings in the extraction of PEEs, fatty acids, aromatic amines, alcohols, phthalate esters, and PAHs. The [TESPMIM][PF₆]- and [TESPMIM][BF₄]-based sol-gel coatings showed relatively lower thermal stability (300 °C and 285 °C, respectively) compared to the [TESPMIM][NTf₂]-based sol-gel coating (454 °C). The PF₆⁻ and BF₄⁻-type coatings exhibited superior extraction efficiency for highly polar analytes and lower extraction efficiency for semi- or nonpolar analytes compared to the NTf₂⁻-type coating. Similarly, it has been reported that PILs comprised of Cl⁻ anions exhibited better extraction of hydrogen-bond acidic analytes compared to analogous PILs containing the NTf₂⁻ anion [118].

IL- and PIL-Based GC Stationary Phases Designed for Environmental Analysis

Application of IL/PIL-Based GC Stationary Phases in Single-Dimensional GC

The first application of an IL-based GC stationary phase was demonstrated by Barber and coworkers in 1959 [119]. In their work, molten stearates of Mn, Co, Ni, Cu, and Zn were applied as stationary phases for the separation of alcohols and amines. Later, quaternary ammonium salts comprised of bromide, picrate, and nitrate anions were exploited as GC stationary phases by Gordon and coworkers [120]. GC stationary phases based on ethylammonium nitrate, ethylpyridinium bromide, and tetraalkylphosphonium salts were developed by Poole and coworkers with wide liquid ranges being reported [121–123]. Unfortunately, the aforementioned stationary phases suffered from limited thermal stability and low separation efficiency.

In order to achieve higher viscosity, broader liquid range, higher thermal stability, and better separation efficiency, different IL-based GC stationary phases including imidazolium-based ILs, cross-linked ILs, dicationic ILs, and tricationic

ILs have been subsequently designed and synthesized [10, 124–128]. ILs have also been applied for the preparation of chiral GC stationary phases by directly applying the chiral ILs as the chiral stationary phase or by dissolving the appropriate chiral selector in the IL [129–132]. The application of ILs/PILs as GC stationary phases has been reviewed in several recent papers [9, 133].

Application of Homemade IL/PIL-Based GC Stationary Phases in Environmental Analysis

Up to date, very few publications have been reported for the analysis of environmental samples on homemade IL/PIL-based GC stationary phases. However, various environmental contaminants including alcohols, anilines, aldehydes, xylenes, and chlorinated compounds have been used as probe molecules for the determination of solvation parameters and the analytical performance of the IL/PIL-based stationary phases [125, 128, 134].

A novel IL-bonded polysiloxane ([PSOMIM][NTf₂]) was applied for the separation of PCBs and aromatic amines [135]. Baseline separation was achieved for PCBs 16, 40, 83, 136, 178, 194, and 208 as well as 15 aromatic amines. Narrow and symmetrical peaks were observed for all aromatic amines which were attributed to the high efficiency of the column. More importantly, the high thermal stability of the stationary phase allowed higher operation temperature up to 300 °C with a slight baseline shift.

Six phthalates were separated on a poly 1-(3-chlorohexyl)imidazolium ([PImC₆][NTf₂]) column, and excellent separation efficiency was obtained [136]. The polymer was prepared by using the 1-(3-chlorohexyl)imidazole (ImC₆Cl) monomer. A metathesis reaction was carried out to replace the Cl[−] anion to NTf₂[−]. A number of PAHs, including dibenzo[a,i]pyrene and coronene, were also separated on the same column. Due to the high thermal stability of the IL stationary phase, the oven temperature could be ramped up to 380 °C without sacrificing the chemical integrity of the IL. This operating temperature is also significantly higher than the normal operating temperature of many commercial columns.

Application of Commercial IL Stationary Phases in Environmental Analysis

The first commercial IL-based GC stationary phase SLB-IL100 (comprised of 1,9-di(3-vinylimidazolium)nonane bis(trifluoromethylsulfonyl)imide) was introduced by Supelco in 2008 [137]. Compared with other commercial GC stationary phases, the SLB-IL100 column exhibited two advantages. Firstly, the polarity of the SLB-IL100 column is much higher than that of the traditional polar GC stationary phases such as polyethylene glycol and bis-cyanopropyl polysiloxane. Additionally, the maximum operating temperature for the SLB-IL100 column is 230 °C, which is significantly higher than that of nonionic high-polarity columns.

A series of custom-tailored SLB-IL100 columns with varying inner diameter and length were evaluated by Ragonese and coworkers for the separation of C₁₈ *cis/trans* fatty acid methyl esters (FAMES) [138]. The separation performance of the IL columns was compared to a popular SP-2560 (bis-cyanopropyl polysiloxane)

column. Under optimized conditions, the longer IL column exhibited higher selectivity than the SP-2560 column.

Mixtures containing volatile suspected allergens, pesticides, and vetiver essential oils were tested by Cagliero and coworkers on IL-based columns [139]. The chromatographic performance of the IL-based stationary phases including peak width, peak asymmetry factor, and separation capability was compared with SE-52, OV-1701, and PEG columns. IL-based columns demonstrated better chromatographic performance for all pesticides compared to OV-1701.

Recently, nitrosamines and caffeine metabolites in wastewater samples were studied using IL-based stationary phases coupled with GC/MS [140]. The SLB-IL111 column had shown good separation efficiency for 7 nitrosamines, and the separation time was shorter compared to a cyanopropyl phenyl polysiloxane column. For caffeine metabolites, the best resolution and peak asymmetry factors were obtained using the SLB-IL59 column. These IL stationary phases were also applied for the determination of benzothiazoles and benzotriazoles in wastewaters [141].

Application of IL/PIL-Based GC Stationary Phases for Two-Dimensional GC

Two-dimensional GC (2D GC) was first demonstrated by Phillips and coworkers in 1990 [142]. Compared with the classical single-dimensional gas chromatography (1D GC), 2D GC provides many advantages, such as improved peak capacity and “structured” chromatograms [143]. 2D GC processes are generally achieved through the use of a modulation device situated between the two GC columns. The key to successful 2D GC separation is to select two types of stationary phases that possess complementary selectivity. In most applications, samples are first separated on a column containing a nonpolar stationary phase and then separated on a much shorter, narrower column containing a semipolar, polar, or shape-selective stationary phase. This column arrangement will allow analytes to be firstly separated based on boiling points, followed by separation based on polarity [143].

Due to the dual-nature retention mechanism of the IL-based stationary phases, they can be applied as selective columns in both the first and second dimensions in 2D GC. More importantly, the application of IL-based stationary phases enables higher operating temperature in 2D GC separations since many conventional polar stationary phases cannot be used at temperatures above 280 °C.

Application of the IL/PIL-Based 2D GC Stationary Phases in Environmental Analysis

Two-dimensional GC coupled to mass spectrometry is an excellent method for analyzing highly complex samples. The separation of 209 PCBs posed a significant challenge in 1D GC, and no work was reported for the complete separation of all analytes. Zapadlo and coworkers used a polar DB-5 column as the first column and

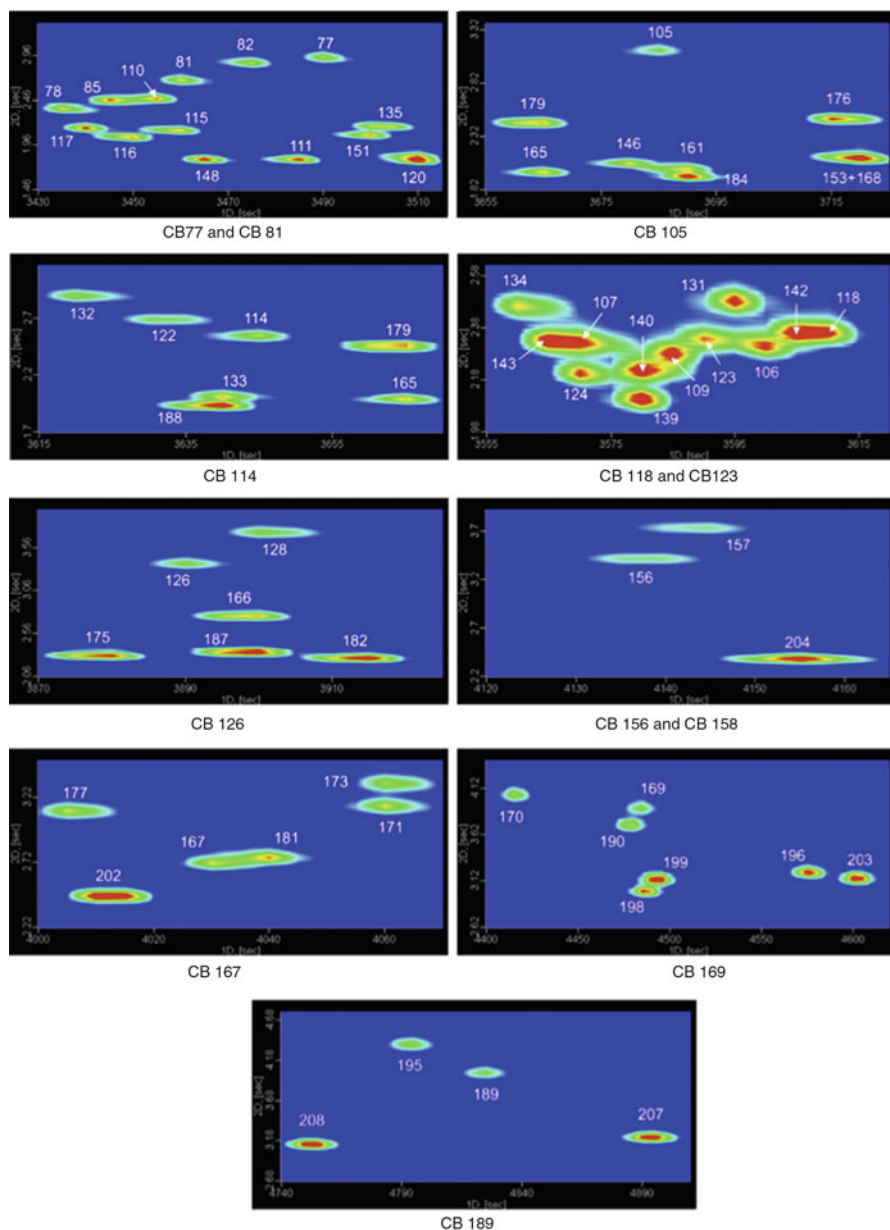


Fig. 7.6 Contour plots obtained by GC $\times$ GC-TOFMS for the toxic "dioxin-like" PCBs on an SPB-Octyl/SLB-IL59 column series (Reprinted with permission from [145])

a SIB-IL59 ionic liquid column as the second column for the 2D GC separation of PCBs [144]. All 209 PCBs, with the exception of PCB 118 and PCB 106, were resolved using 2D GC separation. Columns coupled with a polar phase and IL-based stationary phase were almost orthogonal for the separation of PCBs [144]. Subsequently, in order to enhance the separation of the PCBs by GC $\times$ GC-TOFMS, the same group used an SPB-Octyl column as the first nonpolar column in 2D GC separation [145]. The polarity of the SPB-Octyl column was much lower than the polydimethylsiloxane column, which offered stronger dispersion interactions with the PCBs. Approximately, 196 out of 209 PCBs were resolved on this SPB-Octyl/SLB-IL59 column series, as shown in Fig. 7.6.

A number of different examples in the GC $\times$ GC analysis of real samples were reported. Sciarrone and coworkers developed a GC $\times$ GC-MS method for the determination of oxygenated compounds and BTEX in gasoline [146]. An SLB-IL100 column was used as the first dimension column and an SLB-5MS column was employed as a second dimension column. Using a Deans switch-based transfer system, multiple heart-cut transfers were achieved with no observable shifts in retention time.

The 2D GC technique has also been coupled with SPME for the analysis of pesticides in water. A PDMS fiber was applied for the extraction of pesticides in direct immersion mode [147]. Subsequent to analyte desorption, separation was achieved by using an SLB-5 ms column as the first dimension column and a custom SLB-IL59 column as the second dimension column. This method showed high resolution, selectivity, and sensitivity in the analysis of 28 pesticides.

Conclusions

In environmental studies, ILs and PILs have been applied as extraction phases for various microextraction techniques. Due to their tunable properties, these compounds provide high extraction efficiency and excellent selectivity for a multitude of analyte classes. Compared to the conventional solvent extraction techniques, the IL/PIL-based microextraction methods significantly reduced the usage of toxic organic solvents. Additionally, ILs and PILs can be widely applied in a variety of separation techniques including GC stationary phases. Moreover, the applicability of IL/PIL-based stationary phases in multidimensional GC analyses was demonstrated in a number of studies.

Nevertheless, there are several challenges that should be addressed to expand the applicability of ILs and PILs in environmental analysis. The toxicity of ILs and PILs should be further scrutinized to determine their acute effects on both the environment and living organisms. Similarly, proper handling and disposal of IL/PILs is another concern that should be further investigated to avoid accumulation within the environment. The physicochemical properties and selectivity of ILs and PILs can be significantly altered in the presence of impurities formed during their synthesis. As a result, the synthesis of ultrapure ILs/PILs by employing various chromatographic separation techniques can provide better analytical performance and lab-to-lab reproducibility.

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G.A. Tiruye • R. Marcilla (✉)
 IMDEA Energy Institute, Móstoles, Madrid, Spain
 e-mail: rebeca.marcilla@imdea.org

Abstract

A general overview of the recent advances of the combination of ionic liquids and polymers to create innovative polymer electrolytes and their applications in energy production and storage is presented. These materials have advantages over the conventional polymer electrolytes in terms of ionic conductivity and thermal, chemical, and electrochemical stability, and they will turn over a new leaf for the new-generation energy production and storage devices.

Keywords

Ionic liquids • Polymer electrolytes • Polymeric ionic liquids • Electrochemistry
• Energy conversion and storage

Introduction

Ionic liquids (ILs) are organic salts with a low melting point ($<100\text{ }^{\circ}\text{C}$) which are widely investigated due to their chemical stability, low flammability, negligible vapor pressure, high ionic conductivity, and wide electrochemical window. In the last decade, ionic liquids have emerged as one of the most promising candidates as liquid electrolytes in advanced electrochemical devices such as batteries, supercapacitors, fuel cells, electrochromic devices, and solar cells [1, 2]. However, ionic liquids are intrinsically liquids, so the problems associated with the leakage of the electrolyte are still present in those devices. One of the most dynamic research topics in the field of energy storage devices such as batteries or supercapacitors is the replacement of the liquid electrolyte by safer and mechanically stable polymer electrolytes.

Polymer electrolytes are all those materials where a supramolecular system is doped with ions and presents a significant conductivity. There are many possible classifications of polymer electrolytes depending on the nature of the polymer matrix and the presence of surfactants, plasticizers, or solvents in their structure. Over the last few years, the combination of polymers with ionic liquids has emerged as a hot topic in the field of polymer science in general and in the field of polymer electrolytes in particular [3–6]. Some advantages of this interesting combination stem from the fact that ionic liquids can serve both as ion suppliers to the polymer and also as solvents but avoid flammability or evaporation problems commonly observed in the case of molecular organic solvents [7]. Polymer electrolytes containing ionic liquids present higher ionic conductivity, higher thermal stability, and improved electrochemical stability than other polymer electrolytes.

In this chapter, a general overview of the recent advances of the combination of ionic liquids and polymers to create innovative polymer electrolytes and their applications in energy production and storage will be presented. The first half of the chapter will be focused on the application of ionic liquids (ILs) to energy production and storage and will summarize what are the current approaches to

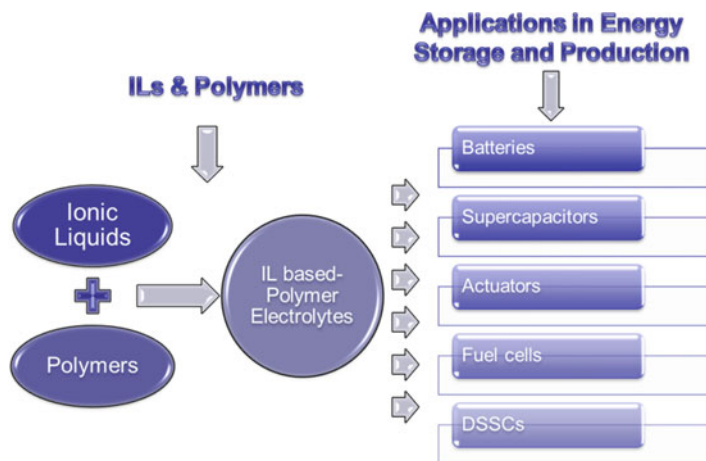


Fig. 8.1 Scheme showing the table of contents of the chapter

incorporate ILs to polymer matrixes depending on the chemical nature and the varied architecture of different polymer networks. The second part of the chapter will be focused on the recent developments of ionic liquid-based polymer electrolytes in batteries, supercapacitors, actuators, fuel cells, and solar cells. Special attention will be paid to the development of polymeric ionic liquids (PILs) and their combination with ionic liquids for application in energy storage and production. The final aim of this chapter is to describe the current trends in the development of these innovative materials and to identify the most challenging future application in the interesting topic of energy storage and production (Fig. 8.1).

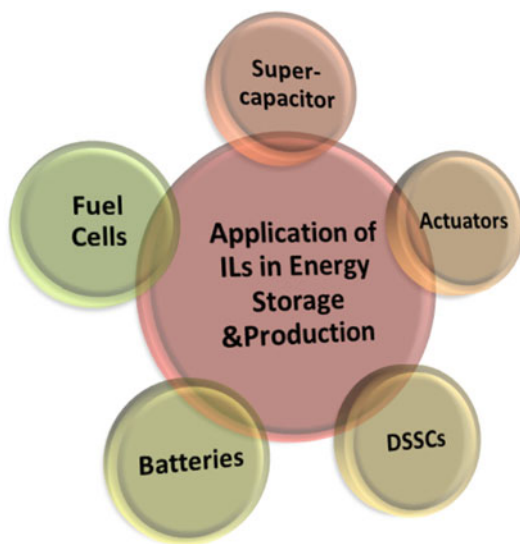
Ionic Liquids as Electrolytes in Energy Storage and Production

Ionic liquids offer a unique collection of properties that make them important candidates for a number of energy-related applications including energy storage and energy production (Fig. 8.2) [8]. Countless cation/anion combinations that exhibit low volatility, low flammability, high electrochemical and thermal stability, as well as ionic conductivity create the possibility of designing ideal tailor-made electrolytes for batteries, supercapacitors, actuators, dye-sensitized solar cells, and fuel cells.

Li-Ion Batteries

The exothermic reaction taking place in the Li-ion battery with organic electrolytes accelerates the heat evolution and may lead to the explosion of the battery. Therefore, it is of essential importance to replace the volatile and flammable electrolytes with safer materials. Due to the nonflammable nature of ILs, their use as electrolytes in Li-ion batteries aims to overcome the drawbacks related with the

Fig. 8.2 Application of ILs in energy storage and production



safety aspects present with conventional organic electrolytes [9]. As a first approach, ILs were used as an additive to organic electrolytes minimizing their flammability character [10]. However, the presence of organic solvents still presents other disadvantages such as the evaporation of the solvent and the associated pollution. Therefore, in a further approach, ILs were investigated in Li-ion batteries as solvent-free electrolytes. Selection of ILs among the vast variety of anions and cations should be made by taking into consideration the ionic conductivity, the thermal stability, and, more importantly, the electrochemical stability of ILs versus Li/Li^+ . Due to the low cathodic stability of imidazolium-based cations, other cations such as quaternary asymmetric ammonium systems [11], pyrazolium [12], and pyrrolidinium [13–15] are preferred. Concerning the anion, those bearing fluorinated imide anions such as bis(trifluoromethanesulfonyl)imide (TFSI) and very recently the bis(fluorosulfonyl)imide (FSI) become the most successful [16, 17].

Supercapacitors

Supercapacitors (SCs) present on the market make use of electrolyte solutions containing either aqueous solutions or organic solvent, which permits relatively higher operating voltages (about 2.5–2.7 V vs. 1 V for aqueous). Nowadays, the main challenge in SC technology is to improve the energy density delivered by the present SCs, limited to few watt hours per kilogram, without sacrificing power density, cycle life, and safety. The maximum energy density of SCs is determined by the intrinsic capacitance of electrode material (C) and by the operating voltage (V) following this equation: $E_{\text{max}} = 1/2CV^2$. Many investigations have been devoted to the development of ionic liquids (ILs) that make it possible to increase

the operational voltage of the EDLCs to about 3.5 V with the subsequent increase of specific energy [18–22]. However, due to the high viscosity and low ionic conductivity of most ILs, the equivalent series resistance (ESR) of IL-based EDLCs is considerably high which results in poor values of specific power: $P_{\max} = V^2/4\text{ESR}$. In this regard, two different strategies have been proposed in the literature to reduce the ESR and improve the power of IL-based EDLCs: increasing the operating temperature to as high as 60 °C [18, 23, 24] and using mixtures of ionic liquids and molecular solvents such as propylene carbonate (PC) [25] and acetonitrile (ACN) [26, 27].

Actuators

Recently, electroactive polymer actuators based on electrochemical processes have received much attention. The performance of these actuators is based on redox reactions of the electroactive polymer or charging/discharging of the double layer between the electroactive polymer and the electrolyte. By these processes, the input electric energy changes into mechanical work. The electrolyte is essential for these actuators as other electrochemical devices and ILs are considered as ideal electrolytes for actuators that can operate in air [28–30]. There are many examples in the literature in which ILs have been successfully used in combination with PEDOT [29, 31] or carbon nanotube-based electrodes [32–35] to build stable actuators.

Fuel Cells

Ionic liquids that show ionic conductivity of more than $10^{-2} \text{ S cm}^{-1}$ at room temperature have been reported close to the level required for fuel cell applications. However, this value corresponds to the IL itself, and they do not include target ions such as the proton. Most of the current investigations are focused on the development of “Brønsted acid–base ILs” synthesized by the simple blend of ternary amines and acids, resulting in ILs with free proton that can be transported from one electrode to the other [36–38]. These ILs, named protic ionic liquids, have been studied vigorously for proton transfer in fuel cell electrolytes under dry conditions [39].

Dye-Sensitized Solar Cells (DSSCs)

Due to their nonvolatility and nonflammability, ILs are possible candidates to resolve the long-term stability problems associated with the use of conventional solvents in dye-sensitized solar cells (DSSCs). The first IL used in this kind of devices was based on imidazolium cation bearing a redox iodide anion [40]. Other ILs with reduced viscosity such as those bearing tetracyanoborate anion have been used [41]. Recently, iodine-free DSSCs using ionic liquids containing different redox pairs such as $\text{SeCN}^-/(\text{SeCN})^{3-}$ or polysulfides have been also investigated [42–44].

Ionic Liquid-Based Polymer Electrolytes

Preparation Methods

As mentioned before, ILs have found application as liquid electrolytes in different electrochemical devices. However, most of the current research in many of these applications is devoted to the development of solid or quasi-solid electrolytes. One of the most successful approaches is the incorporation of ILs to polymer electrolytes because most of the attractive properties of ILs might be translated to the polymer electrolyte. Here, we will focus on three synthetic strategies reported in bibliography toward the design of polymer electrolytes incorporating ionic liquids: casting technique, impregnation, and “in situ” polymerization. Selection of one or other synthetic procedures depends both in the chemical nature of the polymer–IL couple and in the final application of the polymer electrolyte.

- Casting Technique

This technique starts with the solubilization of the selected polymeric matrix and the ionic liquid in a common solvent. After casting the solution by using different techniques (simple casting, doctor blade, ink-jet printing) and drying to evaporate the solvent, the polymer electrolyte is obtained. Phase separation and even leakage or exudation of the IL will occur if the compatibility of IL and polymer matrix is not optimized. Therefore, the most important issue is the nature of polymer and IL that will determine their mutual compatibility and, consequently, their properties and potential applications. Other variables that affect the final properties of the polymer electrolytes are the ratio between polymer and IL and the molecular weight of the polymer. Those variables should be adjusted for each particular application having into consideration that a higher content of IL will result in higher conductivity but will cause lower mechanical stability of IL-based polymer electrolytes.

- Impregnation

The first step here consists of the preparation of a polymer membrane, which can be dense or porous, by film casting or any other method. In a second step, the membrane is impregnated with IL by simply soaking it in a solution containing the IL. The maximum content of IL in the final polymer electrolyte depends on the swelling capability of the precursor polymer membrane by the IL, the presence of pores in the precursor membrane, and the impregnation temperature.

- Polymerization in ILs (“In Situ” Synthesis)

This approach was first developed by Prof. Watanabe et al. and consists on the polymerization of a monomer using the IL as reaction media [45]. The initial requirement is that the monomer, initiator, and cross-linker agent should be soluble in the IL. After complete mixture, the polymerization and/or cross-linking will take place, resulting in the formation of an *ion gel* or *ionogel* [46, 47]. The ion gels can softly bend, and they showed a high ionic conductivity of 10^{-2} S cm⁻¹ at room temperature.

Families of Matrix Polymers

The different polymeric matrices and polymer architectures that have been intensively investigated in combination with ILs to obtain IL-based polymer electrolytes could be classified as:

- *Hydrocarbon polymers* including poly(ethylene oxide) (PEO) [48, 49], polyethylene glycol (PEG), poly(methyl methacrylate) [50] (PMMA), and poly(vinyl alcohol) (PVA). PEO-based electrolytes are one of the most promising and most widely investigated families due to their ability to coordinate ions. In particular, the combination of pyrrolidinium-based ILs with PEO matrix and Li salt was first reported by Prof. Passerini and has been extensively applied to Li-ion batteries [51–53]. Other families of ILs including those bearing piperidinium [54] and imidazolium [55] cations have been also investigated for lithium-ion batteries. The main advantage of the incorporation of ionic liquid to PEO is that it decreases the crystallization of PEO and enhances the ionic conductivity and the electrochemical stability of the final membranes. Similar type of PEO-based electrolytes has been also synthesized for use in dye-sensitized solar cells (DSSCs) [56–60]. For that application, imidazolium-based ILs are the most studied, and Li salt was substituted by a mixture of iodine salt and I_2 that act as redox mediator in the device. Incorporation of ILs to PVA or PMMA polymer matrixes is less extended than in the case of PEO, but there are some examples in the literature [61, 62]. While in the case of PEO-based polymer electrolytes the most common synthetic route is the solvent casting technique, in the case of PMMA, “in situ” polymerization is preferred [46, 47].
- *Perfluorinated polymers* such as polyvinylidene fluoride (PVDF), copolymers of PVDF (PVDF/HFP), and Nafion have been synthesized in combination with ILs both by casting and by impregnation techniques [63–65]. The target applications of those electrolytes are mainly Li-ion batteries in the case of PVDF and proton exchange membrane fuel cells (PEMFCs) for Nafion. Due to the selectivity toward Li^+ and H^+ in each application, lithium salt is necessarily added in the first case [66–69], and protic ionic liquids, and in some cases some strong acids, are commonly used to increase the proton conductivity of the polymer electrolytes in the second case [70–74].
- *Sulfonated aromatic and hetero-aromatic polymers* such as sulfonated poly(ether ether ketone) (SPEEK) [75, 76], sulfonated polyimides [39, 77], and polybenzimidazole (PBI) [78, 79] have been used in combination with protic ionic liquid for application in fuel cells operating above 80 °C. The ionic conductivity of those sulfonated polymer electrolytes increases with the IL content and with the degree of sulfonation since the sulfonic acid groups of the polymer facilitate the ionic mobility of the protic ionic liquids. A further increase of ionic conductivity was obtained by adding strong phosphoric acid (H_3PO_4) to the IL/sulfonated polymer blend. In order to avoid the significant phase separation that occurs when mixing conventional ILs such as 1-ethyl-3-methylimidazolium

triflate (EMImTf) or 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMImTFSI) with H_3PO_4 and PBI, a new IL bearing a more compatible dihydrogen phosphate anion (H_2PO_4^-) was synthesized [80].

- *Polymeric Ionic Liquids*

The design and synthesis of polymeric ionic liquids (PILs), polymers bearing ionic liquid features in their structure, have attracted a growing interest in the last years, becoming one of the most promising topics in the field [81–83]. In fact, this book contains a chapter completely dedicated to describe the chemistry and applications of these new functional polymers. The formulation of these PILs with their IL counterparts to create polymer electrolytes with application in energy storage and production will be addressed in the second half of this chapter.

- *Block Copolymers*

Di-block copolymers usually comprise a microdomain containing the ionic moiety to facilitate transport, while the other nonionic microdomain provides mechanical support to the membrane. Those ionic and nonionic microdomains are usually named as soft and hard domain, respectively. Some examples of these di-block copolymers which are composed of conventional hydrocarbon monomers and contain ionic liquids are poly(styrene-*b*-ethylene oxide) (PS-PEO) [84], poly(styrene-*b*-methyl methacrylate) (PS-PMMA) [85], and poly(1,2-butadiene-*b*-ethylene oxide) (PB-PEO) [86]. The IL was preferentially miscible within the soft domains – PMMA or PEO blocks – and the conductivity increased with the IL content and with the molecular weight of the soft domains. Both the composition and molecular weight of the di-block copolymer have significant effects on the resulting morphology, conductivity, and mechanical properties. Rational di-block copolymer design requires the molecular weight for each segment to be balanced to obtain a persistent gel with high ionic conductivity at the desired temperature. Ionic liquids have been also incorporated into sulfonated block copolymers such as poly(styrenesulfonate-*b*-methylbutylene) (S_nMB_m) for implementation as electrolyte in high-temperature proton exchange membrane fuel cells (PEMFCs) [87, 88]. Park et al. reported the enormous influence of morphologies in through-plane and in-plane conductivity and how this morphology depends on the kind of IL counteranion, the IL content, and the degree of sulfonation (see Fig. 8.3). Hexagonally perforated lamellar-forming samples exhibited the highest conductivities in both through-plane and in-plane directions due to the better connectivity of ionic domains along the perforated hydrophilic phases.

Novel di-block copolymers have been synthesized with one of the blocks being a polymeric ionic liquid (PIL) [89], PS-*b*-PHMA membranes [90], PMAA-*b*-PIL [91], and P2VP-*b*-PMMA [92]. However, no examples in the literature have been found incorporating ILs to those membranes.

The use of tri-block copolymer architectures rather than di-block copolymers may be beneficial in achieving better mechanical stability by creating the physical cross-links, as investigated by Lodge et al. [93–95]. Through the self-assembly of ABA tri-block copolymers, for instance, PS-PEO-PS, PS-PMMA-PS, and PNIPAm-PEO-PNIPAm swollen with different ILs such as BMIm-PF6 or TFSI, transparent gels with as little as about 5 wt% tri-block

Fig. 8.3 Through-plane and in-plane conductivities of IL-incorporated sulfonated block copolymers [88]

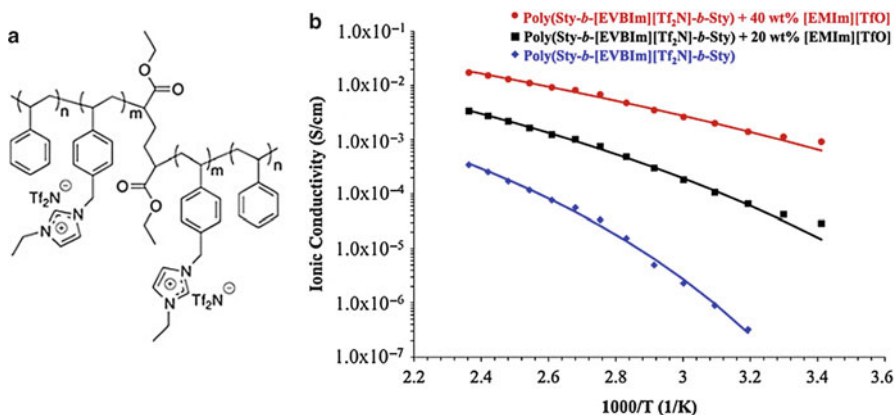
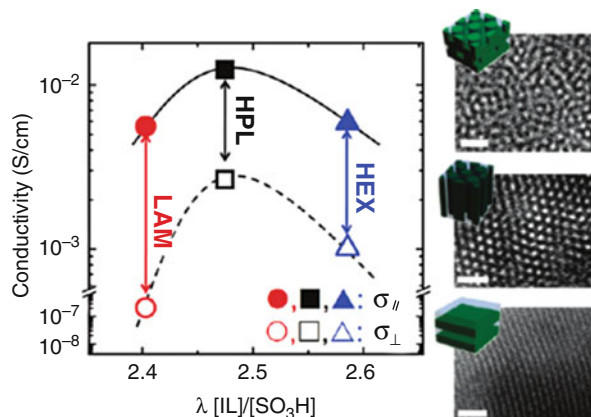


Fig. 8.4 (a) Chemical formula of poly(Sty-*b*-[EVBIm][TfSI]-*b*-Sty) tri-block copolymer. (b) Ionic conductivity versus temperature of this tri-block copolymer with different content of [EMIm][TfO] [98]

copolymers and high ionic conductivity (1.1–1.6 mS cm⁻¹) were obtained. Those tri-block copolymers have been successfully used in thin film transistors, gas separation, and polymer actuators [96, 97]. Recently, the effect of the incorporation of [EMIm][TfO] to ABA tri-block copolymer containing imidazolium-based or novel phosphonium polymeric ionic liquid (PS-PIL (Im)-PS) on the ionic conductivity was investigated (see (Fig. 8.4) [98–100].

By incorporating solvophobic blocks of polystyrene (PS) into the PNIPAm-PEO-PNIPAm tri-block copolymers, Lodge et al. obtained *penta-block copolymers* containing ILs that exhibited adjustable T_{gel} over a significant range (17–48 °C) [101].

Application of IL–Polymer Electrolytes in Energy Storage

The demand for higher-performance electrochemical energy storage technologies is becoming more and more critical due to the emergence of two related issues: the need for harvesting renewable energy effectively (“smart grid concept”) and the development of hybrid and electric vehicles. Moreover, next generations of portable devices will require solid-state supercapacitors and batteries with high-energy and power densities and flexibility to meet various design and power needs. The main drawback of liquid electrolytes (aqueous, organic, and IL-based) in electrochemical storage systems (both batteries and supercapacitors) is the need of additional encapsulation that limits its flexibility and integration in printed circuits or textiles. Although the research on polymer electrolytes has been more concentrated in Li-ion batteries, research on solid electrolytes is starting to be applied in supercapacitors.

Li-ion Batteries

The ion conductive property of a semicrystalline PEO/alkali metal salt complex was first reported by Wright in 1973 [102]. Michel Armand proposed the use of polyethers (PEO) as solid polymer electrolytes (SPE) for lithium batteries in 1979, which immediately spurred an enormous amount of research worldwide [103]. Several strategies were developed in the last decades to avoid the crystallinity of this polymer since crystalline phases hinder the ionic conductivity of the polymer electrolytes. In the last years, some researchers observed that PEO oligomers in combination with ionic liquids became an amorphous fluid showing no T_m and increasing the conductivity of polymer electrolytes [7, 52]. From those pioneering investigations, the research field has experienced a nonstop growing by using mainly PEO-based polymers and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF/HFP) [67, 69, 104–107] in combination with lithium salts and ionic liquids (Fig. 8.5).

The lithium-ion battery is an energy-related topic to which polymeric ionic liquid-based electrolytes have been applied. Mecerreyes et al. reported the electrochemical properties of solvent-free, ternary polymer electrolytes based on the use of a novel poly(diallyldimethylammonium TFSI) as a polymer host blended with $\text{PYR}_{14}\text{TFSI}$ and LiTFSI salt [108]. The ternary electrolyte membranes were found to be chemically and thermally stable. Particularly, the PIL-based polymer electrolytes exhibited ionic conductivities above $10^{-4} \text{ S cm}^{-1}$ at room temperature, electrochemical stability windows of up to 5.0 V versus Li^+/Li , time-stable interfacial resistance values, and good lithium stripping/plating performance. This PIL-based polymer electrolyte was used in $\text{Li}/\text{LiFePO}_4$ solid-state batteries delivering more than 140 mAh g^{-1} with very good capacity retention (up to medium rates (C/5)) (Fig. 8.6).

In general, the mechanical stability of the solid polymer electrolyte (SPE) membrane suffers at increasing IL content, where sticky materials are obtained.

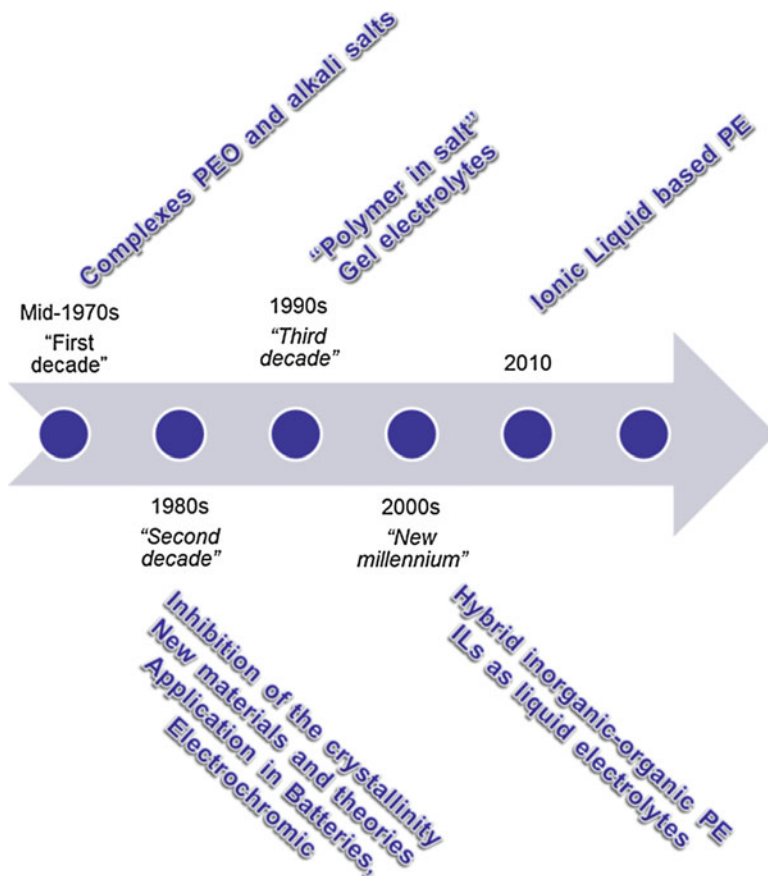


Fig. 8.5 Timeline of polymer electrolytes development for lithium-ion batteries

Different approaches are being investigated to obtain highly conductive polymer electrolytes without depleting their mechanical properties: (1) cross-linking of polymer matrices in the presence of ionic liquid [109], (2) use of inorganic fillers, and (3) design of block copolymers with a block providing extra mechanical strength. Some interesting results are mentioned below:

1. *Cross-linking of polymer matrices*: UV photo-cross-linking PEO was performed in the presence of LiTFSI and PYR₁₄TFSI to obtain chemically cross-linked membranes that exhibit better electrochemical and mechanical properties reaching conductivities of $3 \times 10^{-4} \text{ S cm}^{-1}$ at 20 °C and $10^{-3} \text{ S cm}^{-1}$ at 40 °C (see Fig. 8.7). Charge and discharge tests in battery prototypes (Li/SPE/LiFePO₄) at a C/20 rate yielded more than 100 mAh g⁻¹ at 20 °C, 150 mAh g⁻¹ at 30 °C, and 164 mAh g⁻¹ at 40 °C at a C/10 rate, thus indicating that these batteries were applicable at temperatures higher than 30 °C [110, 111].

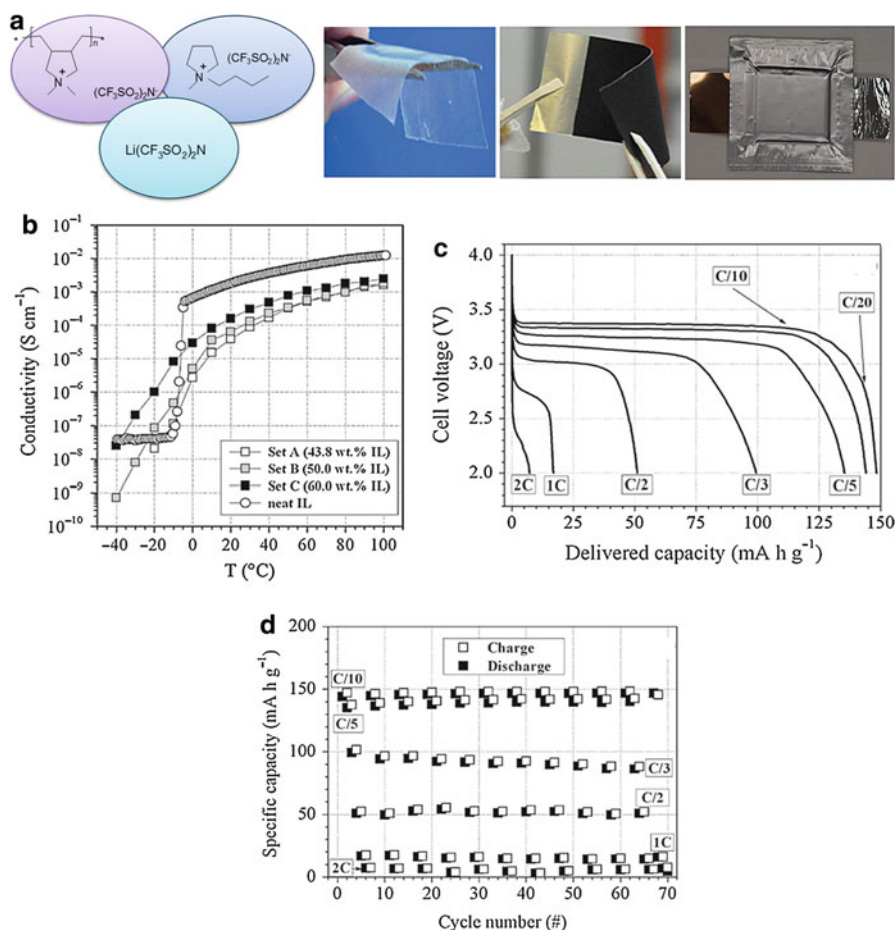
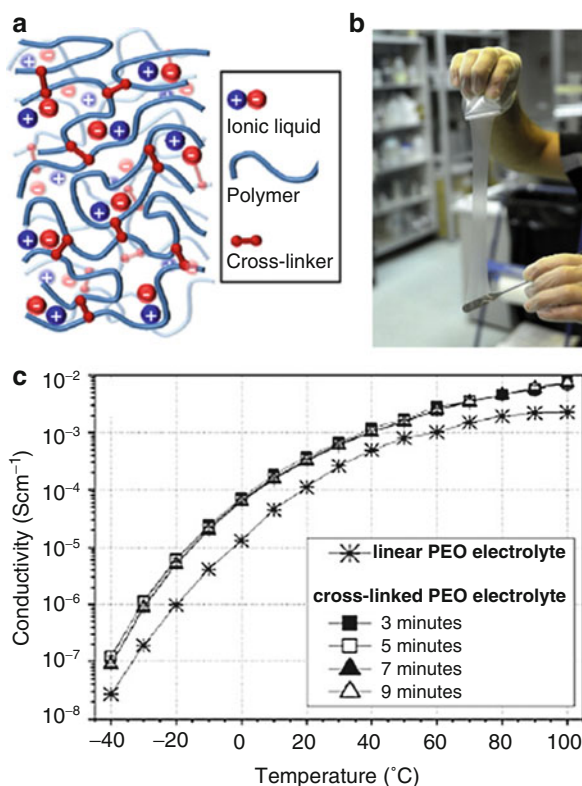


Fig. 8.6 (a) Polymer electrolyte composition and pictures of the membrane, the cathode and the battery prototype, (b) ionic conductivity versus T of PIL-LiTFSI-PYR₁₄TFSI electrolytes with different IL contents, (c) voltage versus capacity profile of selected discharge half cycles, and (d) cycling performance of a Li/SPE/LiFePO₄ polymer battery at 40 °C [108]

Another cross-linking procedure is the use of hyper-branched PEOs to create a gel connected by triazine linkages by a sol-gel process [112] or the copolymerization of PEGM and PEGDM in the presence of PYR₁₃TFSI [50]. It was found that the ionic conductivity of the gel polymer electrolytes was influenced by the cross-link density, the molecular weight of the polymers, as well as the content of the IL.

2. *Addition of inorganic fillers:* This could provide the polymer electrolyte with additional properties such as improved mechanical stability or enhanced ionic conductivity. Ahn et al. reported the synthesis of nanocomposite polymer electrolytes comprising BMImTFSI and nano-sized ceramic fillers (SiO_2 , Al_2O_3 or

Fig. 8.7 (a) Graphical representation [5] and (b) picture of UV-cross-linked PEO + LiTFSI + $\text{PYR}_{14}\text{TFSI}$. (c) Ionic conductivity versus temperature of linear and cross-linked PEO electrolyte [110]



BaTiO₃) hosted in electrospun P(VdF-HFP) membranes [113]. The evaluation of Li/FePO₄ batteries showed that the polymer electrolyte containing BaTiO₃ delivers high initial discharge capacity of 165.8 mAh g⁻¹ and showed the least % capacity fade after prolonged cycling. Another recent example is the development of quaternary polymer electrolyte membranes that comprise PEO, LiTFSI, PYR_{A4}TFSI, and a SiO₂ filler [48]. The authors claim that the addition of SiO₂ and ILs induces a decrease in the PEO melting enthalpy, which thereby increases the ionic conductivity and the Li transference number. Galvanostatic cycling of Li/LiFePO₄ cells revealed superior performance of this quaternary polymer electrolyte compared to conventional PEO–Li salt electrolytes.

3. *Design of block copolymers:* If the ionic liquid used to swell the copolymer selectively interacts with one block over the other, then the majority of the liquid will be confined to that region of the copolymer microstructure. Therefore, organizing the ion-conduction domains of polymers in self-assembled nanostructures is expected to be beneficial to increase ion transport rate due to the creation of preferential pathways. However, although there are many examples in the literature relating the morphology and ionic conductivity of these kinds of materials, there are only a few examples in which those block

copolymers (PS-PEO [114], PEO-PMAALi [115]) were applied into Li-ion batteries. In fact, the main drawback is associated with the formation of the SEI layer that disrupts the self-assembled morphologies blocking the ion-conduction pathways [114].

Lithium/Sulfur Batteries

Lithium/sulfur (Li/S) battery is considered as the next-generation lithium battery because its theoretical specific capacity ($1,670 \text{ mAh g}^{-1}$) and specific energy ($2,600 \text{ Wh kg}^{-1}$) are very high. However, one of the main drawbacks of this technology is the reaction of intermediary polysulfides with conventional liquid electrolytes, which causes irreversible loss of active material (cathode dissolution) and, irretrievably, loss of capacity after cycling. Wu et al. reported that the use of ionic liquid-based polymer electrolytes (porous PVdF/HFP, LiTFSI, and $\text{PYR}_{14}\text{TFSI}$) could minimize the dissolution of sulfur into the electrolyte compared with liquid electrolytes. In fact, the Li/S battery operating with IL-based polymer electrolytes delivers high initial discharge capacity and maintains a reversible capacity of 818 mAh g^{-1} after 20 cycles [116]. Unfortunately, those numbers show that success was limited and these problems have not been alleviated by going to the solid state yet.

Lithium/Air Batteries

The demonstrated unsuitability of the organic carbonates and many other solvents for lithium/air (Li/air) and Li/O_2 batteries is moving the research interest toward the all-solid-state Li/air cells. The solid electrolyte provides some potential advantages in terms of increased interfacial stability, safety, and longer cycle life, due to the protecting role of the solid electrolyte. In this sense, the use of IL-based polymer electrolytes is being also explored. A propylimidazolium TFSI-silica-PVdF/HFP gel was recently prepared and tested as electrolyte for Li/air batteries [117]. Discharge capacity of $2,800 \text{ mAh g}^{-1}$ was delivered, which is higher than that obtained in the case of pure ionic liquid system ($1,500 \text{ mAh g}^{-1}$). This improvement has been interpreted by invoking a more stabilized interface in consequence of the polymer presence, which acts as a protecting layer of the Li anode against moisture.

Supercapacitors

In the past years, different types of polymer or gel electrolytes containing PVA, chitosan, Nafion, etc., have been investigated since they provide high values of conductivity [118–121]. However, due to the water present in the electrolyte, the operating voltage does not exceed about 1.0 V so the specific energy was not particularly high. In order to further improve the performance of polymer

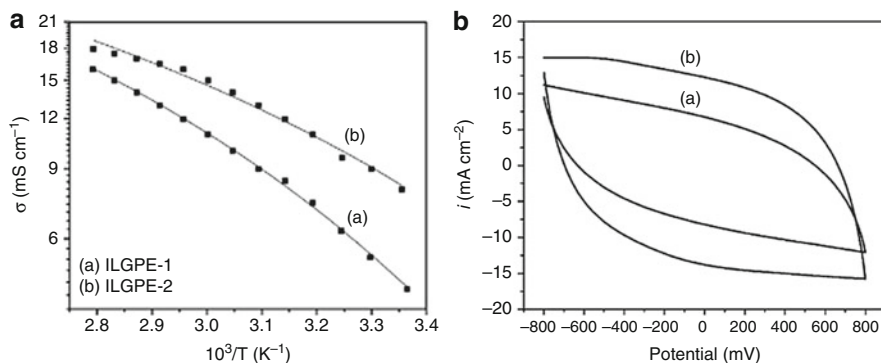


Fig. 8.8 (a) Ionic conductivity (σ) of gel polymer electrolyte as a function of temperature. (b) Cyclic voltammograms of supercapacitor assembled with activated carbon electrodes and polymer electrolytes. Electrolyte composition: (a) 0.3 M LiTf in EMITf–PVdF/HFP 80:20, w/w, (b) 0.3 M LiTf in EMITf–PVdF/HFP/(EC:PC) 65:20:15, w/w [129]

electrolyte-based SCs, an increase of the operating voltage is a must, since such an increase would lead to an enhancement of the specific energy. In that sense the use of ionic liquids is becoming a growing area of research to achieve supercapacitors with high-energy densities. In the field of polymer electrolytes, the most recent and promising results were achieved by embedding ILs in a polymer matrix. Several polymer matrices, including conventional PAN [122], PVdF/HFP [123, 124], PEO [125–127], PVA [128], and PMMA [128], have been investigated in combination with ionic liquids to develop solid supercapacitors. As an example, supercapacitors based on the multiwalled carbon nanotube (MWCNT) electrodes and using an IL-incorporated poly(ethylene oxide) (PEO) with magnesium and lithium salts have been studied by Hashmi et al. [125]. The SCs with the polymer electrolytes containing 40 % of IL (EMImTf) show low specific capacitance values of about $2\text{--}3 \text{ F g}^{-1}$ of MWCNTs. However, much lower values of $\sim 0.01\text{--}0.03 \text{ F g}^{-1}$ were obtained for PEO–Li/Mg salt-based electrolytes without IL.

To improve the ionic conductivity, interfacial stability, etc., some researchers reported the addition of EC or EC:PC mixture in small amounts to substitute partially the ionic liquids in polymer electrolytes. As shown in Fig. 8.8, the addition of EC:PC into the polymer electrolytes resulted not only in the enhancement of the ionic conductivity but also in the enhancement of electrochemical properties such as capacitance in the supercapacitor [129].

In another example, Lu et al. reported the synthesis of PVdF/HFP–EMImTf–SI–zeolite (1:2.5:0.06) IL-based polymer electrolytes having wide electrochemical window up to 4 V and high ionic conductivity (3.5 mS cm^{-1} at room temperature). Addition of small amount of inorganic particle fillers was probed to enhance the mechanical strength of the electrolyte. These polymer electrolytes were used to fabricate SCs showing energy density values as high as 20 Wh kg^{-1} and power density of about $8,000 \text{ W kg}^{-1}$ [130]. These figures of merit, although lower than that for pure ionic liquid electrolytes, are still promising for solid-state

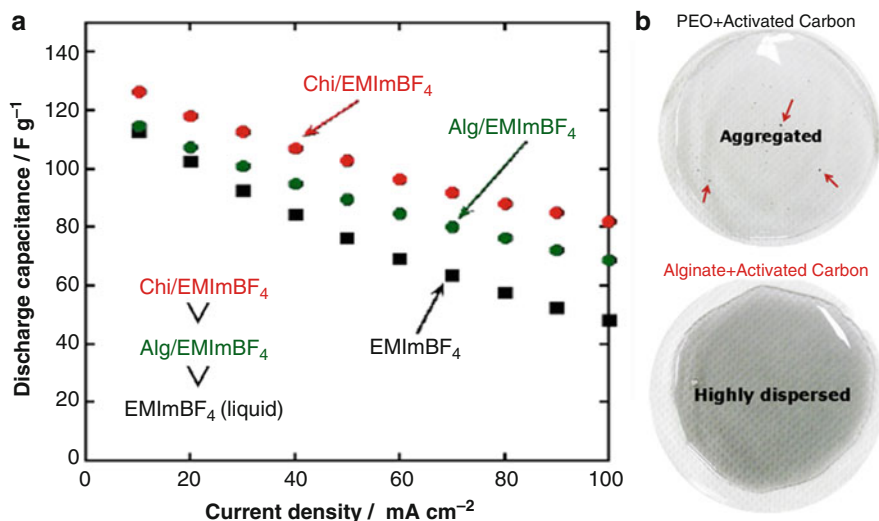


Fig. 8.9 (a) Discharge capacitance of carbon-based supercapacitor using different polysaccharides containing EMImBF₄ [133]. (b) Mixture of activated carbon powder with PEO (*above*) and polysaccharide (*below*) aqueous solution

electrolyte-based capacitors, especially when considering the overall advantages of the solid-state electrolytes over liquid ones.

Only few of the mentioned examples showed a specific capacitance and rate capability close to the corresponding ionic liquid itself, presumably owing to their lower ionic conductivity, which hinders the development of fully solid-state EDLC systems. However, very promising results have been obtained recently by Ishikawa et al. by incorporating EMImBF₄ to different polysaccharides such as alginate and chitosan [131–133]. As shown in Fig. 8.9, those polymer electrolytes exhibited even better electrochemical performance than pure EMImBF₄, especially at high current densities. The authors explained this as a consequence of the high affinity of polysaccharides for the activated carbon electrode that leads to a decrease in the electrode/electrolyte interfacial resistance. Moreover, the operating voltage of those SCs reached 2.0–2.5 V, exhibiting high-specific energy performance and good cyclability (coulombic efficiency over 99.8 % was kept during 5,000 cycles).

Actuators

Electronic conducting polymers (ECP) are distinguished by their possible dimensional changes due to the counterions and solvent molecules expulsion/insertion during oxidation or reduction processes. If an ionic conducting medium is available, ECPs can be used as the active component in actuators for robotics, medical devices, etc. In order to operate in open air, solid polymer electrolytes with good mechanical properties and optimum ionic conductivity (directly related with the

actuation rates) are needed. Thus, the development of flexible solid polymer electrolytes combining ionic liquids (tunable ionic conduction) and polymer matrices (mechanical properties) is very promising for the elaboration and integration of ECP actuators. Indeed, poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VDF-*co*-HFP)) [134] and Nafion [135] embedded with different ILs have been mainly investigated in this context. In the recent years, additional knowledge regarding the effects of the polymer structure and properties on the performance of actuators has been developed specially by deep research on two different polymer matrices: interpenetrated polymer networks and block copolymers.

Interpenetrating polymer networks (IPNs) are a special class of networks described as an intimate combination of two (or more) cross-linked polymers. They have become promising polymer matrices for solid electrolytes since the three-dimensional interpenetration radically improves dimensional and morphological stability [136]. By choosing two polymer partners for their specific properties, i.e., one for ionic conduction (soft) and the other one for mechanical properties (hard), a dual-phase continuity is obtained. The incorporation of ILs with good affinity with the soft polymer dramatically improves ionic motion in these IPNs and makes these polymer electrolytes one of the most interesting candidates for actuators [137]. Chevrot et al. developed a PEDOT–IL-based interpenetrating network electrolyte system with good mechanical stability and very long lifetimes [138]. They first synthesized a polybutadiene/poly(ethylene oxide) (PB/PEO) interpenetrating polymer network (IPN) which was then soaked into pure EDOT monomer. After immersion into FeCl₃ aqueous solution for polymerization, a conducting semi-IPN material was obtained which was swollen with the air- and moisture-stable EMImTFSI. They found that the quantity of PEDOT decreases from the outside to the center of the film so the configuration of the system is similar to a conventional three-layered device but it consists of a single layer. The device revealed a maximum bending deformation of about 90° under a 2 V potential and an excellent stability. From that pioneering work, several IPNs have been developed and used in the design of a mechanically robust conducting IPN actuator. A recent example is the work published by Vidal et al. [139] reporting the synthesis of an IPN based on nitrile butadiene rubber (NBR) as first component and PEO as second component and their application in an actuator exhibiting free strains of 2.4 % and blocking forces above 30 mN for an applied voltage of ± 2 V [140].

Block copolymers: The creation of nanoscale morphologies in IL-integrated polymers using block architectures appeared to have a positive influence on improving the conductivity and consequently the performance of different electrochemical devices. In the last years, several ion gels containing *multi-block copolymers* embedded with different ILs have been used in actuators [96–98, 141]. Watanabe et al. [96] investigated the microstructures, rheological properties, and ionic conductivity of ion gels formed by self-assembly of polystyrene-*block*-poly(methyl methacrylate)-*block*-polystyrene tri-block copolymers (PS-*b*-PMA-*b*-PS), prepared by successive atom-transfer radical polymerizations (ATRP). The resulting ion gels, consisting of these tri-block copolymers incorporating EMImTFSI, presented two-phase structures consisting of continuous

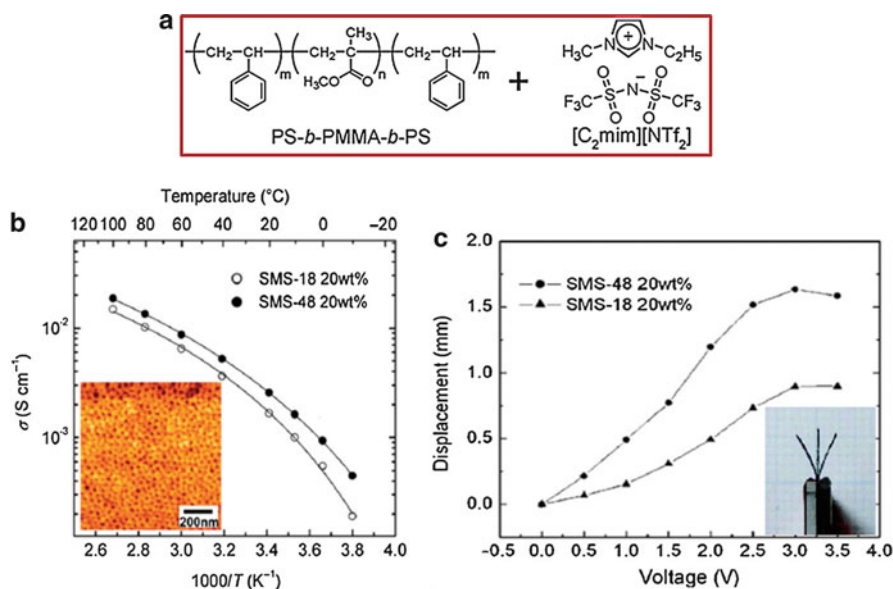


Fig. 8.10 (a) Chemical composition of tri-block ion-gel electrolyte, (b) Arrhenius plots of ionic conductivity, and (c) displacement of ion-gel actuators for the ion gels containing 20 % of EMImTFSI but different block lengths [96]

PMMA phases with preferentially dissolved IL and isolated PS phases that serve as physical cross-linking points of the ion gels. They reported the performance of the actuators based on ion-gel electrolytes sandwiched between two composite carbon electrodes and correlated their performance with the ionic conductivity of the ion gels (see Fig. 8.10).

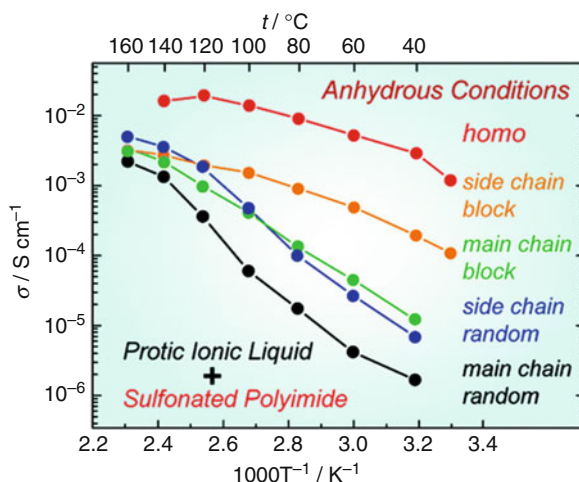
Long et al. [98, 141] reported the synthesis of ionic tri-block and penta-block copolymers with one of the blocks being a polymeric ionic liquid, the preparation of ion gels by addition of an IL (EMImEtSO₄), and the behavior of actuators containing these ion-gel electrolytes. They demonstrated that ILs selectively swell ionic domains in microphase-separated polymers using X-ray scattering and DMA [142].

Application of IL–Polymer Electrolytes in Energy Production

Proton Exchange Membrane Fuel Cells (PEMFCs)

Proton exchange membrane fuel cells (PEMFCs) have the potential to provide power for a variety of applications ranging from electronic devices to transportation vehicles. A major challenge toward economically viable PEMFCs is finding an electrolyte that is durable, has good proton conductivity, and is able to operate at medium temperatures (above 120 °C). Operation of PEMFCs above 120 °C is desirable for a number of reasons: improved CO tolerance, feasibility of using

Fig. 8.11 Effect of polymer structure on the ionic conductivity of membranes [145]



nonprecious metal catalysts, avoidance of flooding, simplified cooling system, and ability to recover waste heat [143]. In this sense, the doping or impregnation of Nafion, current state-of-the-art proton exchange membrane (PEM), with protic ionic liquids has been extensively investigated in the last years [71]. The reported anhydrous conductivity values lie in the range of 0.001–0.1 S cm⁻¹ at 100–200 °C. Based on the efforts to reduce the costs of membranes, the morphologies and proton conductivities of composite systems with other polymer matrices such as PVdF [37], sulfonated poly(aryl ether ketone) (SPAEEK) [144], poly(ether ether ketone) (SPEEK) [75, 76], or polyimide (SPI) have also been investigated [39]. Because [dema][TfO] have suitable properties as protic electrolyte at medium temperature, polymer electrolyte membranes for non-humidified fuel cells were prepared by embedding this IL in sulfonated polyimides with different polymer structures [77, 145]. Figure 8.11 shows the effect of polymer structure on the ionic conductivity of the IL-based polymer electrolytes. The addition of inorganic fillers to the IL–polymer electrolytes has been explored to enhance the ionic conductivity [68] and to promote the ionic liquid retention in PEMFCs [146].

Besides Nafion, polybenzimidazole (PBI) doped with phosphoric acid (H₃PO₄) has been intensively investigated for use in PEMFCs operating at elevated temperature (120–200 °C). Partial or total replacement of phosphoric acid by protic ionic liquids is a promising strategy to increase the performance of the PEMFCs, minimizing the use of corrosive and pollutant electrolytes [78–80, 147].

In an attempt to introduce ordered ionic domains in the membranes to improve the transport properties of PEMFCs, novel anhydrous proton-conducting membranes, formed by incorporating ionic liquids into synthetic block copolymer, poly(styrenesulfonate-*b*-methylbutylene), were investigated [87]. Compared with Nafion 117, the nanostructured membranes revealed over an order of magnitude increase in conductivity with the highest conductivity of 0.045 S cm⁻¹ obtained at 165 °C.

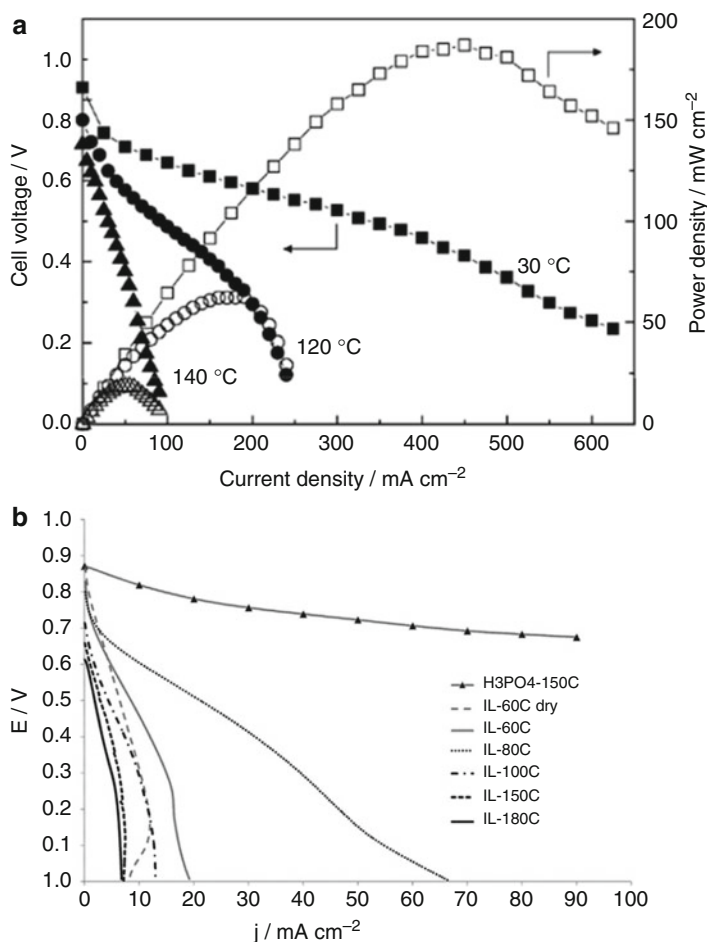


Fig. 8.12 Polarization curves of a PEMFC using (a) polyimide/[dema][TfO] composite membrane [39] and (b) PBI/6DESH(2) at different temperatures [78]

Although there have been many reports on the design of IL-based polymer electrolytes to substitute conventional Nafion or PBI, their use in fuel cell is scarcely reported. Watanabe et al. demonstrated the operation of a PMEFC using the composite membranes (polyimide/[dema][TfO]) under non-humidified conditions (see Fig. 8.12a) [39, 77]. Very recently, the use of diethylamine bisulfate/sulfate IL was incorporated in PBI and tested in a fuel cell (see Fig. 8.12b). The authors reported that the ionic liquid drag limits the life of the cell due to the IL migration from anode and membrane to the cathode. Therefore, further improvements to retain the IL component upon cell operation still need to be carefully considered. Design and synthesis of polymer matrices having strong interaction with IL component might be one of the most effective ways to improve the ionic liquid retention.

Alkaline Polymer Electrolyte Fuel Cells (APEMFCs)

Alkaline polymer electrolyte fuel cells (APEMFCs) have the potential to reduce the cost and weight of current fuel cell technology, but they still have not been broadly commercialized due to poor hydroxide conductivities and mechanical properties, in addition to low chemical stability [148]. One approach to address these limitations is forming a morphologically bicontinuous network of an ion-transporting phase and a hydrophobic phase to provide mechanical strength [149]. Polymeric ionic liquid (PIL)-based membranes have been suggested by several groups as promising candidates for alkali anion exchange membranes in alkaline fuel cells [150–154]. In their fabrication procedure, an IL monomer, 1-vinyl-3-methylimidazolium iodide ([VMIm][I]), was photopolymerized in situ with styrene and acrylonitrile in the presence of 2–10 wt% of the cross-linker divinylbenzene. The resulting membranes were converted to their OH^- forms by exchanging the iodide with hydroxide anions (see Fig. 8.13) [155]. The authors suggested that phase separation in the random copolymer provided both ion transport channels (the imidazolium domain) and a supportive matrix (acrylonitrile domain). The membranes have apparent hydroxide ion conductivities above $10^{-2} \text{ S cm}^{-1}$ at room temperature and excellent chemical stabilities in high pH media at 60°C , fulfilling the basic conductivity and chemical stability requirements. Serious care should be taken because the imidazolium cation ring might undergo a ring-opening reaction under certain strong alkaline conditions at elevated temperature. Other cationic moieties such as tetraalkylammonium or phosphonium are also being investigated, the latter showing stability in 15 M KOH for months [156].

Dye-Sensitized Solar Cells

In addition to conventional polymer matrices such as PEO and PVdF [56, 157–161], there have also been reports on quasi-solid-state dye-sensitized solar cells (DSSCs) based on polymeric ionic liquids (PILs) [162, 163]. In a pioneering work, Mecerreyes et al. [164] reported the use of poly(vinyl propylimidazolium iodide) as a jellifying agent of conventional organic solvents in DSSCs.

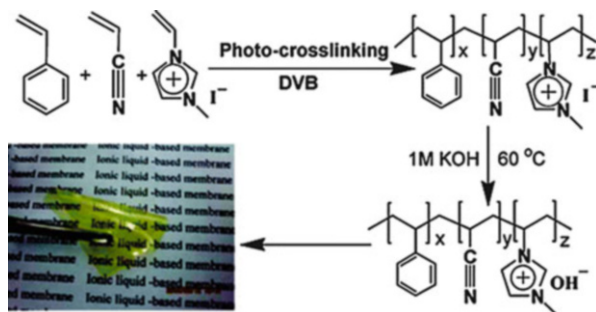
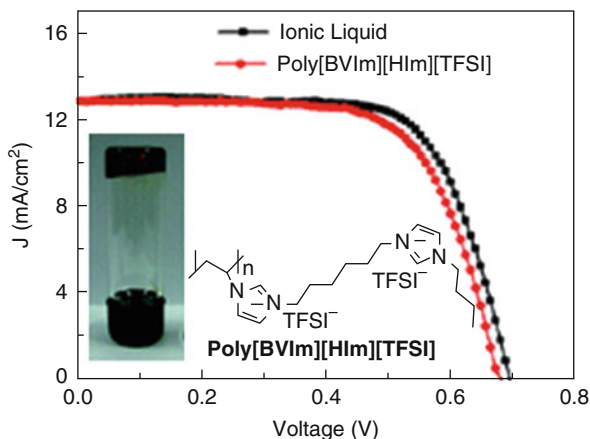


Fig. 8.13 Chemical composition of cross-linked alkaline IL-based polymer electrolytes with a monomer having ionic liquid nature [155]

Fig. 8.14 Chemical composition of bis-imidazolium PIL and comparative I–V curves of DSSCs using IL- or PIL-based electrolytes [166]



The polymer electrolytes were formulated by mixing the PILs with an acetonitrile-based redox electrolyte, which showed PIL content-dependent ionic conductivities in the range of 10^{-3} to 10^{-7} S cm^{-1} at room temperature. Solar cells with 1 cm^2 areas, prepared using this PIL gel electrolyte, yielded a maximum light-to-electricity conversion efficiency of 3.73 %. Other authors extended the use of poly(1-vinyl-3-alkylimidazolium) iodide PILs with different alkyl derivatives, such as methyl, propyl, and perfluorodecyl groups, as quasi-solid electrolytes in DSSCs. For instance, Zhao et al. [165] reported the synthesis of PILs blended with ILs to form gel electrolytes, without using any volatile organic solvent. The DSSCs based on [PBVIm][TFSI] electrolytes displayed maximum efficiency of 4.4 % under simulated air mass 1.5 solar spectrum illumination at 100 mW cm^{-2} as well as superior long-term stability than those with conventional liquid electrolytes, indicating that IL/PIL gel electrolytes are promising candidates for solar cells with good durability. Compared with mono-imidazolium-based poly[BVIm][TFSI], bis-imidazolium-based PIL electrolytes showed a higher thermal stability and conductivity due to the charge transport networks formed in the gel electrolytes via the π – π stacked imidazolium rings [166]. DSSCs based on the bis-imidazolium PIL gel electrolyte showed a superior long-term stability and, as shown in Fig. 8.14, yielded a power conversion efficiency of 5.92 % under the simulated air mass 1.5 solar spectrum illumination at 100 mW cm^{-2} .

Summary

In this chapter the current trends in the design of IL-based polymer electrolytes and their application in energy storage and production have been summarized. Among the different polymer matrices, linear hydrocarbons, perfluorinated polymers, sulfonated aromatic polymers, and, more recently, polymeric ionic liquids have been investigated in combination with ionic liquids. Regarding the innovative polymer architecture, special emphasis has been given to the use of block

copolymers and interpenetrating polymer networks (IPNs) as polymer matrices in IL-based polymer electrolytes. The effect of the polymer electrolyte morphology on the electrochemical performance of the final devices is one of the most active research topics in the field.

In the second half of the chapter, some interesting examples of the application of these IL-based polymer electrolytes in energy storage and production have been gathered. The development of solid electrolytes bearing ionic liquids will pave the way toward the commercialization of safer energy storage technologies, flexible and able to be incorporated into flexible substrates or textiles. In the particular case of actuators, the need of long-cycle operation in air and the intrinsic mechanical requirements are of huge importance and are being addressed by researchers through the incorporation of air-stable ionic liquids into polymer matrices. Regarding the application of these materials in the field of energy production, the development of improved IL-based polymer electrolytes has attracted a lot of attention in an attempt to circumvent the drawbacks of current electrolytes both in dye-sensitized solar cells (DSSCs) and fuel cells. Application of IL-based polymer electrolytes to DSSCs makes it possible to get rid of the current organic electrolyte that is one of the main reasons for short durability of the current devices. In the case of fuel cells, the use of those IL-based polymer electrolytes will allow to operate at higher temperature reducing the high cost of the current technology.

The recent development of polymeric ionic liquids (PILs) and their combination with ionic liquids together with the growing understanding of physicochemical properties of self-assembled IL-based polymer electrolytes are two successful approaches that will help to consolidate the polymer/ionic liquid love history and their final application in energy devices.

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Polymeric Imidazoles and Imidazoliums in Nanomedicine: Comparison to Ammoniums and Phosphoniums

9

Michael H. Allen, Sean T. Hemp, and Timothy E. Long

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Abstract

Polymerized ionic liquids and polyelectrolytes play a major role in a broad range of biological applications including antimicrobials, nonviral gene delivery, synthetic enzymes, metal chelation, and drug delivery. Ammonium- and phosphonium-containing macromolecules will be reviewed with a focus on the literature that examines structure–property relationships of these polyelectrolytes for biological applications. Imidazole-containing macromolecules also receive

M.H. Allen • S.T. Hemp • T.E. Long (✉)

Macromolecules and Interfaces Institute, Department of Chemistry, Virginia Tech, Blacksburg, VA, USA

e-mail: telong@vt.edu

significant focus due to their natural occurrence in nature and their ubiquitous use in nanomedicine. Special attention to imidazole- and imidazolium-containing polymers will focus on vinylimidazole regioisomers in particular.

Keywords

Vinylimidazole • Ammonium • Phosphonium • Polyelectrolytes • Polymerized ionic liquids

Introduction

Ionic liquids typically consist of an ammonium, phosphonium, or imidazolium cation with a bulky, fluorinated counterion, which sufficiently depresses the T_m of the ionic compounds to below 100 °C (Fig. 9.1) [1]. The literature typically directly compares ammonium and phosphonium ionic liquids [2]. Imidazolium ionic liquids are the most common ionic liquids with a broad range of structural diversity through substituent control and counterion structure [3]. Ionic liquids that contain polymerizable functionality enable the generation of polymerized ionic liquids upon polymerization [4]. Typically, researchers examine structure–property relationships of ammonium- and phosphonium-containing polymerized ionic liquids to examine the impact of cation structure on macromolecular properties. This chapter will focus in part on the synthesis, characterization, and biological applications of ammonium and phosphonium polyelectrolytes with a focus on the literature that directly compares ammonium and phosphonium polyelectrolytes.

The imidazole ring remains one of the premiere bioactive molecules utilized significantly for the design and synthesis of functional macromolecules [5, 6]. Found in the amino acid histidine, the imidazole substituent executes vital activities within the human body including oxygen capture, enzymatic catalysis, and metal ion complexation [7, 8]. The intense focus on the ubiquitous imidazole ring has propelled imidazole-containing polymers to the forefront of materials design due to their facile functionalization, biological relevance, and amphoteric nature [4, 9]. Researchers widely utilize the monomers, 1-, 2-, and 4-vinylimidazole regioisomers, which highlight imidazole as a focal point for synthetic macromolecular design [10–12]. Additionally, free radical polymerization of these monomers allows for the development of novel polymer architectures. The propagating

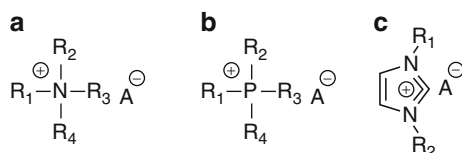


Fig. 9.1 Example structures of ionic liquids: (a) ammonium, (b) phosphonium, and (c) imidazolium

radical instability of 1-vinylimidazole limits the generation of precise polymer structures for future materials, whereas the increased radical stability of 4-vinylimidazole generates polymers with well-defined molecular weights and precise architectures utilizing controlled radical polymerization strategies [10, 13]. These vinyl monomers inspired the generation of synthetic enzymes [14, 15], water purification membranes [16], nucleic acid therapeutics [17, 18], and numerous additional applications. The synthetic versatility afforded through the incorporation of these vinylimidazole regioisomers into macromolecules remains integral as the drive toward a sustainable future continues.

Ammonium- and Phosphonium-Containing Macromolecules

Polyelectrolytes containing ammonium or phosphonium cations are widespread in the literature. They are typically synthesized utilizing two different approaches: a functional monomer route [19] or post-polymerization functionalization [20]. The synthesis of ammonium and phosphonium monomers typically relies on a simple nucleophilic substitution between a haloalkane and a tertiary amine or tertiary phosphine to generate the desired cationic monomer [19]. Monomer stability tends to limit the feasibility of the monomer route approach. Post-polymerization functionalization avoids potential monomer stability issues or polymerization hurdles, but difficulties arise in achieving 100 % functionalization due to steric and neighboring group effects. Halide-containing macromolecules subjected to excess tertiary amines or tertiary phosphines readily generate ammonium and phosphonium macromolecules [20]. Tertiary amine-containing monomers are also common in the literature, and after polymerization, subsequent alkylation using a haloalkane will generate the desired ammonium polyelectrolyte [21]. Tertiary phosphine-containing monomers are rare due to their propensity for oxidation, but 4-(diphenylphosphino)styrene is readily used in the literature [22, 23].

Structural Differences of Ammonium and Phosphonium Cations

Nitrogen is a row 2 element in the periodic table with an atomic weight of 14.01 g/mol, while phosphorus is a row 3 element below nitrogen in the periodic table with an atomic weight of 30.97 g/mol. Atomic radii and electronegativities directly impact the overall structure of the ammonium and phosphonium cations. Phosphorus exhibits a larger atomic radius than nitrogen [24]. Electronegativity differences result in a different charge distribution within the cation. Colby et al. [25] performed *ab initio* calculations to determine the specific charges upon each atom within the ammonium and phosphonium cation. Since nitrogen is more electronegative than carbon, the nitrogen in ammonium cations displayed a slightly negative partial charge of -0.5 eV, while the surrounding alpha carbons exhibited a slightly positive charge of 0.3 eV. Conversely, phosphonium cations contained a reversed charge density because phosphorus is less electronegative than carbon;

therefore, the phosphorus atom displayed a positive charge of +1.1 eV, and the adjacent carbon atoms exhibited a negative charge of -0.2 eV. Ultimately, both atomic radii and electronegativity differences of nitrogen and phosphorus lead to widely different cation structures.

Thermal Stability and Base Stability

Ammonium and phosphonium ionic liquids exhibit significantly different thermal and chemical stabilities. Ammonium ionic liquids typically display poor thermal stability compared to phosphonium ionic liquids [26]. Hoffman elimination is one of the primary degradation pathways for ammonium ionic liquids that leads to this lower thermal stability. Both ammonium and phosphonium ionic liquids also degrade through reverse Menshutkin reactions wherein the halide counterion displaces the tertiary amine or phosphine [26]. Ammonium and phosphonium polymerized ionic liquids exhibit similar trends in thermal stability to their ionic liquid counterparts. Long et al. performed a broad structure–property relationship study focused on poly(vinyl benzyl ammonium)s and poly(vinyl benzyl phosphonium)s [27]. All phosphonium polymerized ionic liquids displayed dramatically higher thermal stabilities than ammonium analogues (Fig. 9.2); longer alkyl substituent lengths also dramatically decreased the thermal stabilities of poly(vinyl benzyl ammonium)s. Thermogravimetric analysis (TGA) studies confirmed the primary degradation pathway of poly(vinyl benzyl ammonium)s was reverse Menshutkin degradation. Ammonium and phosphonium ionic liquids degrade through two different pathways under alkaline conditions [2]. Ammonium ionic liquids degrade through Hoffman elimination, while phosphonium ionic liquids degrade into tertiary phosphine oxides and alkanes. The overall structure of the ammonium or phosphonium cation largely impacts its overall base stability with examples in the literature of alkaline stable ammonium [28] and phosphonium [29, 30] macromolecules.

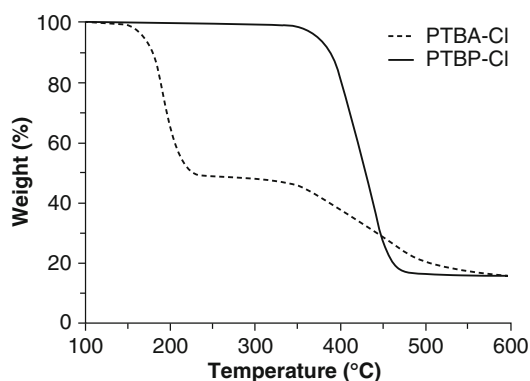


Fig. 9.2 Thermogravimetric analysis of poly(tributylvinylbenzylammonium chloride) (PTBA-Cl) and poly(tributylvinylbenzylphosphonium chloride) (PTBP-Cl) (Reprinted with permission from Ref. [27]. ©2013 John Wiley and Sons, Inc.)

Antimicrobials

Cationic macromolecules electrostatically associate nonspecifically to the negatively charged microbial cell membrane [31]. The lipophilic portions of the cationic macromolecules insert into the cellular membrane upon association to the microbial cell membrane, leading to rupture and cell death. Typical bacteria utilized during efficacy studies include *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). *E. coli* are the prototypical gram-negative bacteria [32], while *S. aureus* are representative gram-positive bacteria [33]. Gram-positive bacteria contain a cell wall consisting of a single cellular membrane with an outer rigid, thick peptidoglycan layer [33]. The peptidoglycan layer consists of a broad mix of peptidoglycans and contains pores, which allow nutrients and particles to reach the inner cell membrane [34]. Cell walls of gram-negative bacteria include an inner cell membrane, a thin peptidoglycan layer, and then another outer cell membrane [32]. The outer cell membrane protects the integrity of the inner cell membrane, increasing the antimicrobial resistance of gram-negative bacteria [35].

Endo and coworkers pioneered structure–property analyses of ammonium- and phosphonium-containing polyelectrolytes for antimicrobial applications. They directly probed the antimicrobial efficacy of ammonium- and phosphonium-containing monomers and polymers against *E. coli* and *S. aureus* [36]. All polyelectrolytes displayed improved antimicrobial activity compared to their respective monomers. Also, phosphonium polyelectrolytes displayed enhanced antimicrobial properties compared to ammonium analogues (Fig. 9.3). Ultimately, longer alkyl substituents attached to the cation resulted in the highest antimicrobial activity with

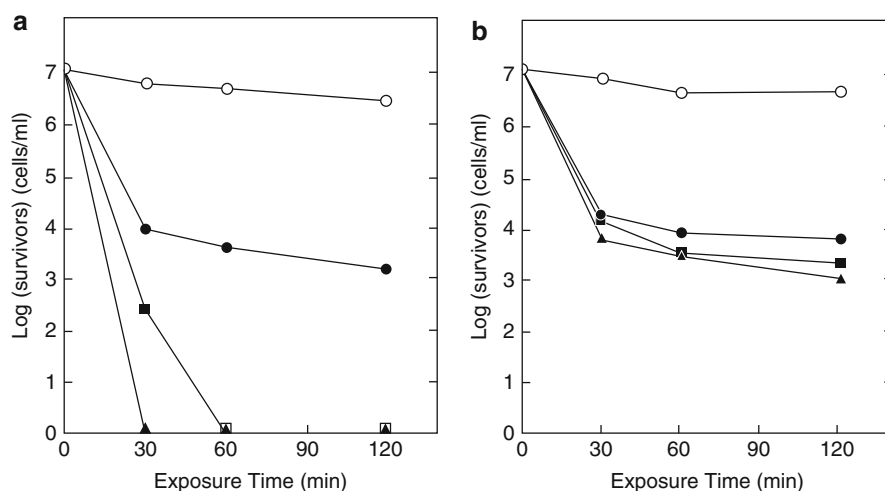


Fig. 9.3 Antimicrobial activity of (a) PTBP-Cl and (b) PTBA-Cl demonstrating the enhanced efficacy of phosphonium macromolecules. Polymer concentrations: 0 μM (open circle), 280 μM (filled triangle), 28 μM (filled square), and 2.8 μM (filled circle) (Reprinted with permission from Ref. [36]. ©1993 John Wiley and Sons, Inc.)

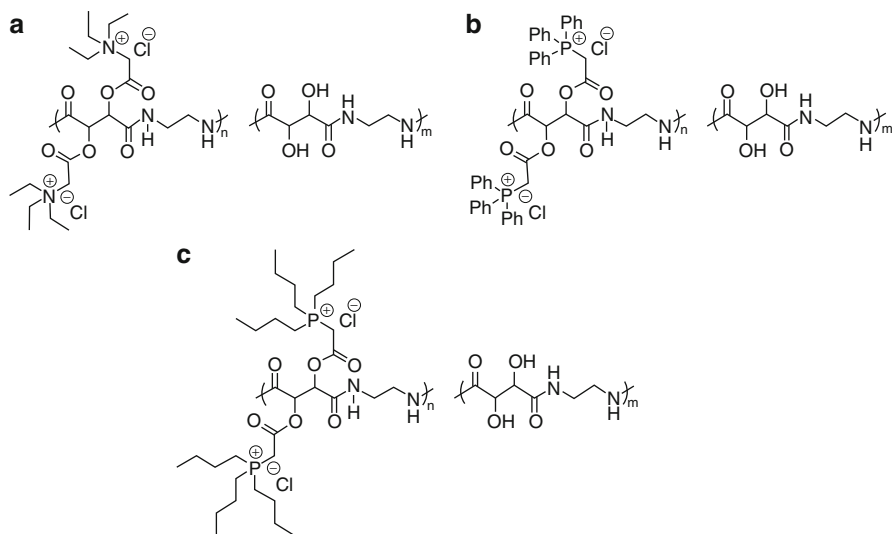


Fig. 9.4 Tartrate-containing polyamides functionalized with (a) triethylammonium, (b) triphenylphosphonium, and (c) tributylphosphonium substituents [38]

n-octyl chains being the most effective at killing both *E. coli* and *S. aureus*. Endo and coworkers also examined ammonium and phosphonium random copolymers and polymer blends [37]. Polymer blends of ammonium and phosphonium polyelectrolytes exhibited a synergistic bactericidal effect, which resulted in improved efficacy. Interestingly, ammonium and phosphonium random copolymers failed to display any synergistic effect and higher phosphonium concentrations in the random copolymers resulting in higher antimicrobial efficacies.

Kenawy and coworkers also extensively examined structure–property relationships of ammonium- and phosphonium-containing polyelectrolytes as antimicrobial agents. They typically generated halide-containing macromolecules and then subsequently performed post-polymerization functionalizations using tertiary amines or phosphines to generate the desired polyelectrolytes. Tartrate-based polyamides with pendant ammonium and phosphonium groups displayed high antibacterial activity, with tributylphosphonium cations exhibiting the highest efficacy (Fig. 9.4) [38]. Cationic poly(glycidyl methacrylate-*co*-hydroxyethyl methacrylate) random copolymers also showed the highest antibacterial and antifungal activity with tributylphosphonium cations attached to the polymer backbone [39]. Kenawy and coworkers also examined cross-linked cationic materials wherein triphenylphosphonium cations displayed the highest antimicrobial efficiency [40]. Finally, they controlled the charge density of ammonium- and phosphonium-containing copolymers, which elucidated improved antimicrobial activity for phosphonium cations and higher charge densities [41].

Nonviral Nucleic Acid Delivery

Nitrogen-based cations such as ammonium, imidazolium, and pyridinium cations are utilized throughout the literature to electrostatically complex nucleic acids and deliver them to cells in vitro and in vivo (Fig. 9.5) [42]. Typical cationic nitrogen-containing macromolecules examined for nonviral nucleic acid delivery include polyethyleneimine [43], poly(amido amine) dendrimers [44], chitosan [45], poly(vinyl imidazolium)s [17, 18], poly(2-dimethylamino)ethyl methacrylate [46], and poly(vinyl pyridinium)s [47]. Nitrogen-based cationic systems also display the advantageous property of typically containing protonatable nitrogens [48]. These protonatable sites provide buffering capacity to the macromolecule, enabling endosomal escape. Endosomal escape is one of the major barriers to nucleic acid delivery [42]. Delivery vehicles that buffer during endosomal acidification enable polyplex escape through the proton-sponge effect, wherein endosomal acidification and polymeric buffering capacity induce an influx of chloride anions [48]. Subsequent osmotic pressure ruptures the endosome. Prior to 2012, researchers failed to examine phosphonium-containing macromolecules for nonviral nucleic acid delivery.

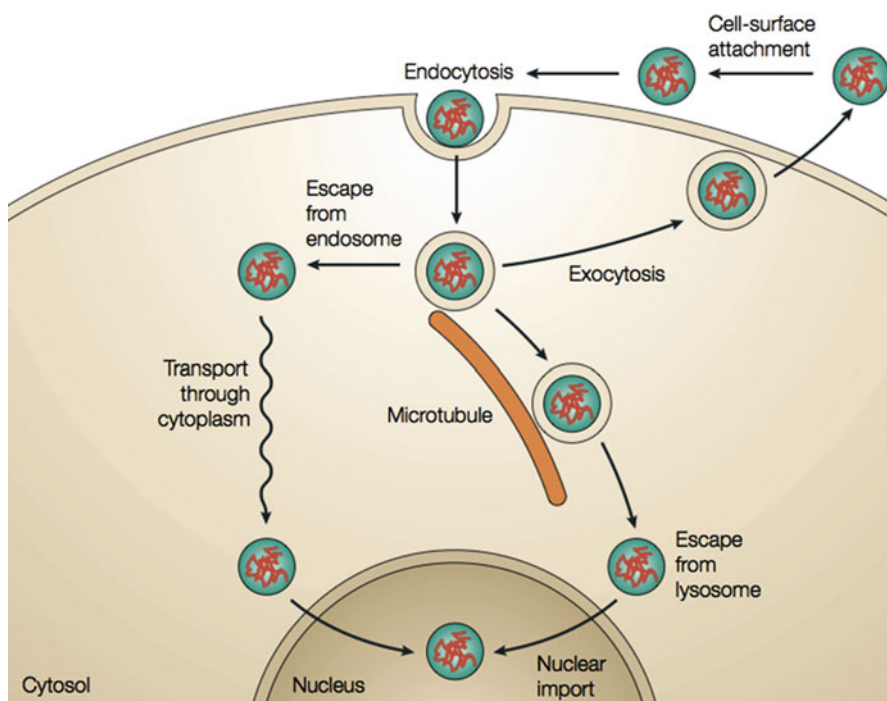


Fig. 9.5 Nonviral gene delivery pathway demonstrating the necessary steps to achieve successful delivery (Reprinted with permission from Ref. [49]. ©2005 Nature Publishing Group)

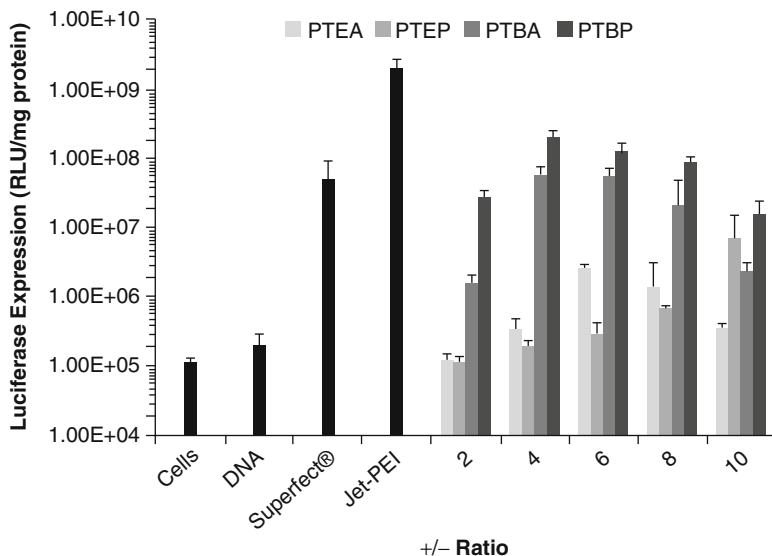


Fig. 9.6 Luciferase transfection assay in serum-free media demonstrating improved efficacy for phosphonium-containing macromolecules (Reprinted with permission from Ref. [50]. ©2012 American Chemical Society)

Long et al. [50] pioneered the utilization of phosphonium macromolecules for nonviral nucleic acid delivery. They examined similar poly(vinyl benzyl ammonium)s and poly(vinyl benzyl phosphonium)s that Endo et al. previously used to highlight the improved antimicrobial properties of phosphonium macromolecules. Phosphonium-containing polystyrenes bound nucleic acids more effectively than ammonium analogues, completely complexing nucleic acids at charge ratios of 2 compared to charge ratios of 4 for ammonium analogues. Luciferase expression assays performed in serum-free media demonstrated improved nucleic acid delivery for phosphonium polystyrenes compared to ammonium polystyrenes (Fig. 9.6). Unfortunately, ammonium and phosphonium polystyrenes performed poorly in serum-containing media, presumably due to aggregation with serum proteins as expected due to the high charge concentration. They also posed significant cytotoxicity *in vitro*, which resulted from their high charge density.

Long et al. [51] aimed to improve nucleic acid delivery under serum-containing conditions and minimize cytotoxicity through the synthesis of phosphonium-containing AB diblock copolymers. The A block consisted of either an oligo (ethylene glycol) methyl ether methacrylate (OEG) or methacryloxyposphoryl choline (MPC) block. Previous literature on OEG and MPC blocks demonstrated their efficacy for enhancing nanoparticle colloidal stability. The B block composed of 4-(vinylbenzyltributyl)phosphonium chloride efficiently bound and compacted nucleic acids, as demonstrated previously. The authors targeted similar molecular

weights for the A block (25 kg/mol) and varied the B block DP (25, 50, or 75). They found all diblock copolymers bound pDNA at charge ratios of 1. Phosphonium diblock copolymer polyplexes also displayed excellent colloidal stability, remaining similar diameters over 24 h under salt or serum conditions. These delivery vehicles deliver pDNA inefficiently to HeLa and COS-7 cells under serum conditions, likely due to the steric stabilizing A block minimizing cellular uptake. In HepaRG cells, a predictive cell line for *in vivo* studies, all phosphonium diblock copolymers delivered pDNA efficiently on the same order of magnitude as jetPEI with minimal cytotoxicity.

siRNA delivery is a rapidly expanding field focused on therapeutic treatment through the siRNA pathway, wherein delivered siRNA induces silencing of a specific protein through cellular machinery [52]. Protein silencing enables treatment of various diseases, including cancer and genetic diseases. Fréchet et al. [53] first examined phosphonium polyacrylates for siRNA delivery and compared them to ammonium polyacrylates. Phosphonium polyacrylates displayed improved gene knockdown and higher cell viabilities compared to ammonium analogues. They also found a significant impact of alkyl substituent on toxicity and transfection efficiency. Finally, Kumar and coworkers [54] reported the elegant design and synthesis of triphenylphosphonium-modified PEI, which displayed improved pDNA and siRNA delivery compared to a linear PEI analogue.

Macromolecules from Vinyl Imidazole Monomers

From delivering therapeutics for the treatment of chronic disease to the fabrication of membranes for electromechanical transducers, imidazole-containing macromolecules comprise an area of intense research focus. The planar, five-membered imidazole ring, contained in the amino acid histidine, serves a variety of bioactive functions due to its amphoteric nature [6]. The acidic N1 and basic N3 nitrogens catalyze ester hydrolysis in the active site of enzymes [7], participate as a coordinating ligand in metalloproteins [55], and aid in protein folding [56]. The biologically relevant molecule histamine contains the imidazole ring to mediate inflammatory responses [57]. Additionally, the imidazole ring undergoes facile modification to generate ionic liquids [58]. The asymmetry associated with this organic cation and bulky counterion lowers the melting point of the ionic salt below 100 °C. Imidazolium ionic liquids exhibit high chemical and thermal stability, negligible vapor pressure, and high ionic conductivity. These properties have resulted in a wide variety of applications including batteries, fuel cells, and catalysis.

The sustained focus to derive fundamental polymer design parameters from nature and the high impact of ionic liquid research fueled the incorporation of the imidazole ring into numerous macromolecules (Fig. 9.7). The amphoteric heterocycle spans various research thrusts in polymer chemistry from components in electroactive devices to building blocks for nucleic acid therapeutics. Taking inspiration from histidine, researchers have designed imidazole-containing

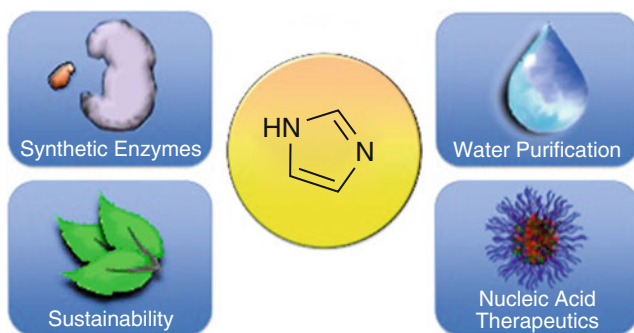


Fig. 9.7 Incorporating the imidazole ring into a wide variety of applications

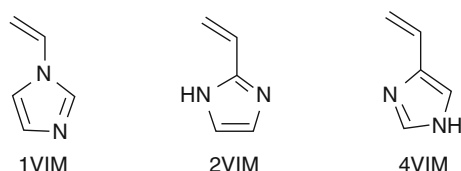


Fig. 9.8 Structures of vinylimidazole regioisomers

polymers for metal complexation to investigate new avenues for water purification [16] and have begun to develop synthetic enzymes for industrial applications [14, 15]. From water purification to CO₂ capturing membranes [59] to renewable feedstocks [60, 61], imidazole-containing macromolecules remain integral as the effort toward increased sustainability continues.

A wide array of synthetic polymers incorporate the imidazole ring including polypeptides, polyesters, polyurethanes, ionenes, meth(acrylics), meth(acrylamides), and styrenics [4, 6, 8]. A unique class of chain growth monomers, vinylimidazoles, incorporates the imidazole ring attached directly to the polymer backbone without the influence of additional functional groups. Three regioisomers exist (Fig. 9.8): *N*- or 1-vinylimidazole (1VIM), 2-vinylimidazole (2VIM), and 4-vinylimidazole (4VIM). The synthetic versatility afforded through the incorporation of these vinylimidazole regioisomers into macromolecules remains integral for the generation of novel materials. 1VIM remains the most heavily investigated monomer due to its inexpensive cost, commercial availability, and facile functionalization; the additional regioisomers currently remain unavailable through commercial resources. The synthesis of 4VIM requires the decarboxylation of urocanic acid [62], whereas the synthesis of 2VIM consists of a complex, multistep procedure [11].

The limited availability of these two regioisomers has prevented the integration of these monomers into an array of macromolecules. This review aims to focus on the polymerization of vinylimidazole monomers in materials science for biological applications.

Macromolecules from 1-Vinylimidazole

1VIM remains the most commonly studied vinylimidazole regioisomer due to its widespread commercial availability. Unlike the amino acid histidine, the vinyl substituent at the 1-position eliminates intermolecular hydrogen bonding, lowering the monomer melting point below $-50\text{ }^{\circ}\text{C}$ [9]. Conventional free radical homopolymerization of 1VIM affords homopolymers with a number-average molecular weight (M_n) less than 100,000 g/mol with a glass transition temperature (T_g) around $180\text{ }^{\circ}\text{C}$. Poly(1VIM) remains thermally stable to $350\text{ }^{\circ}\text{C}$. Copolymers incorporate 1VIM to impart various properties including metal-binding affinity [63], catalytic activity [64], biocompatibility [18], and polyelectrolyte behavior [65].

Application in Metal Chelation

Numerous researchers have investigated the ability of poly(1VIM) to chelate various metal ions. The interest began decades ago, when researchers discovered the binding sites of metal-binding proteins consisted of histidine residues [66–68]. Gurd and Goodman delved deeper into the proteins and attributed metal ion complexation to the imidazole ring [69]. They found four imidazole rings participated in the complexation of Zn^{2+} and Cu^{2+} ions. Gregor and coworkers previously investigated the binding of metallic ions with acrylic and methacrylic polymers and applied this expertise to imidazole-containing macromolecules. They determined poly(1VIM) also displayed a preferred coordination number of four when complexing Cu^{2+} ions, similar to biological enzymes [63, 70]. Poly(1VIM) coordinated additional ions including Ag^+ (N = coordination number = 2) and Zn^{2+} (N = 4) [63, 71]. Pekel et al. studied the complex formation of poly(1VIM) hydrogels with trivalent metal ions in aqueous solution [72]. They found poly(1VIM) formed a $N = 4$ with V (III), Cr (III), and Fe (III). Annenkov et al. investigated the interaction of poly(1VIM) with an additional trivalent metal ion, Al^{3+} [73]. Through the titration of AlCl_3 and $\text{Al}(\text{NO}_3)_3$, they discovered, unlike previous imidazole-metal complexes, the imidazole ring did not complex the Al^{3+} ions. Instead, cooperative hydrogen bonding of the imidazole ring to aluminum hydroxide promoted the formation of alumina particles.

These metal-binding properties of poly(1VIM) more recently generated interest in removal of heavy metals for water purification. Rivas et al. designed poly(1VIM) hydrogels cross-linked with *N,N'*-methylenebisacrylamide to chelate metal ions in aqueous solutions [16]. The hydrogels demonstrated effective binding of Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} ions. Subsequent elution of the metal ions with an acidic aqueous solution regenerated the hydrogel for further metal chelation. Cross-linked copolymers of poly(1VIM) with either acrylic acid or AMPS effectively bound similar ions [74]. The inclusion of the sulfonic acid comonomer increased metal-binding affinity. These same copolymers bound uranyl ions with higher affinity than the respective homopolymers to demonstrate the recovery of uranium from contaminated water sources [75]. The resins underwent four cycles of loading and metal elution but progressively lost metal ion affinity with

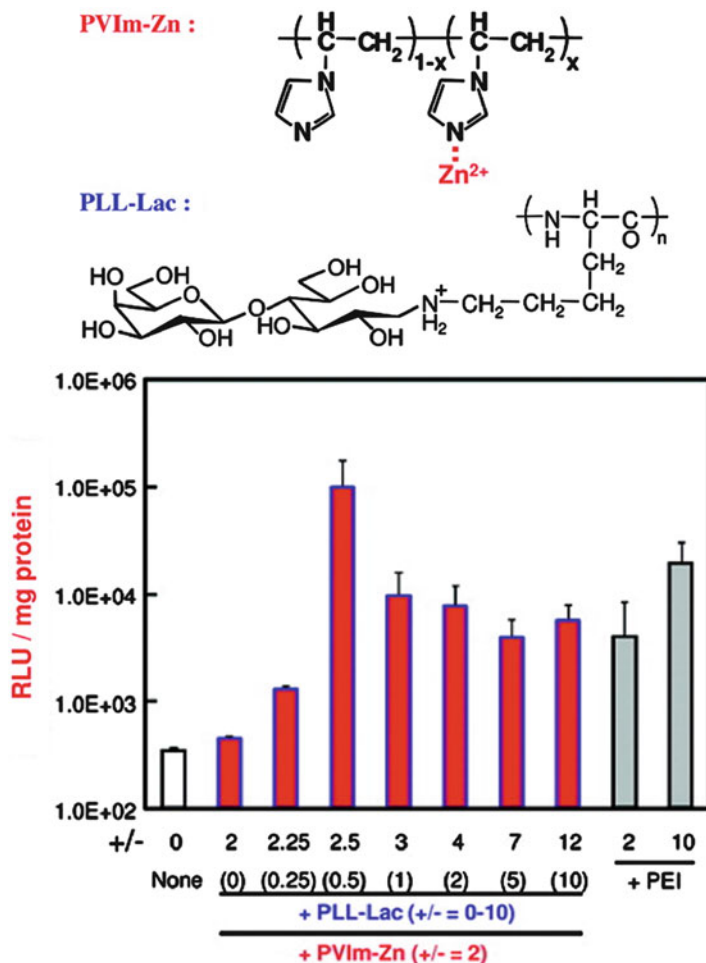


Fig. 9.9 Diagram of poly(1VIM) complexed with Zn^{2+} ions and lactosylated poly(L-lysine) for nonviral gene delivery with subsequent transfection efficiencies (Reprinted with permission from Ref. [78])

each cycle. Tarley et al. synthesized poly(1VIM)-silica hybrid copolymers for Pb^{2+} ion removal, and the copolymers displayed selectivity for $\text{Pb}(\text{II})$ over $\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Zn}(\text{II})$ [76]. Asayama and coworkers complexed Zn^{2+} ions with poly(1VIM) and subsequently bound this complex with DNA for nonviral gene delivery [77]. The complexes displayed stimuli-responsive release of Zn^{2+} at acidic pH and significant transfection efficiency in HepG2 cells with minimal cytotoxicity. Additionally, the incorporation of poly(L-lysine) conjugated with lactose formed ternary complexes for nonviral gene delivery and exhibited higher transfection efficiency than PEI (Fig. 9.9) [78].

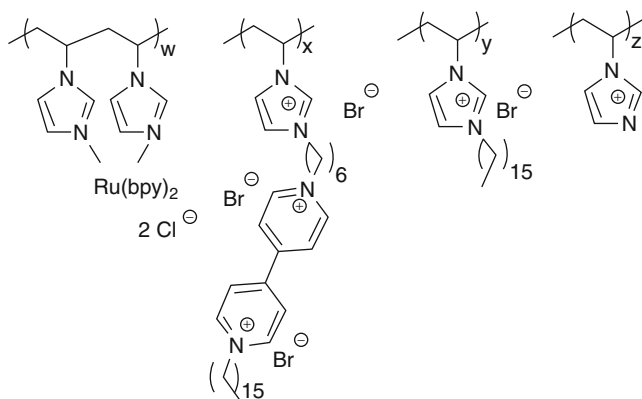


Fig. 9.10 Structures of imidazolium copolymers investigated in photosensitized oxidation–reduction reactions. QPIM terpolymers lack the viologen repeat unit

Vos et al. first coordinated poly(1VIM) with hydrated bis(2,2′-bipyridyl)ruthenium(II) dichloride to form ruthenium–poly(VIM) complexes [79]. This spurred investigations into photoinduced electron transfer reactions involving these complexes to potentially design a synthetic photosynthesis complex. To achieve an artificial photosynthetic complex, the design of a highly efficient oxidation–reduction complex is required. Suzuki and coworkers thoroughly investigated various photosensitive reactions with a poly(1VIM) terpolymer (QPIM) containing repeat units complexed with Rh(II)(bpy)_2 , quaternized repeat units with a long alkyl chain, and unfunctionalized repeat units as shown in Fig. 9.10 [80–100].

They found the rate of viologen radical formation increased as the alkyl chain length increased on the polymer but decreased with the incorporation of higher charge densities. Electrostatic repulsions, sterics, and π – π interactions between the terpolymer and the viologen were identified as three possible factors impacting the rate of the oxidation–reduction reaction [100]. The terpolymers generated hydrogen gas when irradiated in aqueous solution for 25 light cycles after which the platinum catalyst became inactivated; however, the films maintained their photosensitizing ability over 200 cycles [94, 96, 98].

In the 1970s and 1980s, interest in designing artificial oxygen carriers developed. It became necessary to design polymers to interact with the heme group or other porphyrinatoiron complexes to prevent irreversible oxidation. Isolation from myoglobin or hemoglobin resulted in iron's immediate oxidation to its ferric (III) state preventing its use as an oxygen carrier. The iron–porphyrin complexes when attached to a polymer chain or modified to incorporate bulky groups to sterically functionalize the complexes prevented oxidation in aprotic solvents; however, aqueous media caused irreversible oxidation. Pratt and others attempted to understand the coordination chemistry that occurred in the active site of hemoproteins and discovered imidazole and subsequently poly(1VIM) coordinated to Fe(III)

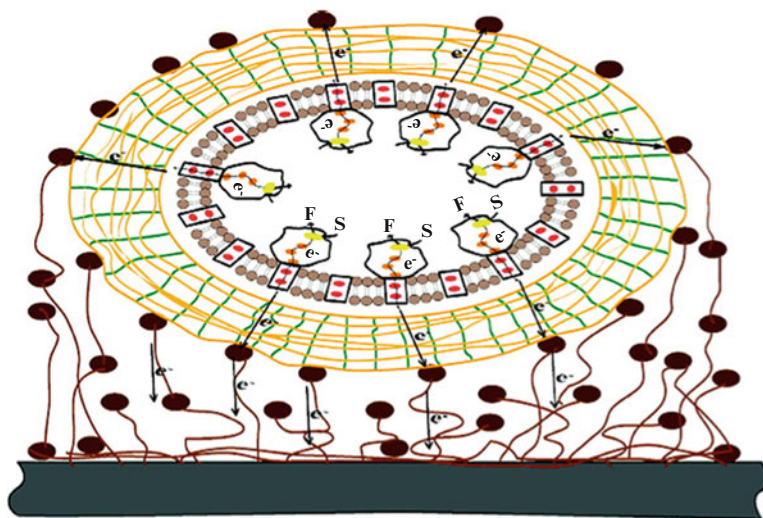
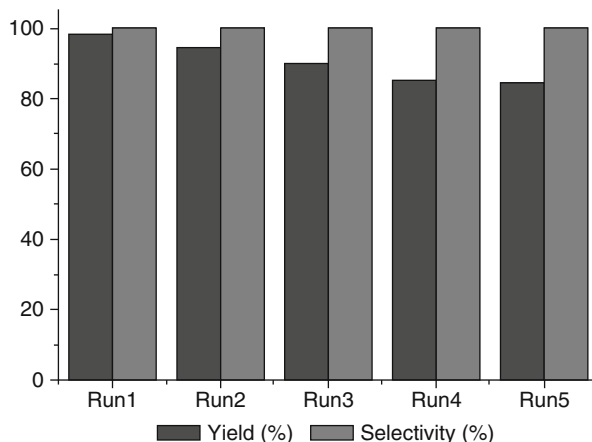


Fig. 9.12 Diagram of *Bacillus subtilis* wired to an electrode with poly(1VIM)-osmium redox polymers to transport electrons from the gram-positive bacteria cell to the electrode (Reprinted with permission from Ref. [112])

Synthetic Enzymes

The design of synthetic enzymes to replace natural proteins for catalytic production of small molecules on an industrial scale with selectivity and specificity remains popular. Enzymes exhibit a high selectivity and efficiency toward structurally similar substrates typically depending on a concerted action between various functional groups in the active site of the enzyme. This includes hydrophobic and electrostatic interactions which promote the binding of a substrate into the active site in an enzyme. Deriving their inspiration from nature, numerous researchers have investigated incorporating the imidazole ring into synthetic macromolecules to mimic the active site of numerous natural enzymes. Poly(2-ethyl-1VIM) quaternized with ethyl bromide and lauryl bromide catalyzed the flavin oxidation of thiols due to the activation of the thiolate anion [126]. Similar copolymers catalyzed the decarboxylation of 6-nitrobenzoxazole-3-carboxylate [127]. The balance of the hydrophobic lauryl domains with the cationic imidazolium rings enabled the tuning of the polymer's catalytic activity [128]. These copolymers also served as apoenzymes binding various thiol-containing coenzymes including coenzyme A and glutathione to catalyze the hydrolysis of PNPA [129]. The coenzymes required binding to an apoenzyme to exhibit high enzymatic reactivities. The lauryl substituents established a hydrophobic environment necessary to bind the thiolate anions on the coenzymes. Additionally, the cationic polyelectrolyte poly(1-butyl-3-vinylimidazolium chloride) strongly bound proteins including lysozyme, and anion exchange tuned the polymer morphology and thermal properties; however, enzymatic studies were not performed [130].

Fig. 9.13 Stability and recyclability of a cross-linked, quaternized imidazolium homopolymer catalyst for cyclic carbonate synthesis (Reprinted with permission from Ref. [133])

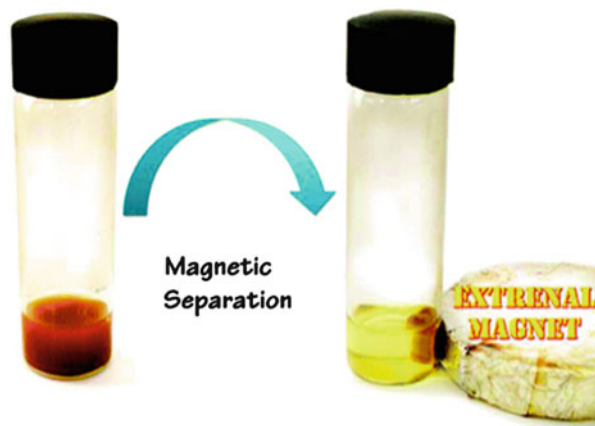


Salamone et al. fully quaternized poly(1VIM) with methyl and hexadecyl substituents to study the effect of the polymer side chains on the alkaline hydrolysis of PNPA and *p*-nitrophenyllaurate (PNPL) [131]. The quaternization failed to influence the hydrolysis of PNPA; however, the hexadecyl-functionalized polymer exhibited an enhanced rate of hydrolysis due to the increased hydrophobicity of the polyelectrolyte. Brembilla confirmed poly(3-alkyl-1-vinylimidazolium)s formed hydrophobic microdomains in aqueous solution with fluorescent probes and viscosity measurements [132]. A highly cross-linked, quaternized imidazolium homopolymer facilitated the one-step synthesis of cyclic carbonates through the catalysis of the coupling of CO₂ with epoxides [133]. As shown in Fig. 9.13, the catalyst retained 100 % selectivity over a period of five cycles but lost approximately 20 % of its activity over the same period.

Additionally, Pourjavadi et al. coated magnetic nanoparticles with a quaternized vinylimidazolium homopolymer which created a recoverable and recyclable heterogeneous catalyst for organic synthesis as shown in Fig. 9.14 [134].

Poly(1VIM) and poly(4-vinylpyridine) effectively catalyzed the ester hydrolysis of nitrophenyl esters containing an anionic charge including 4-acetoxy-3-nitrobenzenesulfonate, but the polymers failed to complex with structurally similar, neutral substrates suggesting an electrostatic interaction between substrate and catalyst [135]. Poly(1VIM) promoted the ester hydrolysis of acrylic acid-2,4-dinitrophenyl *p*-vinylbenzoate copolymeric substrates through the electrostatic complex of the carboxylate anion to the protonated imidazole ring [136]. Neither imidazole nor methylimidazole exhibited similar reactivity toward the polymeric substrate. Additionally, structurally similar substrates (e.g., 2,4-dinitrophenyl *p*-isopropylbenzoate) failed to complex with poly(1VIM) due to the lack of electrostatic interactions demonstrating the importance of electrostatic charge in nucleophilic catalysis in synthetic macromolecular systems. Letsinger et al. also found poly(1VIM) catalyzed the hydrolysis of the nitrophenyl ester derivative of poly(uridylic acid) due to the anionic charges present in the sugar-phosphate backbone [137]. Interestingly, poly(L-histidine) catalyzed the hydrolysis more rapidly than poly(1VIM).

Fig. 9.14 Separation of heterogeneous nanoparticles catalysts from reaction solution through application of an external magnet (Reprinted with permission from Ref. [134])



Khokhlov and coworkers approached the design of synthetic enzymes with inspiration from computer-aided biomimetic design of functional copolymers [138]. They realized two important parameters that were not discussed previously: proteins are globular and soluble in aqueous medium. To mimic these attributes a synthetic polymer requires a hydrophobic core with a hydrophilic shell. *N*-vinylcaprolactam copolymerized with 1VIM in a 10 % aqueous DMSO solution which produced a copolymer that behaved similar to a protein in aqueous media. The copolymers which contained 10–15 mol % 1VIM when heated to 70 °C did not precipitate and at 35 °C underwent a conformation transition from a coil to globule. These copolymers along with poly(NIPAM-*co*-1VIM) exhibited a coil-to-globule transition upon heating in water or water–isopropanol solutions due to the LCST behavior of the hydrophobic monomers. The transition to a globule resulted in enhanced catalytic activity attributed to the existence of numerous hydrophobic polymer/solvent interfaces for the binding of PNPA as shown in Fig. 9.15 [139].

The hydrophilic 1VIM appeared in a high concentration at the water/polymer interface; therefore, a high concentration of the active species (catalyst and substrate) was localized in close proximity to each other enabling a faster rate of catalysis compared to poly(1VIM). At high temperatures, however, the polymers rate of catalysis decreased due to the formation of an unstable globule attributed to the random structure of the copolymer.

To overcome this problem, Liu et al. successfully synthesized NIPAM-1VIM block copolymers with xanthate RAFT agents [140]. These were the first 1VIM block copolymers synthesized to catalyze esterolytic reactions. The block copolymers behaved similarly to the random copolymers (Fig. 9.16) and exhibited enhanced catalytic activity above the LCST of NIPAM.

The blocky nature of the copolymers maintained micellization to high temperatures (>45 °C) unlike the random copolymers. Yuan et al. utilized a similar copolymer system, poly(NIPAM-*co*-1-ethyl-3-vinylimidazolium bromide (EVIM-Br)), to stabilize multi-walled carbon nanotubes in aqueous solution through temperature and ionic strength [141].

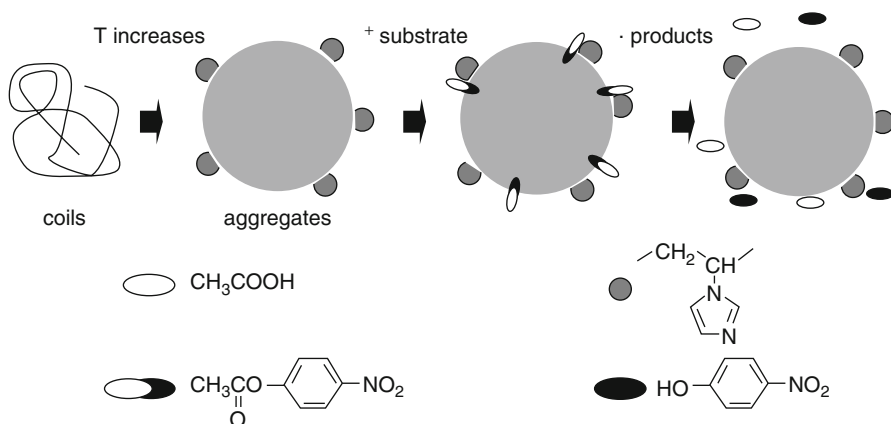


Fig. 9.15 Diagram demonstrating poly(NIPAM-co-1VIM) coil-to-globule transition with subsequent hydrolysis of PNPA at the aggregate surface (Reprinted with permission from Ref. [139])

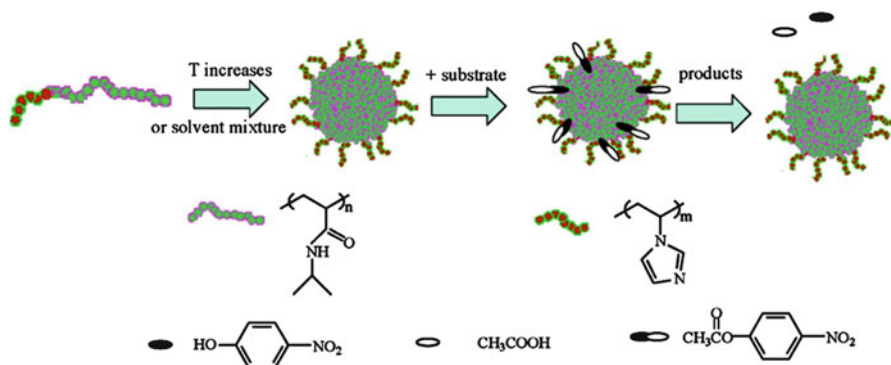


Fig. 9.16 Illustration of NIPAM-1VIM block copolymer nanoreactors for the hydrolysis of PNPA (Reprinted with permission from Ref. [140])

Biological Applications of 1-Vinylimidazole-Containing Macromolecules

Polymer nanoparticles which self-assemble into various compartments enable the design of advanced drug delivery vehicles. Yuan and coworkers have focused extensively on the self-assembly of vinylimidazolium homopolymers into highly ordered nanoparticles [142]. The dispersion polymerization of 3-dodecyl-1-vinylimidazolium bromide and the corresponding C14–18 derivatives afforded colloidally stable polymer nanoparticles (20–40 nm in diameter) in water with concentric multi- and unilamellar inner structures as shown in Fig. 9.17 [143].

The dispersion polymerization did not require the addition of a dispersing agent or stabilizers due to the monomer and oligomers behaving as effective

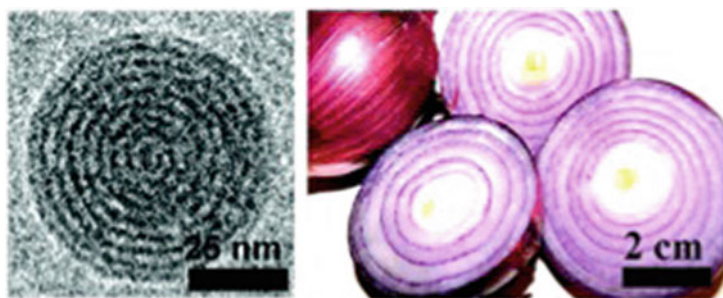


Fig. 9.17 Cryo-TEM image of polymerized ionic liquid nanoparticles in aqueous solution (Reprinted with permission from Ref. [143])

stabilizers [144]. The C12 and larger substituents monomers formed smectic A mesophases [145]. Varying alkyl chain length and counter ion size ($\text{Br}^- < \text{I}^- < \text{BF}_4^- < \text{PF}_6^-$) enabled tuning of the phase transition temperature. A zwitterionic monomer, sulfobetaine 1-vinylimidazole (SBVIM), underwent free radical homopolymerization with the addition of a cross-linker to form a nonfouling hydrogel [146]. The hydrogels resisted protein adsorption similarly to a zwitterionic methacrylate monomer and advantageously showed improved tensile and compressive mechanical properties for potential tissue engineering scaffolds.

Midoux and coworkers recently published a review on nucleic acid delivery vehicles containing histidine [5]. Polymers containing the amino acid histidine or imidazole commonly improve nonviral gene delivery compared to unmodified macromolecules due to imidazole's buffering capacity ($\text{pK}_a \sim 6$) near endosomal pH. Midoux and coworkers functionalized poly(L-lysine) with histidine residues and found a 3–4 order of magnitude increase in transfection efficiency compared to the unfunctionalized homopolymer [147].

Asayama and coworkers have explored numerous derivatives of poly(1VIM) for nonviral DNA delivery. Unfunctionalized poly(1VIM) does not complex DNA in aqueous solutions at physiological pH, therefore requiring quaternization to impart a permanent positive charge. Initially, lactosylated poly(L-lysine) (PLL) grafted onto poly(1VIM) produced a comb-like copolymer which bound DNA effectively, but these systems were not delivered to cells [148]. As discussed previously, poly(1VIM) complexed with Zn^{2+} ions and PLL delivered DNA more effectively than PEI to HepG2 cells [78]. Additionally, Asayama and coworkers functionalized poly(1VIM) with amine and alkyl groups for nucleic acid delivery [149, 150]. Amine functionalization produced a minimal effect on gene transfection due to 2.5 mol % quaternization on poly(1VIM). Oligomerization of bromoethylamine hydrobromide prevented higher functionalization percentages on the homopolymer. Functionalization with alkyl groups (ethyl, butyl, octyl) generated imidazolium copolymers containing a maximum of 50 % cationic charge. The butyl-functionalized imidazolium copolymers displayed the highest luciferase expression in HepG2 cells as shown in Fig. 9.18. The copolymers remained nontoxic due to the low amount of charge density in these systems.

Fig. 9.18 Luciferase expression of HepG2 as a function of various nonviral gene delivery vectors (Reprinted with permission from Ref. [149])

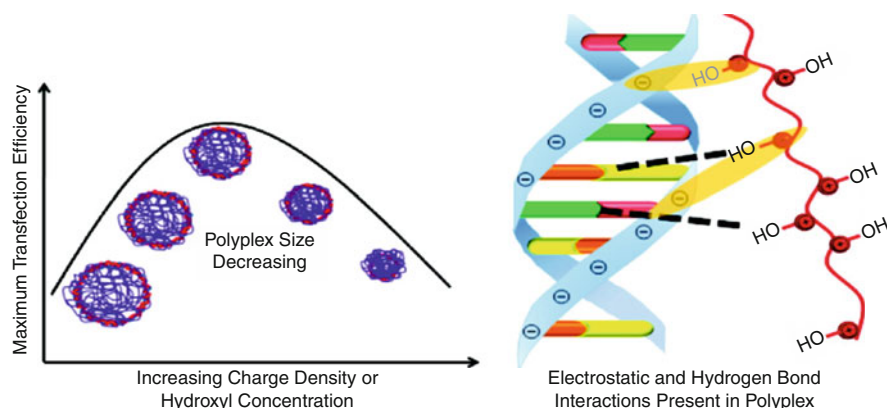
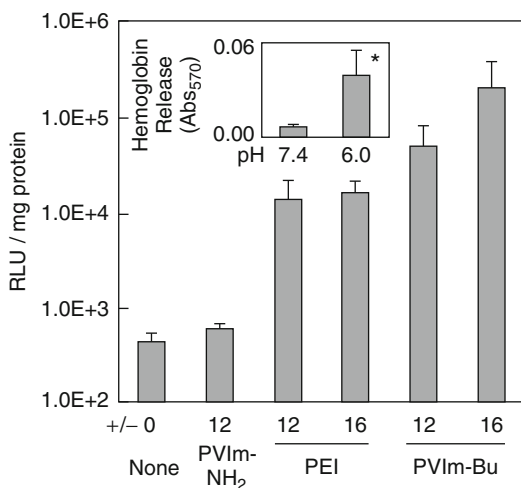


Fig. 9.19 Diagram depicting the importance of controlling polymer-DNA binding affinity for optimized DNA delivery through electrostatic or hydrogen-bonding interactions (Reprinted with permission from Ref. [18])

Long et al. later functionalized poly(1VIM) with hydrogen-bonding substituents to investigate the effects of charge density and hydrogen bonding on nucleic acid delivery [18]. As charge density and hydrogen bonding increased, the polymer-DNA binding affinity increased. However, increased charge density increased copolymer cytotoxicity, whereas copolymers containing increased hydrogen bonding remained nontoxic. Copolymers which displayed an intermediate polymer-DNA binding affinity through controlling charge density and hydrogen bonding exhibited the highest transfection efficiencies as shown in Fig. 9.19.

Controlled Radical Polymerization

N-vinyl monomers including 1VIM form an unstable propagating radical during polymerization. The lack of resonance stabilization produces an increased likelihood of chain transfer and chain termination events, limiting polymer molecular weight. The controlled radical polymerization of these monomers is often difficult due to the decreased stability of the propagating radical. Numerous *N*-vinyl monomers including *N*-vinylcarbazole, *N*-vinylindole, *N*-vinylpyrrolidone, and *N*-vinylphthalimide were polymerized in a controlled fashion with various controlled radical polymerization processes [9]. Bamford et al. studied the conventional free radical polymerization of 1VIM in the early 1980s and determined a degradative addition reaction between monomers and the propagating polymer radical occurred [151]. The propagating polymer chain added to the 2-position on the 1VIM monomer forming a resonance stabilized radical on the 3-position. When the 2-position contained a methyl group (2-methyl-1-vinylimidazole), the degradative addition was significantly reduced. They also determined polymerization of 1VIM in an acidic aqueous solution, protonated the monomer, and increased the polymer molecular weight due to resonance stabilization of the cationic charge. Dambatta and Ebdon further confirmed these observations and determined 1VIM polymerizations initiated with benzoyl peroxide (BPO) induced decomposition of the initiator [152].

The difficulties mentioned above have resulted in limited success to control the polymerization of 1VIM and its quaternized analogues. Nakamura et al. synthesized 1VIM homopolymers in a controlled fashion (PDIs < 1.2) utilizing UV irradiation and a tellurium-based chain transfer agent [153]. Endo et al. employed MADIX (macromolecular design via interchange of xanthate) polymerization, a more common polymerization strategy previously applied to various *N*-vinyl monomers [154]. This class of reversible addition-fragmentation chain transfer (RAFT) polymerizations used active xanthate chain transfer agents (CTAs) to attempt to control the polymerization of three quaternized 1VIM monomers. The molecular weights varied significantly from theoretical values; however, kinetics studies and subsequent chain extension/blocking experiments to synthesize block copolymers confirmed controlled behavior. These monomers also successfully produced diblock copolymers when reacted with a poly(NIPAM) macroCTA. Yuan et al. employed this synthetic strategy to produce poly(NIPAM) and poly(*N,N*-dimethylacrylamide) macroCTAs which were subsequently copolymerized with vinylimidazolium monomers [155]. These dually responsive diblock copolymers to temperature and ionic strength were employed as carbon precursors for the generation of graphitic nanostructures.

Recently, cobalt-mediated polymerization controlled the homopolymerization of 3-ethyl-1-vinylimidazolium bromide with controlled molecular weight growth and narrow PDIs in methanol [156]. The metal-mediated polymerizations (i.e., ATRP) of uncharged 1VIM proved unsuccessful due to the coordination of 1VIM to the metal catalyst. Jiang et al. attempted ATRP of a zwitterionic sulfonated vinylimidazolium monomer but failed to characterize the resulting polymer [146]. Previously, our group attempted the control of 1VIM utilizing

nitroxide-mediated polymerization (NMP); however, size exclusion chromatography and blocking experiments indicated a lack of control [9]. These few reports on the controlled radical polymerization of 1VIM and its quaternized analogues indicated difficulties which continue to impede the progress of designing 1VIM-containing block copolymers. A more radically stable monomer is required to overcome these obstacles to generate polymers that contain imidazole connected directly to the polymer backbone. As shown previously in Figure 3.2, 4VIM and 2VIM present potential solutions to this issue.

Macromolecules Containing 4-Vinylimidazole

Overberger and coworkers first synthesized 4VIM, a crystalline solid with a melting point of 86–88 °C, from histidine but later developed a more direct synthesis involving a one-step decarboxylation of urocanic acid [62]. Others investigated different routes to synthesize 4VIM in gram scale quantities with few synthetic steps; however, the reactions proved unsuccessful or more complex than a one-step decarboxylation reaction [157, 158]. Overberger et al. performed heterogeneous homopolymerizations in benzene and copolymerized 4VIM with a variety of comonomers including vinyl acetate, methyl acrylate, and acrylic acid.

One of the main research thrusts involving the polymerization of 4VIM was for the design of synthetic enzymes. As discussed previously, the histidine residue is widely found in the active site of numerous natural enzymes. The development of synthetic enzyme mimics remains important industrially and academically. Natural enzymes for industrial applications denature easily in harsh conditions and are impractical due to the high costs associated with these systems. A synthetic replacement would reduce cost, provide increased stability, and allow for catalyst reusability. Overberger and coworkers synthesized a variety of 4VIM copolymers to investigate the esterolytic activity of these systems [159–165]. Various properties studied included the effect of copolymer functional groups [160], charge density [163], and alkyl groups attached to 4VIM repeat units on the rate of catalysis [165–168]. Trityl protection on the 1-position failed to produce poly(4VIM) with different stereochemistries to investigate the effect of tacticity on catalysis [169]. The amphoteric nature of poly(4VIM) resulted in a more active catalysis of PNPA hydrolysis compared to poly(1VIM). Kunitake et al. prepared a bifunctional catalyst through free radical copolymerization of 4VIM with *N*-methyl-*N*-hydroxyacrylamide to hydrolyze PNPA similar to serine proteases [170]. The copolymerization of 4VIM with itaconic acid and a cross-linking agent produced microspheres for the catalysis of transesterification reactions [171]. Song et al. copolymerized 4VIM with acrylamide to investigate the interaction of polymer chains containing reactive substituents with catalytic polymers. The 4VIM copolymers failed to catalyze the hydrolysis of poly(acrylamide-*co-p*-nitrophenyl acrylate) which was attributed to steric hindrance preventing the groups from interacting [172]. Placement of the imidazole ring further from the polymer backbone successfully promoted hydrolysis of the *p*-nitrophenyl acrylate repeat unit.

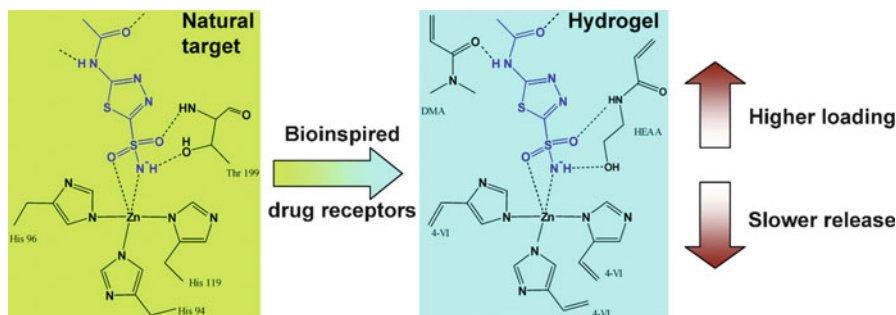


Fig. 9.20 Bioinspired design of hydrogels for ocular drug delivery (Reprinted with permission from Ref. [174])

4VIM resembles imidazole compounds which occur in biology (i.e., histidine, histamine) as both are connected to their respective functionalities at the 4-position on the imidazole ring. Alvarez-Lorenzo et al. prepared biomimetic hydroxyethyl methacrylate and *N,N*-dimethylacrylamide hydrogels to optimize ocular delivery of carbonic anhydrase inhibitor drugs [173, 174]. They incorporated 1VIM and 4VIM into the hydrogels to coordinate Zn^{2+} ions to mimic the cone-shaped cavity of carbonic anhydrase (Fig. 9.20) and found 4VIM-containing hydrogels more effectively hosted the Zn^{2+} ions and antiglaucoma drugs for the development of medicated soft contact lenses. Oner et al. utilized poly(4VIM-co-vinylphosphonic acid) copolymers to study the biomimetic mineralization of hydroxyapatite crystals on the copolymer surface [175]. The rates of hydroxyapatite crystal growth depended on the phosphate content of the copolymer.

Cho et al. explored poly(4VIM) as a nonviral delivery vehicle [176, 177]. The polymer bound DNA at a pH of 7.4 due to approximately 25 % protonation of the imidazole repeat units. Poly(4VIM) transfected HeLa cells about 50 % less effectively than PEI, but PEI exhibited greater cytotoxicity. Figure 9.21 shows the successful transfection of HeLa and MC3T3-E1 cells with both poly(4VIM) and PEI. Qualitatively, the cell morphology also suggested the high toxicity of PEI and the low toxicity of poly(4VIM).

Despite the limited amount of publications incorporating 4VIM into macromolecules compared to 1VIM, 4VIM remains a better mimic of biological imidazole-containing systems. As mentioned previously, 1VIM's propagating radical instability limited its incorporation into a variety of macromolecules with advanced architectures. Recently, we reported on the unprecedented controlled radical polymerization of 4VIM utilizing RAFT polymerization strategies [10]. The polymerizations in acetic acid displayed linear pseudo-first-order kinetics and linear molecular weight growth with monomer conversion through systematic variation of polymerization parameters as shown in Fig. 9.22.

Effectively controlling 4VIM homopolymerizations enables the future design of block copolymers for numerous emerging applications including synthetic enzymes, gene delivery vehicles, and anticorrosive agents.

Fig. 9.21 In vitro transfection of (a) HeLa and (b) MC3T3-E1 cells with poly(4VIM) and PEI with GFP. Nuclei were stained red with propidium iodide (Reprinted with permission from Ref. [176])

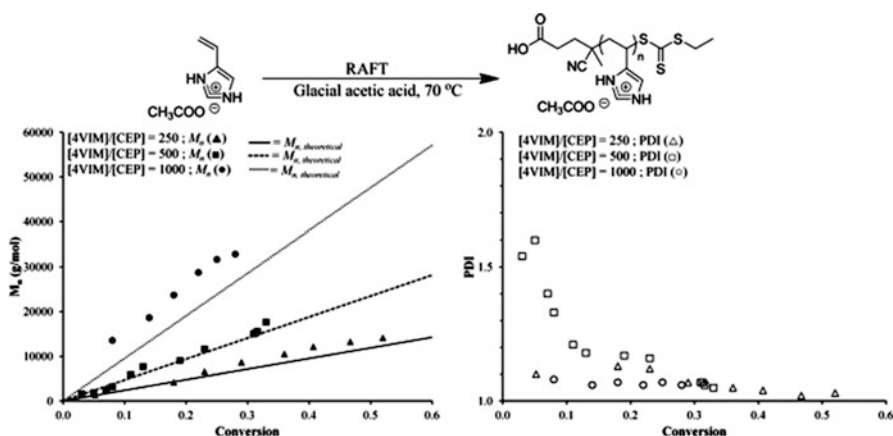
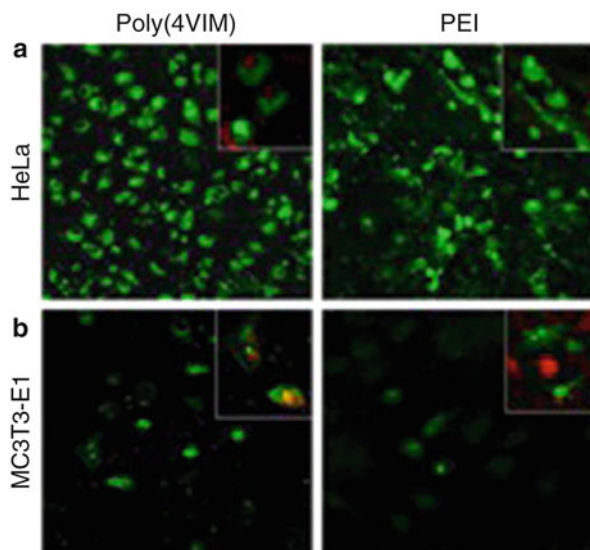


Fig. 9.22 RAFT polymerization of 4VIM in glacial acetic acid with well-defined molecular weight and narrow polydispersities (Reprinted with permission from Ref. [10])

Macromolecules Containing 2-Vinylimidazole

2VIM publications remain extremely limited due to its difficult synthesis. Although 2VIM exhibits increased radical stability compared to 4VIM and 1VIM due to its additional resonance contributors, no publications on the controlled radical

polymerization of 2VIM exist. Lawson first synthesized 2VIM (melting point = 128–129 °C) through the dehydration of 2-hydroxyethylimidazole [178]. The synthesis of 2-hydroxyethylimidazole proved complicated, and the difficult purifications limited yields (<15 %). 2VIM successfully copolymerized with acrylonitrile, styrene, and methyl methacrylate; however, the copolymer properties were not determined. Overberger et al. improved the yield of 2VIM through a dehydrohalogenation of 2-bromoethylimidazole; however, the procedure still required the complicated synthesis of 2-hydroxyethylimidazole [11]. Shimko et al. polymerized 2VIM using cobalt 60 gamma irradiation and found the hydrogen bonding of the solvent impacted the tacticity of the resulting polymer [179]. A more facile synthesis would enable the design of numerous polymers incorporating 2VIM as these three publications remain the only reports on 2VIM. The increased radical stability of 2VIM opens a variety of possibilities for the design of amphoteric macromolecules utilizing both conventional and controlled radical polymerization strategies.

Other Cations

Traditionally, polymerized ionic liquids rely primarily on phosphonium cations and nitrogen-based cations such as ammonium and imidazolium cations. Alternative cations with a broad potential for research include arsenium and sulfonium cations. Arsenium ionic liquids and polyelectrolytes are completely absent from the literature to our knowledge primarily due to the low commercial availability of suitable tertiary arsines. Triphenylarsine is the most available tertiary arsine, which unfortunately displays poor nucleophilicity in comparison to triphenylphosphine [180]. Sulfonium cations are widely important in biological systems with the most important sulfonium cation being S-adenosylmethionine [181]. S-adenosylmethionine acts as a methylating agent in a broad range of biological process such as nucleic acid methylation. Multiple reports of sulfonium ionic liquids are widespread in the literature [182–184]. Examples of sulfonium macromolecules exist in the literature with a primary focus on post-polymerization functionalization [185–187]. Endo et al. [188] examined the antimicrobial activity of a sulfonium-containing polystyrene and its monomer; they revealed improved antimicrobial activity of the sulfonium polymer compared to the sulfonium monomer. Deming et al. [189] demonstrated a wide range of sulfonium poly(L-methionine)s utilizing different alkyl halides and alkylation procedures to generate functional sulfonium-containing polyelectrolytes. Activated halides such as methyl iodide or other strategies were necessary to achieve high alkylation efficiencies. Long et al. [190] utilized similar procedures to Deming and coworkers to alkylate poly(2-methylthioethyl methacrylate) with methyl iodide to generate poly(2-dimethylsulfoniummethyl methacrylate). For the first time, sulfonium macromolecules bound nucleic acids effectively and delivered nucleic acids to HeLa cells more effectively than cells and DNA-only negative controls [190].

Conclusions

Ammonium and phosphonium polyelectrolytes display a broad range of properties suitable for many biological applications including antimicrobials and nonviral nucleic acid delivery. Atomic radii and electronegativities dramatically alter the cation structure when the cationic atom is nitrogen or phosphorus. Monomer synthesis and post-polymerization functionalization are the two primary methods to generate ammonium and phosphonium polyelectrolytes. Phosphonium polyelectrolytes displayed enhanced thermal stability due to their resistance to Hoffman elimination. Cationic macromolecules exhibit significant antimicrobial activity, and researchers found phosphonium macromolecules generally displayed higher antimicrobial efficiency. Ammonium and phosphonium macromolecules also effectively bound and delivered nucleic acids to cells; phosphonium polyelectrolytes displayed enhanced nucleic acid binding and delivery efficiency compared to ammonium analogues.

The intense focus on the ubiquitous imidazole ring has propelled imidazole-containing polymers to the forefront of materials design. Researchers widely utilize the monomers, 1-, 2-, and 4-vinylimidazole regioisomers, and free radical polymerization of these monomers allows for the development of novel polymer architectures. Polymers based on 1VIM are utilized in a wide variety of applications including metal chelation, catalysis, and nonviral gene delivery. The commercial availability of 1VIM has spurred copolymerizations with numerous comonomers and novel derivatives of 1VIM through its facile functionalization which affords the tailoring of polymer properties for numerous technologies. The propagating radical stability of 1VIM limits the generation of novel architectures with controlled radical polymerization strategies. 4VIM, a better synthetic mimic to biological molecules containing imidazole rings, exhibits an increased radical stability enabling controlled radical polymerization. Although a lack of commercial production limits the use of 2VIM and 4VIM, the recent success utilizing RAFT polymerization strategies to produce well-defined polymers facilitates the future generation of novel polymer architectures for emerging applications.

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Abstract

Taking into account the extremely broad range of chemical and structural possibilities of ionic liquid (IL) chemistry, and the undeniable economical and engineering advantages of membrane technology, the CO₂ separation performance of membranes based on poly(ionic liquid)s (PILs) is here discussed. A perspective of the different membrane-designing strategies, including neat PIL membranes having polycation backbones, PIL/IL composites, different frameworks of PIL copolymer membranes, and PIL/IL/zeolite mixed matrix membranes, will be presented. Due to the promising data obtained for this new

L.C. Tomé • I.M. Marrucho (✉)

Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Oeiras, Portugal

e-mail: liliana.tome@itqb.unl.pt; imarrucho@itqb.unl.pt

class of functional polymers, combining some of the exceptional and unique properties of ILs with the macromolecular architecture of polymers, it is foreseen that PIL-based membranes will play a especial role in CO₂ separation.

Keywords

Polymeric ionic liquids • Membranes • CO₂ separation performance • Permeability • Permselectivity

Motivation

Climate change and renewable energy are two of the most important societal challenges that our world faces today [1]. The search for new environmentally acceptable solutions is being urged by governments through the implementation of stricter legislation and the development of new collaborative research programs. In the field of energy, natural gas stands today as an essential bridge to a clean, low-carbon, renewable energy era. In order to maintain and expand the availability of this clean burning and efficient fuel source, natural gas processing regulations require the removal of contaminants such as hydrogen sulfide (H₂S) and carbon dioxide (CO₂), since they not only reduce the heating value of the methane (CH₄) gas streams in power plants, but also cause corrosion in pipes and equipment [2]. On the other hand, the increasing atmospheric concentrations of greenhouse gases, specifically CO₂, are of particular concern due to the resulting environmental risks which are largely associated to unpredictable climate changes. Billions of tons of annual CO₂ emissions are currently a direct sub-product of fossil fuel combustion for the generation of energy and heat [3].

As the transition to more sustainable energy processes progresses, there is a great interest in the development of highly efficient technologies to curb CO₂ emissions of current energy sources. The CO₂ capture from large point sources is a viable strategy that provides a short- to medium-term solution until renewable energy technologies mature [4]. Carbon capture and storage schemes comprise a group of technologies for CO₂ capture, followed by compression, transport, and permanent storage [5]. Since the CO₂ separation is the first and the most energy-intensive step, new cost-effective and high-performance technologies for carbon capture need to be researched. In this context, the design of materials with the ability to efficiently separate CO₂ from other gases is of vital importance.

Contextualization

Different industrial processes emit CO₂ streams with distinct compositions, and consequently the development of processes for CO₂ removal from light gases (e.g., CH₄, N₂, and H₂) is a key technical, economical, and environmental challenge in applications such as natural gas sweetening (CO₂/CH₄), carbon dioxide recovery from power plant flue streams (predominantly CO₂/N₂), and hydrogen

production (CO₂/H₂). The most relevant technologies currently used for CO₂ removal from natural gas and power plant flue gas include solvent-based chemical absorption, physical solvent absorption, pressure swing adsorption, and membrane and cryogenic distillation [6–11], where amine-based absorption is undoubtedly the most efficient technology [12]. Despite their advantages, such as high reactivity and good absorption capacity, the use of amines is of environmental and economical concern due to their corrosive nature, volatility, and high energy demand for regeneration [3, 7, 10]. Thus, research targeted at developing new approaches has been undertaken and currently the goal is to design attractive sorbent materials with high CO₂ capacity for energy-saving CO₂ separation processes.

A quite recent approach to CO₂ removal from gas streams makes use of ILs, a class of materials widely promoted as “design” solvents. Ionic liquids are low-melting-point salts and, apart from their broad definition as compounds with an exceptional combination of properties such as negligible volatility [13], thermal stability [14], low flammability [15], and high ion conductivity [16], their tunability makes them absolutely unique and incomparable to other solvents. While ILs have been attracting much interest as new solvents in chemical synthesis and catalysis [17, 18], the development of novel functional materials for distinct applications [19–23], including gas separation processes, particularly in CO₂ separation applications [24–28], has also been playing a crucial role in the wide dissemination of ILs. It is important to emphasize here that perhaps the most important features of ILs within the CO₂ separation context are their remarkable CO₂ solubility and selectivity over other light gases (N₂, CH₄, H₂, and O₂), the ability to tailor many of their physical and chemical properties, as well as their CO₂ affinity by combining different cations and anions or by adding functional groups.

A great deal of effort has been put on the experimental determination and theoretical understanding of gas solubilities in ILs [28–31]. For example, Brennecke and co-authors carefully studied the CO₂ solubility in several commonly used ILs and concluded that the anion of the IL has a larger influence on CO₂ solubility than the cation [32–35]. The influence of different functional groups, such as alkyl, ether, hydroxyl, amine, nitrile, and fluorine, on the gas solubility properties of ILs has also been intensively investigated by different authors [36–41]. Indeed, a quick search in the open literature on the subject of CO₂ solubility in ILs clearly shows the chemical diversity of ILs researched up to now. From amine-inspired reactive ILs to aprotic heterocyclic anion ILs [42], the most recent studies focus on task-specific ILs by using basic anions, such as acetate [43, 44], amino acids [45, 46], imidazolate, or pyrrolide [47].

Supported ionic liquid membranes (SILMs), where the desired IL is immobilized into the pores of a solid membrane by capillary forces, are a very attractive approach compared to bulk-fluid ILs, since much smaller amounts of IL are needed [48]. Moreover, the inherent simplicity of membranes can bring many advantages compared to other conventional separation technologies, namely the small scale of the equipment, reduced environmental impact, ease of incorporation into existing processes, low energy consumption, and operating costs [49].

A broad diversity of ILs has already been used to develop SILM for CO₂ separation. Several studies on gas permeation properties through SILMs have investigated the effect of the IL chemical structure, covering diverse cations, such as imidazolium [50–65], pyrrolidinium [64], phosphonium [66, 67], sulfonium [67], pyridinium [68, 69], ammonium [69–71], or thiazolium [72, 73], combined with halogens, fluorinated anions, sulfonates, carboxylates, and nitrile-containing anions. In order to tune the CO₂ selectivity of SILMs, other studies have explored different structural variations of the imidazolium cation [39, 74, 75]. It is worthy to note that SILMs have good CO₂ separation performances, with permeabilities/selectivities that are consistently close or above the “Robeson 2008 upper bound” [76]. Nevertheless, the application of such membranes in industry is limited due to their inadequate long-term stability since they are susceptible to failure if the pressure differential across the membrane is high enough to push out the IL phase from the pores of the membrane support [48]. Actually, SILM stability is still an open issue as different behaviors have been found depending on the nature of both the IL and the membrane support, as well as on the pore size [77]. In order to overcome the limitation inherent to SILMs, research has been carried out on the fabrication of CO₂ separation membranes using ILs through three different approaches, namely, (i) polymer/IL composite membranes, (ii) gelled IL membranes, and (iii) polymerized IL-based membranes.

The first approach has explored the blending of ILs with polymers to make homogeneous composite membranes [78–84]. Although these composite materials have shown enhanced mechanical strength and favorable gas transport properties, a limiting working pressure difference across the membrane was also observed. Given that the IL is entrapped in the tight spaces between the polymer chains, there is no chemical bonds tethering the IL to the polymer, and consequently high-pressure differentials compress the membrane and can cast out the IL. The second approach to design membranes making use of ILs is the formation of gelled structures using either low-molecular-weight gelators or compatible macromolecules [85–89]. Gelled IL membranes have improved mechanical properties and exhibited higher burst pressures compared to SILMs, while the solubility characteristics remain very similar to those of ILs. Gelation is a suitable method for preparing pseudo-solid membranes with gas transport properties close to pure ILs and polymer-like mechanical stability. However, the CO₂ permeance of the gelled IL membranes prepared so far is limited by their thickness, and thus the use of a support reduces their CO₂ separation efficiency. Alternatively and considering that ILs present a unique platform for monomer design, where functional groups can be easily introduced for a specific application, the third and most promising way to take advantage of ILs for CO₂ separation and simultaneously overcome the inherent disadvantages of the previous two approaches is to polymerize IL monomers and prepare solid thin polymer membranes [90].

In the past few years, there has been growing interest in the polymeric form of ionic liquids since this new class of functional polymers combines some of the exceptional and unique properties of ILs with the macromolecular architecture of polymers. It is generally accepted that poly(ionic liquid)s (PILs) are a subclass of polyelectrolytes that comprise IL species connected through a polymeric backbone to form a macromolecular architecture. The field of PILs has recently been object of

several valuable reviews [91–95] describing different aspects of the synthetic strategies used to prepare these polymers, their chemical structures, physical properties, as well as their application as new polymeric materials in many technological fields such as in catalyses, energy, and environment, among others.

Although pioneering studies anticipated the use of PILs as advanced polymer electrolytes [96–99], a number of studies have been carried out to investigate CO₂ sorption in PILs [100–110]. In 2005, Radosz and coworkers first reported the study of CO₂ absorption by imidazolium-based PILs combining tetrafluoroborate (BF₄) or hexafluorophosphate (PF₆) anions and showed that those materials exhibit even higher CO₂ absorption capacity and faster absorption/desorption rates than the corresponding ILs [100, 101]. Later, the same group demonstrated that ammonium-based PILs have higher CO₂ sorption capacity than the imidazolium-based ones [102]. It has also observed that the CO₂ sorption properties of pyrrolidinium-based PILs are significantly affected by the nature of the counter-anion [107]. Furthermore, Noble's group established the potential of PILs as promising materials for membrane-based CO₂ separations with CO₂/CH₄ and CO₂/N₂ permeability selectivities on par or greater than those observed for conventional SILMs [111–114]. Even though PILs afford solid stable membranes, their major drawback is the substantial drop in both gas permeability and diffusivity when compared to those of their IL analogues in SILMs. To this end, different strategies have been investigated for designing robust PIL-based membranes with improved CO₂ separation performances.

This chapter covers the advances on the design of several PIL-based membranes for CO₂ separation, in particular for flue gas separation (CO₂/N₂) and natural gas purification (CO₂/CH₄). These separations are greatly important for energy production and climate change concerns, as evidenced by the numerous studies available in the literature. Initially, a brief overview of the general fundamentals on membrane gas separation is provided. Then, we focus on the evolution of gas permeation properties, as well as CO₂ separation performances obtained during the progressive development of PILs as new alternative materials for CO₂ separation membranes. Four different membrane arrangements are highlighted herein: (i) neat PIL membranes having different functional groups attached to their polycation backbones [111–118], (ii) the blending of free ILs with PILs to form homogeneous composite membranes [115–123], (iii) synthesis of PIL copolymers to control segmental motion and chain packing for increasing the gas permeability and mechanical stability of the membranes [124–129], and (iv) the incorporation of zeolites into PILs to form mixed matrix membranes [130–132].

Membrane Gas Separation

In the past decades, membrane technology has been attracting rising interest owing their advantages over conventional separation processes such as reduced environmental impact, lower energy consumption, and operating costs [133]. The fast progress in this field enabled the current use of membrane-based systems on an

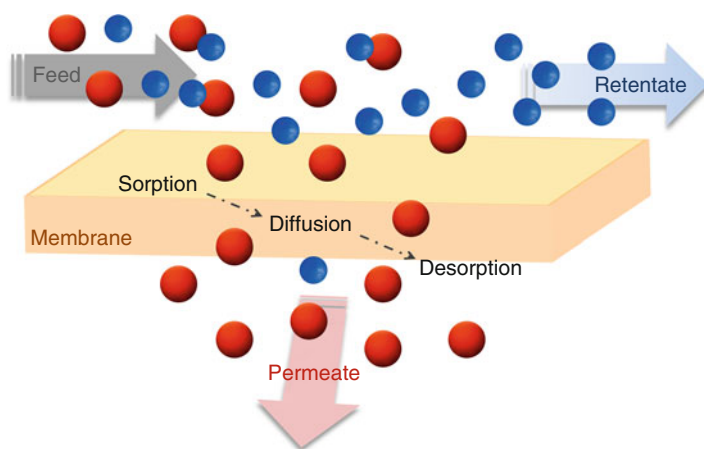


Fig. 10.1 Gas transport mechanism through dense polymer membranes

industrial scale for different gas separations [49]. In particular, great effort is being put in the development of CO_2 permeable and selective membrane materials for application in natural gas sweetening (CO_2/CH_4) and CO_2 separation from post-combustion flue gases (CO_2/N_2), as these processes can improve the efficiency of natural gas and reduce anthropogenic CO_2 emissions, respectively [134–136]. Nevertheless, to fully compete with well-established separation processes, membranes with high gas permeability and selectivity to specific gases, good thermal/chemical resistance, and sufficient mechanical stability for withstanding the harsh environments of separation processes, need to be developed [49]. Three types of membranes, polymeric membranes [137], inorganic membranes [138], and inorganic–organic composite membranes [139], have been researched to meet these criteria. Even though polymer membranes have achieved important success because they possess advantages of mechanical properties, reproducibility, and relative economical processing capability [137], large improvements in CO_2 separation efficiency require novel materials with enhanced separation performances. As a highly versatile and tunable platform for designing a broad range of different polymer chemical structures, poly(ionic liquid)s present an enormous potential as alternative materials to improve existing membrane-based CO_2 separation processes. The progress and scientific results obtained for membranes based on this novel class of polymeric materials are highlighted in this chapter.

The principal property of membranes used in gas separation applications is their ability to control the permeation of different species. In gas separation processes through nonporous or dense membranes, the feed gas mixture is driven by a difference in concentration or pressure across the membrane, which works as a semi-permeable barrier that restricts the movement of some gas molecules while letting other pass through, as it is depicted in Fig. 10.1. The equations and

terminology presented below illustrate the general principles and basic concepts used to describe gas transport, as well as to evaluate the membrane material performance.

Permeability, Diffusivity, and Solubility

It is generally accepted that gas transport through a dense polymeric film or membrane occurs according to the solution–diffusion mass transfer mechanism, where the permeability coefficient or permeability (P), a measure of the membrane's ability to permeate gas, is the product of the diffusion coefficient or diffusivity (D) and the solubility coefficient or solubility (S) as follows [140]:

$$P = D \times S \quad (10.1)$$

As it is schematically represented in Fig. 10.1, the solution–diffusion mechanism is described by three steps: (1) gas absorption or adsorption on the upstream side of the membrane, (2) diffusion of the absorbed species through the membrane driven by the concentration gradient (partial pressure difference), and (3) gas desorption on the downstream side of the membrane [140]. Consequently, permeability depends on both thermodynamic factors, such as condensability of the gas specie and its interaction with the membrane, and kinetic factors that are mainly governed by the size of the permeant species, membrane material segmental mobility and packaging, fractional free volume or other structural features that permit permeant diffusion.

Permeability (P) is defined as the steady-state gas flux (J) through a membrane under a transmembrane pressure drop ($p_2 - p_1$) and normalized to the unit thickness of the membrane [141]:

$$P = J \frac{\ell}{\Delta p} \quad (10.2)$$

where p_2 is the upstream pressure, p_1 is the downstream pressure, and ℓ is the membrane thickness. Gas permeability is often expressed in Barrer [142]:

$$1 \text{ Barrer} = \frac{10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm}}{\text{cm}^2 \text{ s cmHg}} \quad (10.3)$$

Diffusivity is an indication of the gas mobility through the membrane material and is usually expressed in cm²/s. Solubility (cm³(STP)cm⁻³cmHg⁻¹) is a thermodynamic parameter, which reflects the number of gas molecules dissolved in the membrane when equilibrated at a given gas pressure and temperature [142]. While solubility depends mainly on gas molecule condensability (as characterized, for example, by gas critical temperature, normal boiling point,

enthalpy of vaporization, etc.), the gas-material interactions and membrane morphological features, such as crystallinity, can also influence gas solubility.

Selectivity

Selectivity is a widely used parameter to evaluate the feasibility of using a membrane for a specific separation. It is defined as its ability to separate two gases. Membranes have different permeabilities for different gases, and the faster permeation of some gases relative to others provides the selectivity basis for using membranes in gas separation. The ideal permeability selectivity (or ideal separation factor), also commonly called permselectivity, $\alpha_{A/B}$, is a measure of how well a membrane discerns one gas from another and, for dense polymer membranes, can be determined dividing the permeability of the more permeable specie A by the permeability of the less permeable specie B [143]. Permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity as follows:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \times \left(\frac{S_A}{S_B} \right) \quad (10.4)$$

Likewise permeability, the permselectivity is a material property of the membrane and thus independent of its thickness.

Separation Performance

The materials used to make membranes are crucial to their specific gas separation performance. Membranes for gas separation preferably have both high permeability for a specific component of the gas mixture and high permselectivity. Higher permeability decreases the membrane area needed to treat a given amount of gas, hence decreasing the capital cost of the process, while higher permselectivity leads to gas products with higher purity. Nevertheless, a trade-off relationship exists between these two parameters as polymer membranes that are more permeable are generally less selective and vice versa [144–146]. In 1991, Robeson graphically quantified this concept and showed that such trade-off relationship can be described by the existence of an upper bound in the log-log plot of permselectivity versus permeability of the more permeable gas [147]. Due to the large amount of data available since 1991, revised upper bounds for several gas pairs were published in 2008 [76]. Robeson described the correlation as:

$$P_A = k\alpha_{A/B}^n \quad (10.5)$$

where P_A is the permeability of the fast gas, $\alpha_{A/B}^n$ is the permselectivity, and n is the slope of the upper bound of the noted relationship. Below this line, virtually all the

data points exists [76]. The upper bound relationship is an empirical correlation based on large amounts of experimental results. However, a theoretical analysis performed by Freeman [143] yielded good agreement with the observed empirical results. In fact, a new concept called “upper bound” has emerged in the literature, and currently this type of plots, also known as “Robeson plots,” is widely used to evaluate the performance of membranes given a particular gas separation, illustrating the progress in membrane science for gas separation applications.

CO₂ Separation Membranes Based on Poly(ionic liquid)s

The main strategies proposed to increase both the CO₂ permeability and separation performance of PIL-based membranes will be here discussed. As illustrated in Fig. 10.2, different membrane arrangements have been explored, including neat PIL membranes having polycation backbones (a), PIL/IL composites (b), different frameworks of PIL copolymer membranes (c), and PIL/IL/zeolite mixed matrix membranes (d).

Neat PIL Membranes

The potential performance of PILs as gas separation membranes was initially addressed in 2006 by Camper et al. [111]. Using CO₂, CH₄, and N₂ solubility data and taking into account the solution–diffusion mass transfer mechanism, permeabilities of immobilized ILs were predicted by lowering the gas diffusion coefficients by subsequent orders of magnitude, in a trial and error manner.

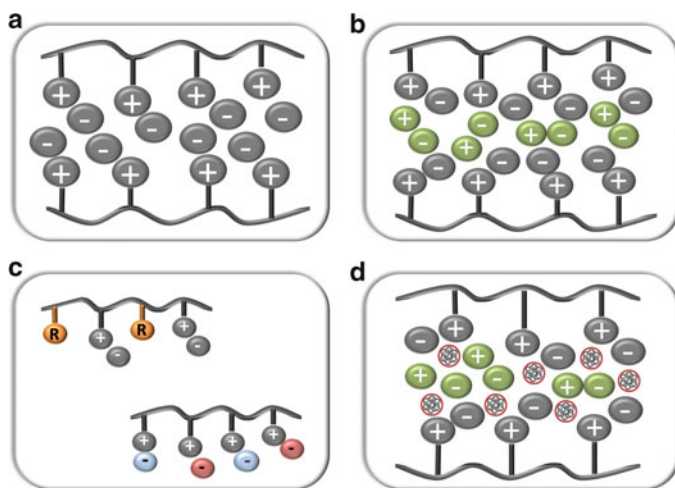


Fig. 10.2 Schematic illustration of (a) neat PIL membrane, (b) PIL/IL composite membrane, (c) PIL copolymer membranes, and (d) PIL/IL/zeolite mixed matrix membrane. Note that the free ionic liquid is illustrated in green in (b) and (c)

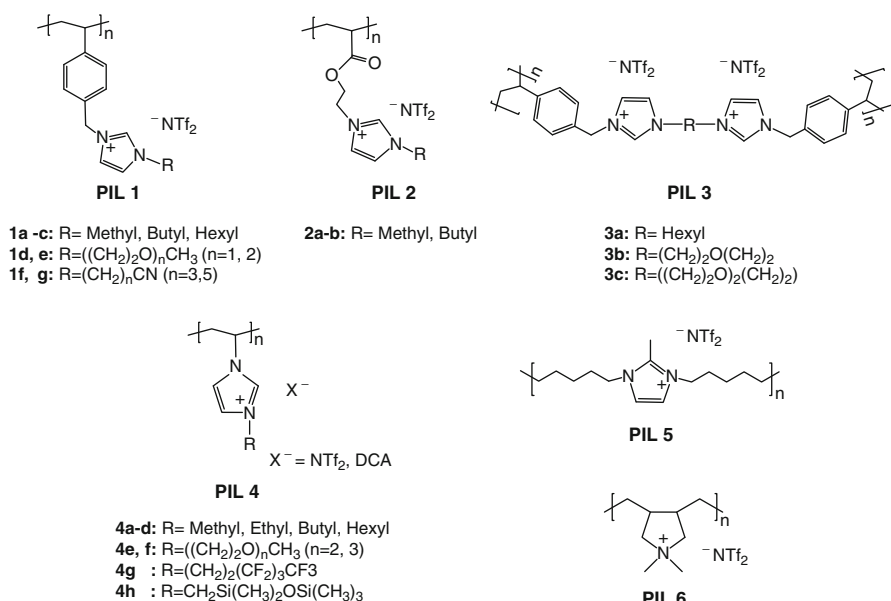


Fig. 10.3 Chemical structures of cationic poly(ionic liquid)s that have been evaluated as CO₂ separation membranes

The authors postulated that if solubility remains the same, the performance of those hypothetical stabilized IL membranes would be promising for CO₂ separations [111]. The best way to “make those membranes come true” was to use polymerizable IL monomers to prepare neat PIL membranes (Fig. 10.2a). The radical chain-addition polymerization of IL monomers combining a polymerizable group is the most commonly used route to prepare PILs, which can be easily converted into dense polymer membranes. The chemical structures of the neat PILs synthesized so far to prepare CO₂ separation membranes are shown in Fig. 10.3. Among the PILs used, all comprising cation moieties in their polymeric backbone, the most studied are the imidazolium-based PILs combined with the bis(trifluoromethylsulfonyl)imide (NTf₂) anion.

The first neat PIL membranes for CO₂ separation were presented by Noble’s group [112]. Five PILs featuring alkyl imidazolium cations tethered to a polystyrene (**PIL 1a-c**) or polyacrylate backbone (**PIL 2a,b**) were synthesized by UV polymerization using a photo-initiator and a cross-linking agent, and subsequently the CO₂, CH₄, and N₂ permeation properties of the prepared neat PIL membranes were evaluated. The chemical structure of the polymer backbone had little effect on the gas permeation properties of the membranes, whereas both the permeability of all gases and the CO₂ permselectivity were largely dependent of the alkyl chain length attached to the imidazolium polycation [112]. For instance, the CO₂ permeability increased from 9 to 32 Barrer as the alkyl group was lengthened from methyl

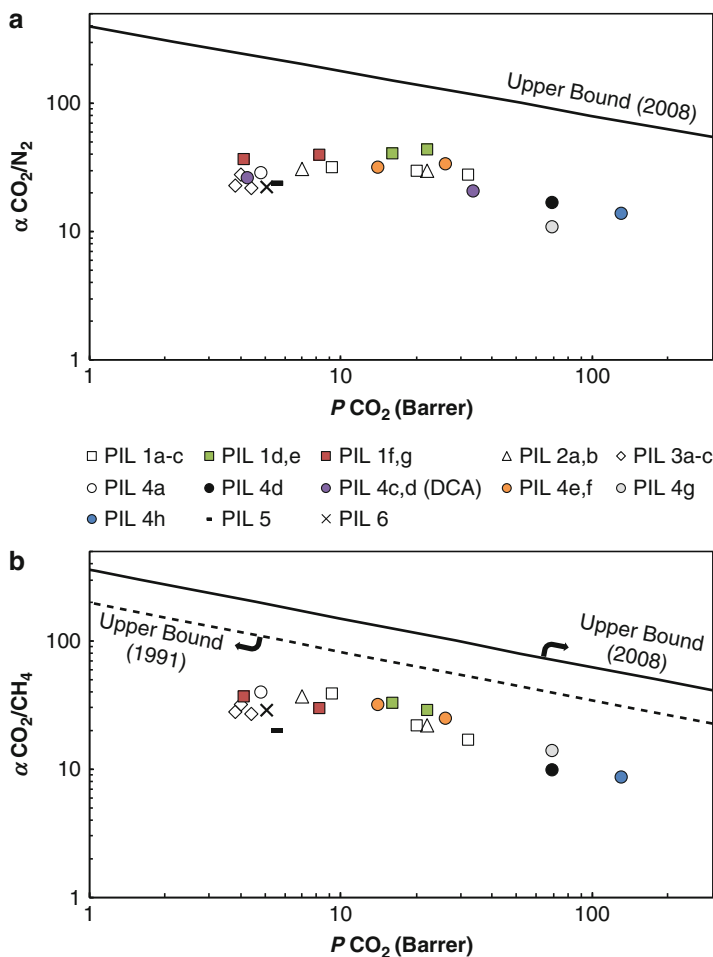


Fig. 10.4 CO₂ separation performance of the neat PIL membranes plotted on (a) CO₂/N₂ and (b) CO₂/CH₄ Robeson plots. Data from References [111–118] are plotted on a log-log scale and the *upper bounds* for each gas pair are adapted from Robeson [76, 147]

to hexyl in the styrene-based systems (**PIL 1a–c**), but their permselectivities for CO₂/N₂ decreased from 32 to 28 and for CO₂/CH₄ from 39 to 17 [112]. The CO₂ separation performances of this first generation of neat PIL membranes are shown in the form of Robeson plots in Fig. 10.4.

In order to improve the CO₂ separation performance of these membranes, Noble and coworkers proposed a second generation of functionalized imidazolium-based PILs containing polar groups, namely, oligo(ethylene glycol) (**PIL 1d,e**) or alkyl-terminated nitrile (**PIL 1f,g**) [113]. The inclusion of pendant nitrile groups decreased the CO₂ permeabilities (4–8 Barrer), while PILs combining oligo(ethylene glycol) units exhibited CO₂ permeabilities (16–22 Barrer) that were on par with

their alkyl analogues (9–32 Barrer) [113]. As it can be seen in Fig. 10.4, these functionalized PILs (**PIL 1d,e** and **PIL 1f,g**) generally have improved CO_2/N_2 (37–44) and CO_2/CH_4 (29–37) permselectivities when compared to those with alkyl chain substituents (**PIL 1a-c**) [113].

Cross-linked PIL membranes with different spacer groups (**PIL 3a-c**) were also synthesized from the corresponding multifunctional styrene IL monomers [114]. However, this approach is less successful to prepare PIL membranes due to their highly cross-linked structures. Although these membranes exhibited similar CO_2/N_2 (22–28) and CO_2/CH_4 (22–28) permselectivities, the obtained CO_2 permeabilities through the cross-linked PIL membranes were significantly lower (3.8–4.4 Barrer) [114] compared to those observed in the imidazolium-based PILs previously studied.

In addition to polystyrene and polyacrylate backbone-based PILs, several PILs featuring functionalized imidazolium cations tethered to a polyethylene backbone (**PIL 4a-h**) have also been tested. Considering that vinylimidazolium monomers are easier to synthesize than their styrene analogues, Carlisle et al. [115] evaluated the gas permeabilities and CO_2 separation performance of six vinylimidazolium-based PILs (**PIL 4a** and **PIL 4d-h**) combined with the NTf_2 anion. The results showed that the primary factor differentiating CO_2 permeability in **PIL 4a** from both **PIL 1a** and **PIL 2a** was its diffusivity, which suggests that **PIL 4a** possesses a much rigid polymer matrix [115]. PIL having disiloxane-functionalized vinylimidazolium cation (**PIL 4 h**) was found to be the most CO_2 permeable membrane (130 Barrer), although less selective ($\text{CO}_2/\text{N}_2 = 14$, $\text{CO}_2/\text{CH}_4 = 8.7$) [115]. Conversely, fluoroalkyl substituents (**PIL 4g**) contributed only to a slight increase in the CO_2/CH_4 permselectivity, without changing the CO_2 permeability (Fig. 10.4). Furthermore, Li et al. [116] synthesized three new alkyl-functionalized vinylimidazolium-based PIL using dicyanamide (DCA) as counter-anion (**PIL 4b-d**). Likewise, Bara et al. [112] previously observed for styrene and acrylate backbone-based PILs, increasing the alkyl chain substituent from ethyl to hexyl in the vinylimidazolium-based systems, increased the CO_2 permeability but reduced the CO_2/N_2 permselectivity of the membranes [116]. Even though PILs with DCA as counter-anion were less CO_2 permeable (0.09–33.5 Barrer) than their corresponding analogues with the NTf_2 anion, the authors observed that **PIL 4d** with DCA presents higher CO_2/N_2 permselectivity (21) than that of **PIL 4d** with the NTf_2 anion (17).

Main-chain cationic PILs (**PIL 5**) have also been developed by Noble's group [117]. In this case, the imidazolium functionality is located in the main polymer backbone between alkyl spacers instead of within the side groups, and consequently it endorses a different polymer architecture [117]. In Fig. 10.4, it can be observed that **PIL 5** does not significantly outperform the PIL membranes previously tested for CO_2/N_2 and CO_2/CH_4 separations. In fact, the permselectivity of **PIL 5** ($\text{CO}_2/\text{N}_2 = 24$, $\text{CO}_2/\text{CH}_4 = 20$) is in the same range of most imidazolium-based PILs with side chains, but its CO_2 permeability (5.3 Barrer) lies in the least permeable neat PIL membranes area [117].

More recently, the use of a PIL combining the pyrrolidinium cation and the NTf_2 anion (**PIL 6**) to prepare CO_2 separation membranes was proposed by us [118].

Neat **PIL6**-based membrane was prepared and it was shown that its permselectivity/permeability properties are of the same order of magnitude as those of imidazolium-based PILs, also containing NTf₂ as counter-anion. It is worthy to note that the pyrrolidinium-based PIL used was synthesized by carrying out the anion exchange directly into the commercially available poly(diallyldimethylammonium chloride) [148] and the membrane was afterwards prepared by the film-casting method. This route is clearly less complicated than that used to prepare the imidazolium-based PILs, which involve a number of organic syntheses and purification steps at the monomer level, as well as the need to control polymerization conditions.

At this stage, it is evident that functionalization of the imidazolium-PIL polycation alone cannot promote the large improvement in gas permeability required for neat PIL membranes to be technologically competitive. Nevertheless, the knowledge gained from these studies, particularly regarding structure–property relationships, was undoubtedly a necessary step for the development of improved PIL-based membranes.

PIL/IL Composite Membranes

The major factor retarding the gas transport through PIL membranes compared to SILMs, is the large decrease in both gas permeability and diffusivity through the solid polymer matrix. Actually, an ideal membrane should combine adequate CO₂ permeability and permselectivity of a SILM with the mechanical stability and robustness of a polymer. The low gas permeabilities in neat PIL membranes encouraged Noble's group to re-examine the role of ILs in CO₂ separation membranes, this time by incorporating them in PILs. This concept started as a way to achieve membranes with higher gas permeabilities while maintaining their mechanical stability. ILs within PILs are different from traditional plasticizers in conventional polymers due, not only to their negligible volatility [13], but also to their ability to strongly interact with the charged backbone of the PIL through electrostatic interactions. This means that the large degree of electrostatic forces holding the IL within the PIL matrix should not be overcome by applied pressure. A schematic illustration of PIL/IL composite membranes is shown in Fig. 10.2b. The chemical structures of several PILs and ILs, which have been used to prepare composite membranes, are shown in Figs. 10.3 and 10.5, respectively.

The proof-of-concept for PIL-IL composite membranes for gas separation was published by Bara et al. [119], who prepared solid stable PIL/IL composite membranes by the polymerization of an IL monomer in the presence of a non-polymerizable IL (also called “free IL”). The incorporation of 20 wt% of free **IL 1** into **PIL 1a** increased its CO₂ permeability by approximately 400 % compared to the neat **PIL 1a** membrane, while permselectivities of 39 for CO₂/N₂ and 27 for CO₂/CH₄ were obtained, displaying differences of 33 % and minus 25 %, respectively [119]. Afterwards, Bara et al. [120] also changed the anion of the free IL component. They combined the **PIL 1d** with 20 wt% of free imidazolium-based ILs having different anions (**IL 1-4**). The composite membrane containing 20 wt%

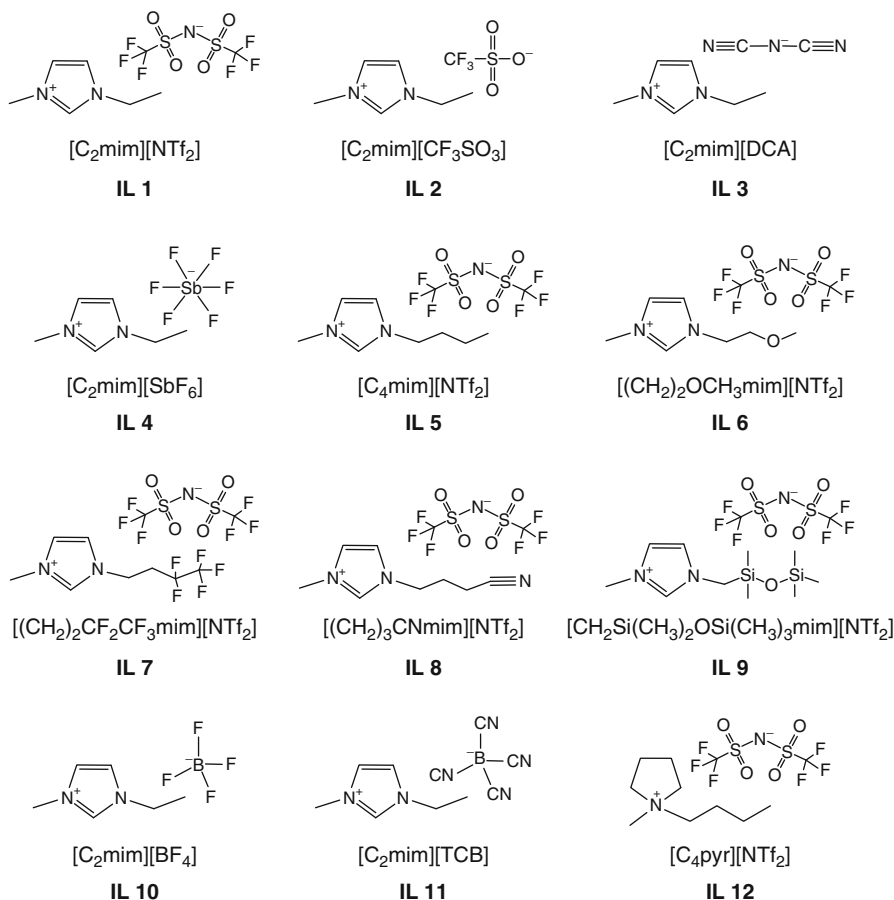


Fig. 10.5 Chemical structures and short names of the ionic liquids that have been used to prepare PIL/IL composite membranes

of free $[C_2mim][NTf_2]$ (**IL 1**) exhibited the highest CO_2 permeability (60 Barrer) compared to the other prepared composites (which varied from 41 to 43 Barrer). Owing to the fact that $[C_2mim][NTf_2]$ has the largest molar volume, this composite membrane has higher free volume, allowing for a faster gas diffusion [120]. What is more, CO_2/N_2 (36–39) and CO_2/CH_4 (24–27) permselectivities of the PIL/IL composites are only slightly smaller than those of the neat **PIL 1d** membrane ($CO_2/N_2 = 41$, $CO_2/CH_4 = 33$), meaning that only a minimal permeability/permselectivity trade-off exists for these membranes (Fig. 10.6). In the same line of research, Bara et al. [121] assessed the effect of functionalized imidazolium cation species of the free IL constituent. Imidazolium-based ILs containing alkyl, ether, fluoroalkyl, nitrile, and siloxane groups (**IL 5–9**) were incorporated into **PIL 1d**. For composites containing alkyl, ether, and fluoroalkyl groups, similar CO_2 permeabilities (47–53 Barrer) and permselectivities ($CO_2/N_2 \approx 37$ and $CO_2/CH_4 \approx 26$)

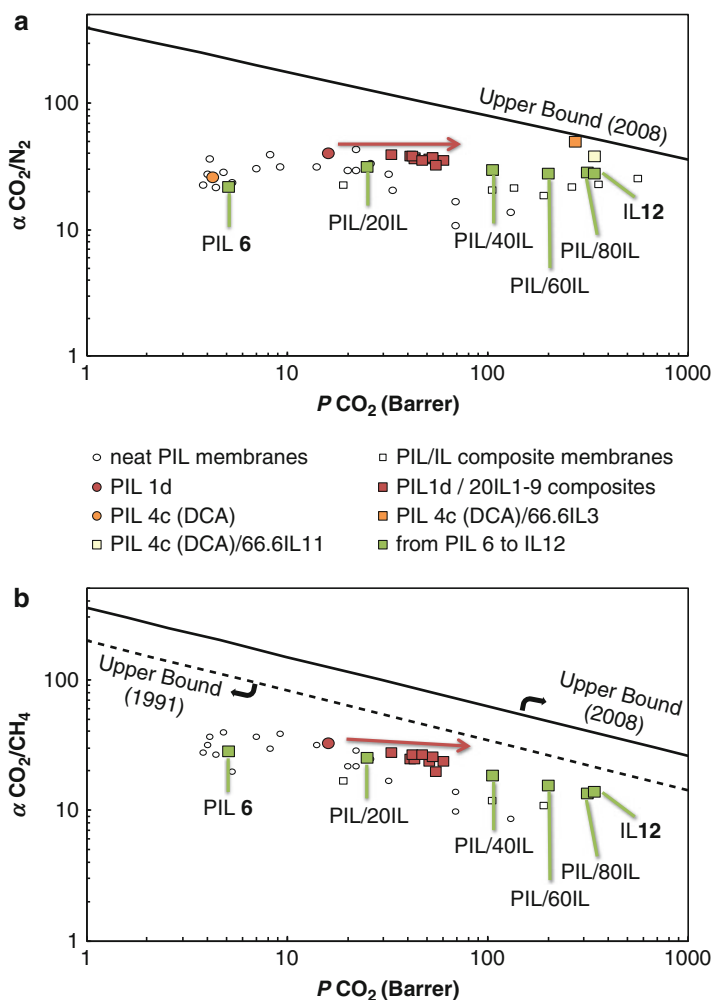


Fig. 10.6 CO₂ separation performance of the PIL/IL composite membranes plotted on (a) CO₂/N₂ and (b) CO₂/CH₄ Robeson plots. Data from References [115–123] are plotted on a log-log scale and the upper bounds for each gas pair are adapted from Robeson [76, 147]

were obtained [121]. The composite bearing the nitrile groups attached to the free cation displayed the highest CO₂/N₂ (40) and CO₂/CH₄ (28) permselectivities, but also the smallest CO₂ permeability (33 Barrer). Conversely, the PIL/IL composite membranes with the siloxane functionality shows the highest CO₂ permeability (55 Barrer), but it exhibited the smallest CO₂/N₂ (33) and CO₂/CH₄ (20) permselectivities [121].

The large gas permeability improvements obtained by the incorporation of free IL into PILs inspired more researchers to pursue this approach. Li et al. [122] synthesized a series of PIL/IL composites with a concentration of free IL ranging from 15 to 60 wt%.

They showed that the incorporation of **IL 5** into **PIL 3** caused an increase in the free volume of the membranes. However, it was observed that increasing the amount of free **IL 5** into **PIL 3c** enhanced the CO₂ and N₂ permeabilities, solubilities, and diffusivities, but did not significantly affect the CO₂/N₂ (22–26) permselectivities of the composites [122]. These composites were found to be stable under transmembrane pressure differential of 10 bar [122]. Later, the same group [116] evaluated the performance of PIL/IL composites based on alkyl-functionalized vinylimidazolium PILs with DCA as counter-anion (**PIL 4b-d**). These PILs were blended with different free ILs, namely, [C₂mim][DCA] (**IL 3**), [C₂mim][BF₄] (**IL 10**), and [C₂mim][B(CN)₄] (**IL 11**), which were chosen due to their high CO₂/N₂ separation performance [60]. In this case, the incorporation of the free ILs not only significantly increased the CO₂ permeability but also enhanced the CO₂/N₂ permselectivity [116]. The best CO₂ separation performances were achieved for the composites of **PIL 4c** with 66.6 wt% of **IL 3** and **IL 11**, presenting CO₂ permeabilities of 273 and 340 Barrer and CO₂/N₂ permselectivities of 51 and 39, respectively [116]. As it can be seen in Fig. 10.6a, these two PIL/IL composite membranes have CO₂/N₂ separation performance very close to the Robeson 2008 upper bound, suggesting their enormous potential for post-combustion flue gas treatment [116].

Since the incorporation of free IL into PIL membranes can considerably improve their performance in CO₂ separation, we also decided to study the gas separation behavior of the whole material range from neat PIL to pure IL, encompassing the PIL/IL composites. For that purpose, membranes based on pyrrolidinium **PIL 6** with different amounts of free **IL 12** (0, 20, 40, 60, 80, and 100 wt%) were prepared [118]. As expected, the results showed that the CO₂, N₂, and CH₄ permeabilities and diffusivities increase dramatically in PIL/IL composites when compared to those of pure **PIL 6**, probably due to the enhancement of polymer chain mobility and consequently a lower resistance to gas diffusion created by the free ion pairs. For instance, the addition of 60 wt% of **IL 12** increased the CO₂, CH₄, and N₂ permeabilities by roughly 3829 %, 7011 %, and 2970 %, respectively [118]. Moreover, the incorporation of 20, 40, and 60 wt% of **IL 12** into **PIL 6** promoted a permselectivity increase of 44 %, 36 %, and 27 %, respectively. In contrast, the CO₂/CH₄ permselectivity decreased 12 %, 53 %, and 82 % in the same composites [118]. The CO₂ separation performance of the whole material range, from pure **PIL 6** to pure **IL 12** passing through their composites, can be clearly appreciated in Fig. 10.6. The Robeson plots showed that CO₂/N₂ is a more favorable separation than CO₂/CH₄ for the prepared composite membranes, mainly due to the intrinsic permselectivity properties of the **IL 12** incorporated. The presence of **IL 12** in the composites promoted the enhancement of the CO₂/N₂ separation performance because the CO₂/N₂ permselectivity in the neat **PIL 6** is lower than that obtained for pure **IL 12** [118]. Indeed, the study of the full material range allows for the selection of the appropriate amount of IL so that PIL/IL composite membrane closest to the upper bound (2008) of the Robeson plot can be thoughtfully prepared.

Carlisle et al. [123] used a different approach that consists on the preparation of cross-linked PIL/IL gel membranes. These authors prepared a series of membranes by photopolymerization of oligo(ethylene glycol)-functionalized cross-linking and

non-cross-linking vinylimidazolium IL monomers in the presence of free **IL 1**. The effect of the cross-linker content as well as the free IL loading on the CO₂ separation performance of these membranes was investigated. The CO₂ permeability was dramatically increased at the three concentrations (45, 65, 75 wt%) of IL loading, while both the CO₂/N₂ and CO₂/CH₄ permselectivity remained nearly constant [123]. The gas diffusivity through the membranes can be increased by decreasing the cross-linker concentration [123]. These cross-linked PIL/IL gel membranes are quite promising since this configuration can stabilize 75 wt% of free IL while presenting “liquid-like” CO₂ separation performance, with CO₂ permeability of 520 Barrer and good CO₂/N₂ and CO₂/CH₄ permselectivities of 37 and 20, respectively.

In summary, all these studies demonstrate that by the addition of free IL enables the increase in the CO₂ permeability of PIL-based membranes with little, if no, sacrifice of their CO₂ permselectivities. It was also observed that the gas permeation properties of the free IL greatly influence the CO₂ separation performance of the composites and as the amount of free IL increases, the CO₂ separation performance of the composite further deviates from the parent neat PIL and approaches that of the analogous SILMs. Consequently, the choice of the appropriate IL is crucial in the tailoring of the PIL/IL membrane properties to improve their CO₂ separation performance.

PIL Copolymer Membranes

The synthesis of PIL copolymers that contain at least one PIL monomeric unit has also been attracting great attention [93, 95] since copolymerization is a general strategy to tune the desired properties of macromolecules. Thus, the synthesis of PIL copolymers is an additional and alternative strategy to design PIL-based CO₂ separation membranes [124–129]. The chemical structures of the PIL copolymers that have been developed for this purpose are shown in Fig. 10.7.

Radosz and coworkers were the first to test PIL copolymers as CO₂ separation membranes [124]. The main objective was to prepare less brittle PIL membranes by grafting poly(ethylene glycol) (PEG) onto glassy ammonium-based PILs to form PIL-PEG membranes (**coPIL 1 and 2**) [124]. The resulting membranes were found to be chemically and mechanically stable, with CO₂ permeabilities as high as 40 Barrer (at 35 °C) and CO₂/N₂ permselectivities up to 70 [124].

More recently, Li and Coleman [125] synthesized random copolymers having diamino functional IL monomeric units within a block copolyimide backbone (**coPIL 3a,b**) and then prepared freestanding membranes by the film-casting method. Nonetheless, the incorporation of IL monomeric units reduced the gas permeabilities, solubilities, and diffusivities and fairly increased (4 %) the CO₂/CH₄ permselectivity compared to the pure block copolyimide [125]. Furthermore, Chi et al. [126] synthesized graft copolymers consisting of poly(vinyl chloride) (PVC) main chains and imidazolium-based PIL side chains (**coPIL 4a,b**) via atom transfer radical polymerization. The resulting membranes maintained good

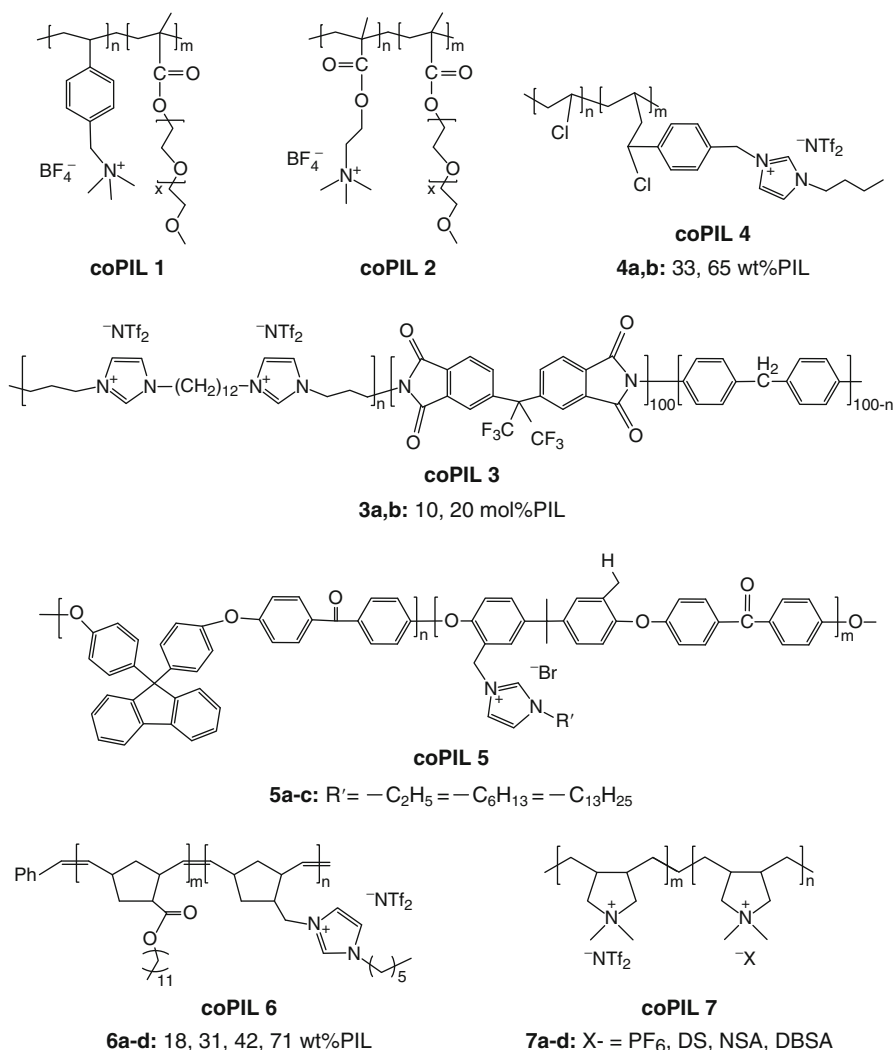


Fig. 10.7 Chemical structure of the PIL copolymers that have been evaluated as CO₂ separation membranes

mechanical properties (lower strength and greater elongation than PVC), the CO₂ permeability increased from 1.7 to 17.9 Barrer, while the CO₂/N₂ permselectivity slightly decreased (from 29 to 25) as the content of PIL increased [126]. Alkyl imidazolium functionalized poly(ether ketone)s (Im-PEKs) were also synthesized by polycondensation [127]. The copolymers combining the pendant imidazolium cations with different alkyl chains (**coPIL 5a-c**) displayed good thermal and mechanical stabilities and showed high CO₂/N₂ permselectivities up to 66. However, the CO₂ permeabilities, between 1.11 and 1.89 Barrer, are very low [127].

Keeping in mind both the advantages of PILs and the effect of nanostructured, phase-separated block copolymers, Noble's group synthesized a new type of block copolymers (**coPIL 6a-d**) combining an imidazolium-based PIL and an alkyl non-ionic polymer. In this work, Nguyen et al. [128] showed that the combined effects of composition and nanostructure of the block copolymers have an important impact on both the CO₂ permeability and CO₂/N₂ permselectivity. For instance, decreasing the IL block amount increased the CO₂ permeability by one to two orders of magnitude up to 9,300 Barrer, and simultaneously decreased the permselectivity, since the diffusion of both CO₂ and N₂ is favored by formation of nanostructures in the "ionic liquid domain" [128]. On the other hand, these new block copolymers have distinctive advantages over the analogous pure homopolymers with respect to membrane preparation since they can be successfully fabricated as defect-free, thin (3–20 μm) supported membranes [128].

In order to increase the flexibility in tailoring the permeability and selectivity of PIL-based membranes, we explored the use of PILs with mixtures of counter-anions employing a straightforward strategy [129]. A new family of PIL random copolymers having pyrrolidinium cation units combined with different counter-anion mixtures was synthesized by a simple and quantitative anion exchange procedure, where only a simple purification step by filtration is required to obtain pure copolymers [129]. Composite membranes of pyrrolidinium random copolymers (**coPIL 7a-d**) with 20 wt% of free **IL 12** were prepared, because the pure copolymers were brittle and broke during the gas permeation experiments. CO₂ permeabilities between 2.74 and 44.2 Barrer were obtained, whereas the membranes exhibited permselectivities ranging from 21.4 to 31.0 for the separation of CO₂/N₂. The results also showed that depending on the structure of the second counter-anion, the polymer chains interact and pack differently, and consequently rigid or further opened polymer networks can be obtained [129]. This study demonstrated that the gas permeation properties of PIL-based membranes can be designed by using pyrrolidinium random copolymers with different counter-anion mixtures as polymer matrices.

The CO₂/CH₄ and CO₂/N₂ separation efficiencies of PIL copolymer membranes developed so far are plotted in Fig. 10.8a and b. These membranes do not outperform the Robeson 2008 upper bounds for CO₂/CH₄ and CO₂/N₂ separations, but Fig. 10.8 clearly shows that CO₂ separation performance as a function of permeability can be tuned by using PIL copolymers. Although considerable research is still required for a complete understanding of the relationship between macromolecular structure and gas permeation properties, these results open new possibilities for designing promising PIL-based CO₂ separation membranes with improved mechanical stability.

PIL/IL/Zelite Mixed Matrix Membranes

Mixed matrix membranes (MMMs), a new class of membrane materials containing inorganic and organic components, have been identified as the potential solution to

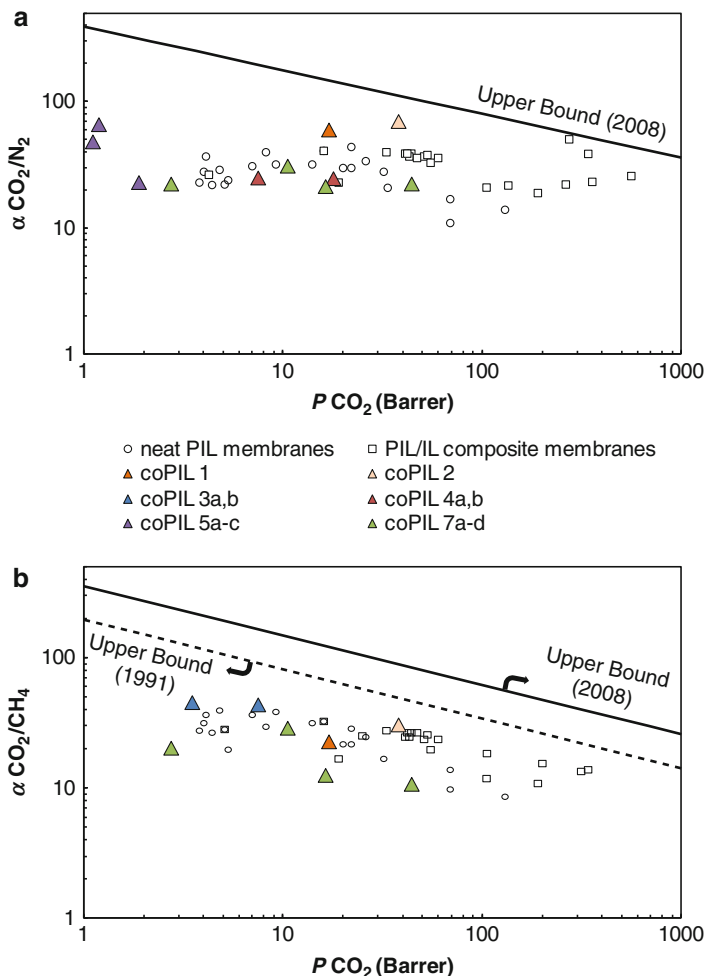


Fig. 10.8 CO₂ separation performance of the PIL copolymer membranes plotted on (a) CO₂/N₂ and (b) CO₂/CH₄ Robeson plots. Data from References [124–129] are plotted on a log-log scale and the upper bounds for each gas pair are adapted from Robeson [76, 147]

the trade-off issues of polymeric membranes [149]. MMMs are normally fabricated by the incorporation of an inorganic solid (dispersed) phase into a continuous polymer matrix. Conceptually, these composite membranes can offer the ease processing inherent to polymeric materials, as well as the enhanced CO₂ permeability and separation performance of inorganic membranes [139].

In light of the abovementioned aspects, MMMs comprising PIL, free IL, and inorganic particles were proposed to improve the CO₂ separation performance of PIL-based membranes [130–132]. The first MMM containing three components of **PIL 1a** (Fig. 10.3), **IL 1** (Fig. 10.5), and zeolite SAPO-34 was studied in 2010 by

Hudiono et al. [130]. A schematic illustration of these composite membranes is shown in Fig. 10.2d. The results showed that the IL component not only increased the permeability of the membrane, but also improved the interfacial adhesion between the zeolite and the PIL [130]. The permeability of CO₂, CH₄, and N₂ through the **PIL 1a/IL 1**/SAPO-34 membrane increased by 65 %, 50 %, and 48 %, respectively, compared to that of the respective PIL/IL composite. The incorporation of SAPO-34 zeolites also increased both the CO₂/N₂ and CO₂/CH₄ permselectivities by roughly 11 %. However, the performance of PIL/IL/SAPO-34 membrane is still below the upper limit (2008) on the Robeson plots for CO₂/N₂ and CO₂/CH₄ separations [130]. Nonetheless, this pioneer work demonstrated that it is possible to improve the organic–inorganic adhesion in an MMM by the addition of free IL, allowing for the fabrication of membranes without defects that are typical to MMMs. Later, Hudiono et al. [131] presented a detailed study of the CO₂ separation performance of three-component MMMs focusing on the effect of varying both SAPO-34 and free IL loadings. These results showed how the system can be tuned.

Recently, Hao et al. [132] synthesized PIL/IL/ZIF-8 composite membrane using **PIL 4c** (Fig. 10.3); free **IL 1**, **10**, and **11** (Fig. 10.5); and different amounts of ZIF-8 (0, 10, 20, and 25 wt%). The prepared membranes exhibited a continuous increase in the CO₂, CH₄, and N₂ permeabilities with increasing ZIF-8 loading in the presence of the three free ILs tested. However, a slight decrease in CO₂/N₂ and CO₂/CH₄ permselectivities was also observed, since the ZIF-8 has intrinsically low CO₂ selectivity [132]. For instance, the CO₂ permeability of **PIL 4c/IL 11** jumped from 365 to 1062 Barrer, about a threefold increment, with the incorporation of 25 wt% of ZIF-8, while the CO₂/N₂ and CO₂/CH₄ permselectivities dropped from 30 to 24 and from 16 to 12, respectively.

Even though the CO₂ separation performance of the PIL/IL/zeolite mixed matrix membranes prepared until now has not yet surpassed the 2008 upper bound on the Robeson plots for CO₂/N₂ and CO₂/CH₄ separations, the three studies described above show that fully heterogeneous membranes embedding inorganic particles uniformly can be prepared using both PILs and ILs. In addition, MMMs are currently considered one of the most potential classes of materials for advancing the current membrane gas separation technology, as well as the inherent brittleness problems found in inorganic membranes. Therefore, MMMs based on PILs constitute a highly interesting approach that deserves to be deeply explored.

Outlook

In the last years, poly(ionic liquid)s have been blossoming at the interface of many disciplines, leading to a renaissance of the field of ionic polymers. Despite all the progress in the different areas, their use as gas separation membranes is still in its infancy. Although the published data for PIL-based membranes shows promising CO₂ separation factors, it also evidences the lack of diversity in what concerns the different chemical structures of cations and anions. PILs having cationic, anionic, and zwitter-ionic moieties in the polymer backbone have already been synthesized and used in other

areas of knowledge, but only the first class has been approached for the preparation of CO₂ separation membranes. It is indispensable to explore the performance of other PIL architectures in order to understand/identify the best performing polymers.

Valuable clues regarding the role of several functional groups can be gathered from the large amount of work available on CO₂ solubility in ionic liquids. Indeed, ILs have been thoroughly researched and specifically designed to perform in a highly efficient manner for CO₂ separation applications, overcoming the drawbacks of some of the ILs initially proposed. The test and careful analysis of specific ILs in SILM configurations can provide important insights into the structure-property relationships, thus allowing a more confident design of PIL analogues.

Another concern is the lack of data under real industrial conditions. The evaluation of the behavior of PIL-based membranes with temperature, at different humidity conditions and exposed to different chemical environments, is crucial for their application in CO₂ separation processes. Additionally, other issue that has been completely neglected so far is the mechanical and chemical stability of the PIL-based membranes.

Taking into account that membranes with CO₂ separation performances in the upper right quadrant of the Robeson plots are very important for industrial applications, the development of PIL-based membranes targeting the critical combination of high CO₂ permeability/permeselectivity and high chemical and mechanical stability is required to place these materials at the doorways of industrially relevant membrane-based CO₂ separation processes.

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Conducting IPNs and Ionic Liquids: Applications to Electroactive Polymer Devices

11

Dominique Teyssié, Claude Chevrot, Pierre-Henri Aubert,
Cédric Plesse, and Frédéric Vidal

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D. Teyssié • C. Chevrot • P.-H. Aubert • C. Plesse • F. Vidal (✉)
Laboratoire de Physicochimie des Polymères et des Interfaces (EA 2528), Fédération “Institut des
Matériaux”, Université de Cergy-Pontoise, Cergy-Pontoise, France
e-mail: frederic.vidal@u-cergy.fr

Abstract

The synthesis of interpenetrating polymer networks (IPNs) is proposed as an alternative to polyether-based (co)polymers or networks for the design of solid polymer electrolytes (SPEs). IPNs were prepared from an elastomer bringing the mechanical properties and poly(ethylene oxide). These IPNs, swollen by *N*-ethylmethylimidazolium bis(trifluoromethanesulfonyl)-imide (EMITFSI), possess an ionic conductivity close to $10^{-3} \text{ S cm}^{-1}$ at 30 °C. In order to form conducting IPNs, chemical polymerization of 3,4-ethylenedioxythiophene (EDOT) has been carried out within the SPE IPN. A pseudo-trilayer configuration has been obtained with the SPE IPN sandwiched between two interpenetrated PEDOT electrodes. Controlling the PEDOT content from 0.3 to 24 wt% in the material, electrochromic, electroreflective, or electromechanical devices is obtained.

Keywords

Actuators • Ionic liquids • Interpenetrating polymer networks • IPNs

Introduction

Electronic conducting polymers (ECPs) have attracted attention because of their promising electronic, electrooptical, and mechanical properties. These materials are characterized by their possible properties changes due to the counterions and solvent molecules' expulsion/insertion during oxidation or reduction processes [1]. Among electronic conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has received much attention recently because of its particularly high stability in the doped state and the reversibility of the doping process [2–4]. Providing an ionic conducting medium is available, PEDOT can be used as the active component in electroactive polymer devices, i.e., electrochromic devices or actuators [5–7]. To operate in air, ECP-based electroactive devices are usually built using a solid polymer electrolyte (SPE) film sandwiched between two ECP film electrodes (ECP//SPE//ECP) [8]. In order to envisage further development for these devices as “active skins,” it is necessary to fabricate electroactive materials with adequate performances and robust mechanical properties for a real integration in practical electrochemical devices. Most efforts have been previously concentrated on ECP synthesis conditions (temperature, nature of the electrolyte and solvent) in order to improve optical or mechanical responses [9–14]. However, performances of open-air electroactive devices are not only depending on ECP performances but also on the SPE partner. Indeed, the SPE medium which provides the ions necessary to the redox process has a major influence both on the electrochemical response and on the mechanical properties of the devices.

Since the discoveries of ionic conduction in polymers containing inorganic salts by Wright [15], and that polymer ionic conductors could be used as electrolytes by Armand [16], a wide range of solid polymer electrolytes (SPEs) have been developed in various electrochemical devices like supercapacitors and rechargeable batteries [17]. Conventional ion-conducting polymers, like poly(ethylene oxide) (PEO) [18],

are solid solution of electrolyte salts in polymers. However the low diffusion coefficient of ion species in the SPE leads to an intrinsically weak ionic conductivity. When the SPE is swollen with an electrolyte solution, the ionic conductivity can be increased, but the evaporation of the solvent must be minimized, which is not an easy matter in devices operating in air. Recently, several authors have shown that ionic liquids can be successfully used as novel electrolytes because of their high ionic conductivity, good electrochemical stability, and nonvolatility [19]. The formation of gel-like films increases the ionic conductivity but causes a poor dimensional stability and weak mechanical properties. Therefore, many efforts have been devoted to improve the mechanical properties of swollen polymer electrolytes. To resolve the dimensional stability, SPE can be designed as a network. In spite of improved mechanical properties and dimensional stability, reducing the mobility of polymer chains decreases the mobility of charges in the material and therefore leads to an ionic conductivity reduction [20, 21]. Although dangling chains can be introduced to increase the proportion of free volume available for the migration of ions [22], it is difficult to combine high ionic conductivity with good mechanical properties. For this purpose, interpenetrating polymer networks (IPNs) are a special class of networks which can be designed to fulfill specific end uses. IPNs are described as an intimate combination of two (or more) cross-linked polymers [23]. The tight entanglement of these networks ensures good interpenetration of the two components, and the 3-dimensional interpenetration in the networks radically improves dimensional and morphological stability. By choosing two polymer partners for their specific properties, i.e., one for ionic conduction and the other one for mechanical properties, and providing that dual-phase continuity are obtained [24], an “ideal” SPE can be designed for electroactive polymer devices (EAPDs).

Conducting interpenetrating polymer networks (C-IPNs) have been prepared from oxidative polymerization of the 3,4-ethylenedioxythiophene (EDOT) monomer within the SPE IPN matrix. A pseudo-trilayer configuration has been obtained with the IPN sandwiched between two interpenetrated PEDOT electrodes. This type of device can operate as electrochromic devices or actuators in air if the IPN provides the source of ions required for the redox reaction. Therefore, before operation, the materials are immersed in an ionic liquid for a given length of time. After the swelling step, the IPN-based SPE can play the role of ion reservoir during operation in air. In fact C-IPNs are similar to an electrochemical cell with a two-electrode configuration where the inner ionic liquid-swollen IPN ensures the ionic conductivity while the comparatively outer PEDOT layers act both as electrodes and active materials.

Synthesis of Interpenetrating Networks as Solid Polymer Electrolyte

Introduction

As mentioned above the SPEs have a major influence on the electrochemical response of ECP-based devices. Therefore the SPE ionic conductivity can be

tuned in order to obtain a high ion diffusion rate within the matrix. On the other hand, ECPs are known to have poor mechanical properties. Thus the mechanical resistance of the device is brought mainly by the SPE central polymeric layer. First a single PEO network was tested as the SPE component in EAPDs. This network was prepared by free radical copolymerization of poly(ethylene glycol) dimethacrylate and poly(ethylene glycol) methacrylate (in 25/75 wt% ratio) leading to an elastomer ($T_g = -41\text{ }^{\circ}\text{C}$) with dangling chains in order to increase the free volume available to further additional salts. It must be stressed first that PEO network on its own although all oxygen atoms are available for ion conductivity cannot be of interest in the elaboration of SPE because of tearing problems leading to the destruction of the material when loaded with ionic liquid as electrolyte. PEO thus must be combined with another polymer into an IPN architecture in order to prevent this problem. In our first tentative synthesis of IPNs containing PEO as the electrolyte support, PEO/polycarbonate was chosen as the SPE component. However for this particular chemical combination, bending deformations lead to crack formations at room temperature since deformations induce stress in the material, although PEO and PC have a strong chemical affinity [25]. In order to prevent cracking, an elastomer in addition to PEO was used instead of rigid polycarbonate. Elastomers were shown to be able to absorb large deformations and the different investigated systems will be described now.

PEO/Polybutadiene IPNs as SPE

IPNs were prepared in a one-pot procedure corresponding to the independent polymerization/cross-linking of each network. PEO network was prepared by free radical copolymerization of poly(ethylene glycol) dimethacrylate and poly(ethylene glycol) methacrylate (in 25/75 wt% ratio). PB network formation was then triggered by α,ω hydroxyl-functionalized polybutadiene cross-linked with a pluriisocyanate (Desmodur[®]) component (with dibutyltin laurate (DBTDL) as catalyst). The kinetics of IPN synthesis were investigated by FT-NIR and the results published elsewhere [24, 26, 27]. In particular these results show that transparent or translucent IPNs can be obtained depending on the rate of polymerization of the PB component with respect to the PEO rate synthesis (as adjusted by DBTDL to OH ratio). Transparent or translucent IPNs can be obtained, i.e., with differing interpenetrating degrees for each PEO/PB chosen weight ratio 30/70, 50/50, and 80/20. In particular IPNs are all transparent when PB is synthesized first. In principle the first formed network will be the continuous phase in the further IPN. The ionic conduction properties are strongly dependent on the morphology of the material. In order to get a better insight in the morphology of these PEO/PB IPNs, test experiments were carried out on each sample, i.e., LiClO_4 -loaded IPN conductivity and TEM imaging.

The morphology of 30/70 PEO/PB transparent IPN can be considered as finely interpenetrated since in the TEM image no contrast at all can be detected (Fig. 11.1b). On the opposite translucent 30/70 PEO/PB IPN, a coarser morphology

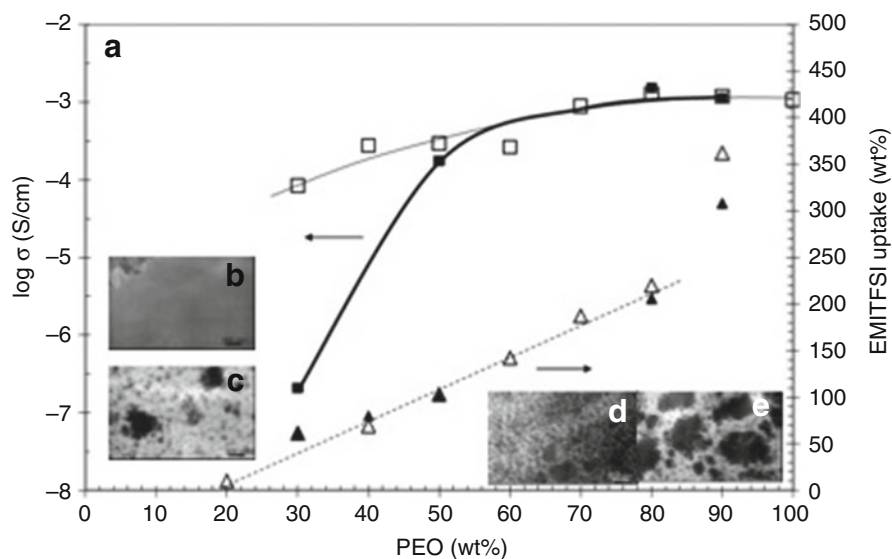


Fig. 11.1 (a) EMITFSI uptake (wt%) and ionic conductivity at 30 °C for PEO/PB IPNs (open signs: transparent material, solid signs: translucent material) as a function of the PEO weight content in the material. Electron micrographs of (b) transparent and (c) translucent 30/70 PEO/PB IPN and (d) transparent and (e) translucent 80/20 PEO/PB IPN. PB phase marked with OsO₄ appears dark (From [27])

is obtained (Fig. 11.1c). Islands of 400 nm diameter in a clearer gray matrix can be observed. The morphology of the translucent PEO/PB IPN exhibits more or less circular domains with a mean 700 nm diameter covering about 40 % of the surface. As far as the transparent 80/20 PEO/PB IPN is concerned, the morphology is almost homogeneous at low magnification (Fig. 11.1d). Whatever the results of TEM, they cannot fully inform about the morphology of the sought IPNs. Thus LiClO₄ loading experiments were carried out in order to make a clear assignment of the morphology of the samples.

LiClO₄ uptake was performed on both transparent and translucent PEO/PB samples. Indeed as we demonstrated previously the specific interaction of Li⁺ cations within PEO/PB, IPNs can be used as a powerful tool in order to study phase co-continuity and possible extent of phase separation in the material [26]. The molar ratio of uptaken Li⁺ cations to ethylene oxide units ($r = [\text{Li}^+] / [\text{CH}_2\text{CH}_2\text{O}-]$) was determined by the Li⁺ uptake by weighing the dried LiClO₄-loaded samples after immersion in the salt aqueous solution. LiClO₄ uptake in PB single network is close to zero as expected. Thus the measurement of r is truly indicative of the accessibility of LiClO₄ to the PEO domains. First for the 30/70 PEO/PB IPN, the r values for the transparent and translucent samples are 0.054 and 0.004 accordingly. As far as 50/50 PEO/PB IPNs are concerned, the r values are 0.141 and 0.115 for transparent and translucent IPNs, respectively, which represents 7 and 8.7 EO unit per Li⁺ cation. When it comes to 80/20 PEO/PB IPN,

the difference in the Li^+/EO ratio is similar 0.168 and 0.174, respectively, meaning that the accessibility of PEO is similar in the two samples on the contrary of lower PEO translucent samples content.

Ionic liquids have been successfully used as electrolytes [19, 20, 28], and particularly performing is 1-ethyl-3-methylimidazolium bis(trifluoroethylsulfonyl) imide due to its high conductivity nonvolatility and low viscosity [29]. Therefore EMITFSI-swollen IPNs have been thoroughly studied. It appears here that the r values translate very finely in the conductivity of EMITFSI-loaded samples as shown in Fig. 11.1a. The maximum EMITFSI content increases from about 60 to 210 wt% with an increase of the PEO content in translucent and transparent IPNs. The increase in the maximum EMITFSI uptake thus curiously only parallels the PEO content in the sample irrespective of its morphology. The corresponding ionic conductivity of 90/10 and 80/20 conductivities is identical for translucent and transparent phases which can be ascribed to the percolation of PEO domains as deduced from LiClO_4 uptake for high PEO contents. Thus in those cases the whole of PEO contributes to the ionic conductivity which amounts to that of the single PEO network ($10^{-3} \text{ S cm}^{-1}$). For the lowest PEO composition –30/70 IPN-, the translucent IPN displays a conductivity at 25 °C two orders of magnitude less ($2.2 \cdot 10^{-7} \text{ S cm}^{-1}$) than the transparent one ($1.4 \cdot 10^{-4} \text{ S cm}^{-1}$). Keeping in mind that the EMITFSI uptake is independent on the morphology for a given IPN, the number of charge carriers is consequently independent of the morphology. Thus any observed difference in the conductivity can only originate in the mobility of the charge carriers which thus arises from the morphology.

The conclusion of this study is that IPNs containing up to 30 wt% of an apolar partner can display ionic conductivity in the presence of ionic liquid in the same range than the single PEO network. Thus a foreign polymer can be introduced in the system in order to improve its mechanical properties without impairing its ionic liquid-conducting properties providing the adequate morphology is attained. This should be possible to be applied to other polymers further on.

PEO/NBR IPNs as SPE

In order to improve the flexibility of the IPN, we proposed to replace PB partner by a nitrile butadiene rubber (NBR) leading to PEO/NBR IPN [30]. The high molecular weight NBR should ensure convenient mechanical properties since PEO/PB IPNs are still too easily tearable which makes them not so convenient in view of their future integration in complex systems. PEO/NBR IPNs are synthesized via a two-step in situ process where PEO network is again composed of 25 wt% PEGDM and 75 wt% PEGM. The starting medium is a solution of NBR, PEGDM, PEGM, and initiators in trichloroethane containing 80 wt% down to 50 wt% PEO. The PEO network is shown to proceed within 3 h at 50 °C. When the proportion of NBR increases, the synthesis of the PEO network slows down, and a postcuring at 100 °C appears necessary to complete the total conversion of methacrylic groups as shown by NIR spectroscopy. In a second step the NBR network is formed by heating

25 min at 180 °C in the presence of dicumyl peroxide (DCP). The NBR content has no influence on the curing time.

First these networks were then subjected to transmission electron microscopy. If a clear difference in the morphology appears as a function of the NBR content, a precise distinction of PEO phase continuities in all samples cannot be inferred yet. Thus additional experiments were required to get insight in the phase continuity of the two partners. As mentioned above the investigation of IPN morphology and phase continuity can be powerfully investigated by LiClO₄ loading. Again Li⁺/EO loading has been investigated on samples containing from 80 to 20 wt% PEO. The LiClO₄ uptake is proportional to the PEO content between 60 and 100 wt% PEO and the Li⁺/EO remaining almost constant ($r = 0.11$). These results show that between 60 and 100 wt% proportion, all PEO domains are available for LiClO₄ insertion with a constant molar proportion with respect to that of ethylene oxide units. These results might be considered as a strong indication of PEO phase continuity in those IPNs. Below 60 wt% PEO, a sharp decrease in the LiClO₄ uptake is observed indicating that the insertion of LiClO₄ is considerably hindered. The Li⁺/EO ratio sharply decreases from $r = 0.11$ to $r = 0.04$. PEO domains are thus presumed being less and less interconnected and dispersed in the continuous NBR phase.

As mentioned previously a critical parameter for targeted applications is the ionic conductivity. EMITFSI has a high affinity for polymers with polar groups which make it compatible for both PEO and NBR. The ionic liquid uptake in NBR is 85 wt% and can reach 180 wt% in PEO (before tearing the network). The synergistic effect of IPNs here is clearly demonstrated since the EMITFSI uptake can reach 250 wt% for an 80 wt% PEO-containing IPN. The ionic conductivity of EMITFSI-swollen IPNs is just below the conductivity of single PEO network, i.e., $1.10^{-3} \text{ S cm}^{-1}$ at 25 °C.

Typical viscoelastic and mechanical behavior have been studied for both single and PEO/NBR IPNs. By DMTA, two α relaxations can be clearly observed in the IPN, one about 0 °C corresponding to NBR-rich phases and one about -40 °C corresponding to PEO-rich phases for all compositions. These results clearly indicate that the IPNs present a dual-phase morphology and are not interpenetrated at molecular level. These results confirm the results obtained by TEM studies. PEO single networks have a 10 % elongation at break and the Young's modulus is around 11 MPa. As already mentioned these properties make PEO network improper to acceptable actuation properties. However NBR single network breaks at 300 % strain for a stress above 1.4 MPa which makes this elastomer interesting for the targeted application. As far as IPNs are concerned, the behavior is intermediate; the Young's moduli are 1.6, 1.3, 1.2, and 1.1 MPa for IPNs containing 20, 30, 40, and 50 wt% NBR, the elongation at break being 45–159 % according to the IPN composition.

A second synthetic pathway was investigated in order to try to improve the interpenetration level [31]. In this two-step sequential procedure, NBR network is synthesized first by cross-linking through DCP at high temperature (>160 °C) and pressure (285 kgcm⁻²) for 20 min. In a second step the NBR network is swollen

Table 11.1 Thermomechanical properties and ionic conductivity (room temperature) data for PEO/NBR containing 50 wt% PEO (25 PEGDM; 75 PEGM) obtained through *in-situ* or *sequential* synthesis pathways

PEO/NBR IPN	T_{α} (°C)	$T_{\alpha 2}$ (°C)	Maximum EMITFSI ionic conductivity ($S\ cm^{-1}$)	Elongation at break (%) (stress at break MPa)
In situ synthesis	−40 strong	0 strong	$8 \cdot 10^{-4}$	150 (1.0)
Sequential synthesis	−36 weak	2 strong	$1 \cdot 10^{-3}$	110 (1.0)

with a cyclohexane solution containing AIBN, 25, 50, or 75 wt% PEGDM, and the corresponding percentages of PEGM in order to vary the cross-linking density of the resulting PEO network. The material is then cured for one hour at 70 °C and 1 h at 100 °C in order to get complete transformation of the methacrylic functions. The thermomechanical analysis of the samples shows one very wide mechanical relaxation instead of the two distinct ones as in the previous synthetic pathway. The main T_{α} is between −4 °C and −2 °C depending on the cross-linking density of the PEO network. The relaxation of the PEO network is thus shifted to higher temperatures due to the interpenetration in the continuous phase of NBR resulting from the synthetic pathway. This high degree of interpenetration appears clearly on the TEM pictures of the networks where the grayish continuous phase suggests that PEO is very finely dispersed in the NBR phase. The sizes of the PEO regions are less than 30 nm which is consistent with the transparency of the sample. Table 11.1 summarizes the thermomechanical properties and the ionic conductivity of the samples obtained through the *in situ* and sequential procedure, respectively.

Other IPNs as SPE

For specific applications, other PEO-based IPNs as SPE have been also studied. First in order to design actuator fibers with linear deformation, PEO/PEO IPNs have been synthesized [32]. The synthesis of the first PEO network is similar to that described previously via free radical copolymerization of PEGM and PEGDM. The second PEO network is synthesized via a polyaddition process between OH groups of the PEO polymer and a pluriisocyanate cross-linker. This specific IPN design allows a better interpenetration of the ECP within the PEO/PEO fiber during the actuator elaboration step (see next section). For microactuator applications, the SPE should be compatible with the photolithography and microsystem processes. Therefore polytetrahydrofuran (PTHF)/PEO IPNs were synthesized through a one-shot *in situ* procedure [33]. The proportions of PEO were varied between 20 wt% and 80 wt %. The 50/50 PTHF/PEO IPN was selected as a trade-off between mechanical properties, ionic conductivity, and low generation rate of hydroxyl radicals at room temperature. Indeed we have demonstrated that PEO partner generates hydroxyl radicals which damage the ECP [34, 35]. Therefore the radical generation rate has to be minimized in the PEO/PTHF IPN. This particular IPN exhibits a 100 % strain

under a 0.8 MPa stress. Its ionic conductivity is $5 \cdot 10^{-4} \text{ S cm}^{-1}$ when loaded with EMITFSI. It will be shown further on that this composition is particularly suitable for microactuators due to fast response when integrated in the device.

Conclusion

A series of solid polymer electrolytes based on interpenetrating polymer networks were synthesized. The IPNs were developed using either the in situ or the sequential procedure. This study reveals that the presence of an elastomer network improves the mechanical properties of PEO single network; i.e., elongation at break is at least 1,000 times higher for PEO/NBR IPNs than that observed with PEO single networks. Moreover, PEO-based IPNs swollen by EMITFSI at saturation exhibit ionic conductivity value (at room temperature) comparable to that of PEO single networks. For example, the PEO/NBR IPN has an ionic conductivity close to $10^{-3} \text{ S cm}^{-1}$ at 30 °C. These values are very promising and demonstrate their suitability for use as base materials in actuators and self-supporting electrochromic devices.

Synthesis of Conducting IPNs to Electroactive Materials

The principle of the synthesis of conducting IPN-based EAPD, although seemingly simple, requires very fine adjustments of the experimental conditions, which will be detailed below. Chemical and electrochemical synthesis of conducting IPN has been investigated.

The Chemical Synthesis Route

Typically it is required that a fine layer of PEDOT be inserted just under the two opposite faces of the SPE film. In order to achieve this, the monomer EDOT is first introduced in the SPE film by swelling in the pure liquid monomer or by vapor absorption. Then the polymerization of EDOT is triggered by dipping for controlled lengths of time the swollen film in an oxidative medium typically aqueous or chloroforms FeCl_3 solution. Then all is a question of how fast EDOT diffuses out of the film because it is very soluble in chloroform or hardly soluble in water. Moreover it must be controlled how fast FeCl_3 enters the films and promotes a PEDOT layer by in situ oxidative polymerization of EDOT. This layer will prevent further entering of FeCl_3 and thus stop polymerization of EDOT leaving only a thin layer of conductive polymer. The central part of the film will be devoid of conducting polymer, thus avoiding any short-circuiting and making the device a mimic of a three-layered device without the drawback of delamination. For longer polymerization time, a feeble quantity of PEDOT is usually present in the central part of the SPE leading to lesser performances of the devices due to the presence of short-circuiting [36].

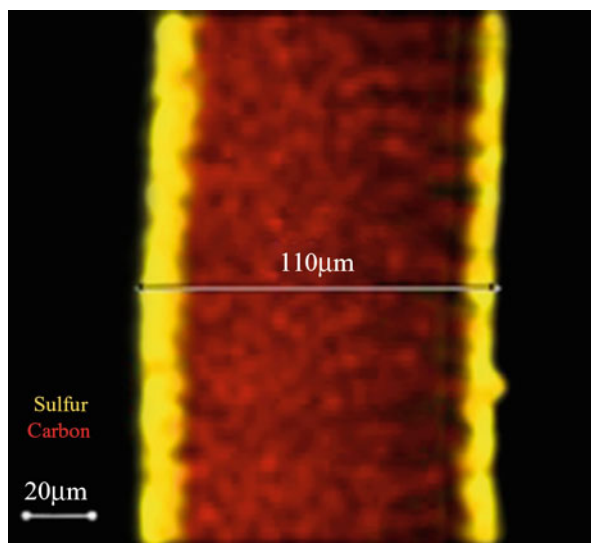
The final amount of PEDOT can be controlled from 0.1 to 22 wt% of the EAPD by tuning the duration of immersion in FeCl_3 . For example, in a 250 μm thick actuator, the PEDOT content is close to 22 wt% with a PEDOT layer thickness of 40 μm in two symmetrical layers near the surface of the C-IPN film [30, 37]. The final PEDOT content has also been studied as a function of the cross-linking degree of the PEO network in the SPE. The more the cross-linking degree the longer the immersion time in FeCl_3 has to be. As shown by cyclic voltammetry [38], the synthetic pathway does not have an adverse effect on the electroactive properties of the PEDOT layers. Anodic peak corresponding to the oxidation of PEDOT and cathodic peak corresponding to the reduction of oxidized PEDOT to a neutral state are easily detected in the film.

The Electrochemical Synthesis Route

This process implies the electrochemical synthesis of a conducting polymer in a SPE matrix. This strategy is interesting since it allows the choice of the electrolytic medium and therefore the nature of the doping ion. Moreover it should bring more regular morphology and also a better control of the electrochemical properties of PEDOT. Some publications have been devoted to the electrochemical incorporation of a conducting polymer inside a linear or a cross-linked polymer [39, 40]. Several groups have reported the preparation of semi-IPN structures either with a direct electropolymerization on an electrode or with an additional spin-coating deposition step on the electrode [41, 42]. However in those publications, the separation of the semi-IPN is difficult contrary to the process presented here, which allows the fabrication of self-supporting materials.

The NBR/PEDOT or PEO/NBR/PEDOT IPN films (100 μm thickness) were prepared by anodic oxidation of EDOT into the NBR (or PEO/NBR IPN) coated on an ITO glass [43]. A three-electrode single-compartment electrochemical cell was used for electropolymerization. The design of the “sandwich” electrochemical cell was adapted from a previous work [44]. The SPE film is deposited on an ITO-coated glass electrode used as the working electrode; the counter electrode was a platinum-coated grid, and a silver wire was used as a reference electrode. A thin cellulose film is added as a separator between the SPE film and the counter electrode in order to favor the diffusion of ions during the electropolymerization. PEDOT was electrochemically deposited into the NBR matrix applying a constant potential of 1.3 V for 30 min and 1.1 V for 14 h. This decrease in the applied potential allows limiting the over-oxidation of the formed PEDOT. After the electropolymerization the PEDOT/NBR film could easily be removed from the ITO electrode as a first confirmation that PEDOT had been grown inside the NBR matrix and not on the ITO electrode. Furthermore the NBR/PEDOT film is flexible since the mechanical properties are still mainly ruled by the elastomeric partner. The electroactivity of the PEDOT in the semi-IPN was checked in a LiClO_4 $10^{-1} \text{ mol L}^{-1}$ /propylene carbonate by cyclic voltamperometry.

Fig. 11.2 EDX picture of PEO/NBR/PEDOT IPN cross section (From [45])



For chemical or electrochemical route, SEM picture analysis gives immediate information about the repartition of PEDOT within the SPE matrix. From SEM picture the thickness of the PEDOT layer is estimated and the PEDOT layer cannot be scratched off the material. Therefore it can be deduced that the PEDOT interpenetrates correctly the SPE matrix. The presence of S in the cross-section of the film observed by EDX mapping reveals also that PEDOT is present in the SPE matrix [45] (Fig. 11.2).

PEDOT-Based IPNs with Electrochromic or Electoreflective Properties

Introduction

Materials which change color reversibly during the electrochemical process of charge and discharge are called electrochromic materials. The first report on the subject was devoted to inorganic oxide films [46]. However commercial applications remain a challenge due to the expensive and complicated synthesis techniques which must be developed. ECPs have drawn a considerable interest due to the potential applications since they offer enhanced processability and present important advantages such as good optical contrast, fast switching times, and broad range of displayable colors [47]. Electrochromic displays are typically assembled by combining a transparent electrode covered with a thin layer of electrochromic materials, transparent solid polymer electrolyte, and a complementary electrochromic material deposited onto a counter electrode. Since PEDOT is

displaying electrochromic properties itself, it seemed an interesting challenge to try and develop such electrochromic devices through our simple one-block-mimicking three-layer system [48].

The variation of electrooptical properties of ECP is also known to be effective in the infrared range. When oxidized, the polaronic and bipolaronic states of the ECP strongly absorb in the near-infrared (NIR) region, while upon reduction, they are transparent in the NIR. When coated on a highly reflective surface such as a gold layer, the ECP provides reversibly the attenuation of the reflectance of the metal electrode. Electroreflective devices (ERDs) in which the conducting polymer is outward facing, hiding a reflective gold layer has been proposed by several authors [49–51]. The ECP is easily accessible to the ionic species of the electrolyte through micropores and the devices operate in reflective mode. The reflective modulation reaches up to 80 % at 2.0 μm upon the application of a low voltage [47]. The above-described systems are all multilayered architecture and remain very complex to upscale, hence limiting the commercial development of large surface areas.

ECPs exhibit also variable reflectance properties in the NIR region beyond the plasma frequency (ω_p) – as metallic conductors do in the visible range – in the course of the doping/dedoping process. This point was investigated in the literature [52, 53] through either chemical or electrochemical doping processes of ECP model layers. The multilayered architecture can be considerably simplified if a large enough amount of ECP is used such that it becomes a thick and opaque film. The film thus acts both as current collector and as the IR tunable reflective layer. A further and final simplification is achieved when the electrolyte and the ECP film are incorporated in a unique hosting matrix. Such a configuration is possible taking advantage of IPNs.

C-IPN-Based Electrochromic Devices

PEO/PEDOT IPN-based electrochromic devices [54–56] were prepared as described in I.1. except that PEGDM and PEGM are included in 1:1 proportion in order to lead to a convenient free volume for the migration of ions and satisfactory mechanical properties. EDOT or 3,4-propylenedioxythiophene (ProDOT) (1 and 2 wt% of the total amount) was added at the beginning. After curing for 4 h at 50 °C and 1 h at 80 °C a free-standing monomer – swollen film is obtained. The film is then immersed in a FeCl_3 chloroform solution in order to promote the polymerization of the conducting monomer. The length of time in FeCl_3 solution is adjusted depending on the required transparency of the final material. The architecture of the final material is a mimic of a three-layer device as already mentioned for other IPNs.

When swollen in ionic liquid solution, the C-IPN film can be clamped between two ITO plates to lead to a symmetrical electrochromic device. When a low voltage is applied ($\Delta E = 1.6$ V) between the two faces, the device becomes dark blue in the visible range due to the reduction of PEDOT layer at only one electrode, the other layer being oxidized (highly transmissive). If $\Delta E = 0$ V, the bleaching of the device

is observed when the two faces are electrically shunted. The maximum optical visible contrast $\Delta T\%$ measured between 380 and 800 nm is close to 33 % with a 60 s switching time for coloring form and 30 s for bleaching one. The simple realization of these electrochromic devices is promising for the development of low-cost devices with large active surface

With one extra methylene group in the dioxane structure compared to PEDOT, π -conjugated polymer from 3,4-propylenedioxythiophene (ProDOT) exhibits higher optical contrast in transmission than EDOT derivatives [57]. It was thus interesting to try and apply the same synthesis pathway to that monomer and search for electrochromic properties [58]. The synthesis of the PEO/PProDOT IPNs was carried out exactly in the same way as PEO/PEDOT IPNs with 1.8 wt% ECP monomer [58]. However it turned out that ProDOT could not polymerize exclusively near the surface of the semi-IPN as in the case of EDOT. Thus a modification of the synthesis was envisaged. Notably PProDOT was trapped in the PEO network because of higher affinity for this polymer. Thus the polymerization of PProDOT promoted by FeCl_3 was carried out in a chloroform/ethyl acetate 95/5 solution which allowed ProDOT to leave sufficiently fast the heart of the PEO network matrix and polymerize on the edges of the film like as described for PEDOT monomer. This particularity demonstrates once more that the synthesis of the ECPs must be tuned very finely in order to obtain the desired properties. Once polymerized in the PEO matrix, PProDOT keeps its electroactivity as shown by cyclic voltammetry. Then the conducting IPN film is swollen in LiClO_4/PC solution and clamped between two ITO plates leading to a symmetrical electrochromic device. The maximum $\Delta T\%$ is 32 % which compares well with reported values [58].

Electroreflective Device Based on C-IPN

Polymer-based electroreflective devices (ERDs) as active thermal control material for satellites are thoroughly investigated [59, 60] in particular as they are light, less expensive, and adaptable to conventional systems and without moving parts as louvers. In this area ECPs draw much attention nowadays due to the fact that they allow active control of IR reflectivity of surfaces and are expected to lead to a significant reduction of onboard power-budget-associated mass. ECP devices should allow avoiding either high temperature when illuminated by the sun or low temperature when the satellite is in the shadow of the earth. An extra asset is that the tunable reflectivity can be programmed or controlled from the ground. Again the device which has just been described for electrochromic applications, one-piece material PEDOT/PEO/PEDOT, seems best convenient for this application providing the right amount of PEDOT (1 wt%) is included in the IPN [61]. The spectroelectrochemical characterization of the material has been made after the film was swollen with EMITFSI. The spectroelectrochemical behavior of the C-IPN demonstrates the tunability in the middle IR (between 2.5 and 7.5 μm) as a function of the applied voltage. The reflectance %R varies from 10 % to 40 % in

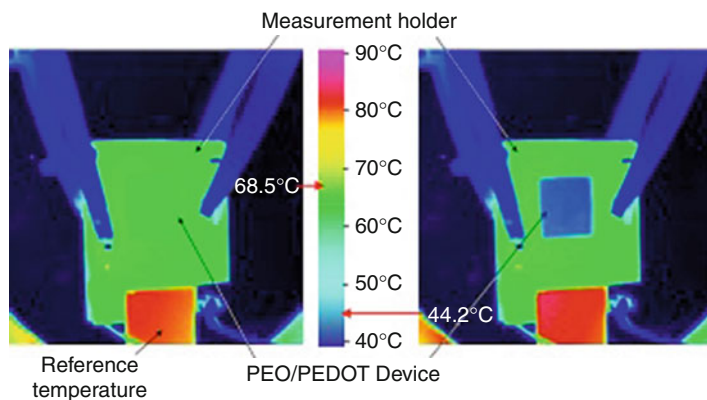


Fig. 11.3 IR picture of the device recorded in band III at 70 °C showing apparent temperature according to the doping level of the active layer, 68.5 °C or 44.2 °C, when reduced or oxidized, respectively (From [61])

this IR range for an applied voltage from -1.2 V to $+1.2$ V. In the same time between 10 and 25 μm , the %R varies from 20 % to 60 %. Although slightly lower than the values reported in the literature, it must be stressed that these values are obtained in the absence of gold layers such as in multilayered devices, i.e., the PEDOT acting as current collector and active material in the device. These reflectance contrasts can be visualized using an IR camera as imaged (Fig. 11.3) which shows the thermal images of an experiment carried out on the C-IPN at thermal equilibrium (70 °C). Applying a $+1.2$ V voltage, the oxidation of the active layer leads to a modification of the reflectivity which in turn modifies the apparent temperature. The active layer then appears at a lower apparent temperature (44.2 °C) demonstrating that the device can also be used for IR camouflage purposes. These results clearly demonstrate that the modulation of the optical properties in the IR range is reached by the control of the oxidation state level of the ECP.

The performances of EMITFSI-swollen PEO/PEDOT IPNs were assessed for space applications [62]. Therefore, a series of thermal balance in high-vacuum chamber (10^{-5} mbar) have been performed on samples to assess their behavior in partially space-like environment. Since it is not possible to measure the reflectivity of the sample in the thermal-vacuum environment, the variation of temperature has been recorded in order to assess the impact of PEO/PEDOT devices on the temperature of the covered surface. Therefore, thermocouples were directly connected with the rear side of the sample, and temperature variations were measured during 7 days thermal-vacuum experiment. After a 3 h conditioning period leading to sample temperature of 15 °C, a voltage of -1.5 V is applied. After 75 min, the temperature of the sample decreases by 4 °C which means that the sample is getting less reflective (or more emissive). When a positive voltage of 1.5 V is applied, an increase in temperature (3 °C) within 60 min is measured due to

Table 11.2 Optical contrasts (%R) for PEO/PEDOT and PEO/NBR/PEDOT IPNs

	PEDOT//PEO//PEDOT	PEDOT//PEO/NBR//PEDOT	PEDOT//PEO/NBR//PEO//PEO/NBR//PEDOT
		EDOT chemically polymerized	EDOT electropolymerized
	Electrolyte: EMITFSI	Electrolyte: EMITFSI	Electrolyte: LiClO ₄ /propylene carbonate
Optical contrast at 2.5 μm	25 %	22 %	14 %
Optical contrast at 7.5 μm	35 %	30 %	18 %
Optical contrast between 10 and 25 μm	40	30 %	17 %

the increase of reflectivity (or the decrease in emissivity). The phenomenon is reversible and reproducible for a given sample up to the end of the test (7 days under vacuum pressure of 10^{-5} mbar), indicating that EMITFSI is still present in the IPN. Therefore the ability of PEO/PEDOT IPN devices, without any encapsulation, to allow temperature change has been evidenced under the application of a low voltage in partially space-like environment. Furthermore the device exhibits low energy consumption in comparison with present systems like louvers.

Under normal pressure, the stability of the device is satisfactory since no electroactivity loss is observed during 5,000 cycles at ambient temperature, and 80 % of the electroactivity is kept after 20,000 cycles. However at 60 °C degradation of the device is observed [34]. At 60 °C, 80 % of the electroactivity is lost after 1,500 cycles. This degradation is believed to originate in $\bullet\text{OH}$ radicals from the PEO which in turn induces a degradation of the PEDOT. One among possible solutions is to reduce the quantity of PEO in the ionic conducting matrix. This has been done by combining PEO with NBR in an IPN architecture as the heart matrix of the device [45]. The concomitant improvement of the mechanical properties allowing making thinner films is another asset of this strategy. Moreover the ionic conductivity is not impaired since NBR is polar enough. However when swollen with EMITFSI, the materials exhibit a slightly lower reflectance than their PEO counterparts (see Table 11.2).

The synthetic route which has been used so far for the preparation of ERD is the chemical oxidative polymerization of the conjugated polymer. Therefore in order to improve the electrooptical properties, we have developed a new synthesis route based on the EDOT electropolymerization within the PEO/NBR IPN. The choice of an electropolymerization of EDOT within the PEO/NBR IPN should bring an improved morphology and also a better control of the electrochemical properties of PEDOT. The electrosynthetic pathway leads to a PEO/NBR//PEDOT film instead of a PEDOT//PEO/NBR//PEDOT configuration. Therefore the device was prepared by the dual association of the two new PEO/NBR//PEDOT IPN films joined by a PEO network to favor the association of the two semi-IPNs [43].

A promising reflectance modulation was observed both in the NIR and the MIR regions even if the optical contrasts are lower compared to the chemical oxidation route.

Surely further improvements can be brought to this material which is on its own an electroreflective cell which can be handled without tearing or other damage, and work is in progress therefore.

Actuator Devices

Actuation Mechanism

Conducting polymers have also attracted considerable attention notably because of possible dimensional changes during redox processes. A large amount of evidence has been presented in the literature showing that the reversible expansion during redox switching is the result of mass transfer between the polymer film and electrolyte. Typically ions (and solvent molecules) enter or leave CP film in order to maintain electroneutrality during redox reactions. Therefore, CP can be used as the active material in actuators or artificial muscles and lead to interesting potential applications (robotics, prosthetics, microvalves, etc.) (Fig. 11.4).

Air-working actuators are generally built in a configuration, where the internal layer is a solid polymer electrolyte (SPE) sandwiched between two CP layers (CP//SPE//CP), and the relative differential expansion between conducting polymer layers results in bending [63]. However, when a conductive polymer film is deposited onto a flexible polymer film sputtered with a thin layer of metal, a delamination process which limits the actuator's lifetime is almost always observed. This problem can be overcome if the actuator is designed as a conducting IPN. The IPN matrix is made from poly(ethylene oxide) (PEO) and an elastomer as PB, PTHF, or NBR [25, 28, 30, 33, 36–38, 54, 64–71]. The mechanism of actuation is similar whatever the elastomer used in the C-IPN. After EMITFSI uptake, a strip of C-IPN is subjected to an applied low voltage, typically ± 2 V between the two faces of the actuator film. One conducting layer is connected to the working electrode, whereas the second one

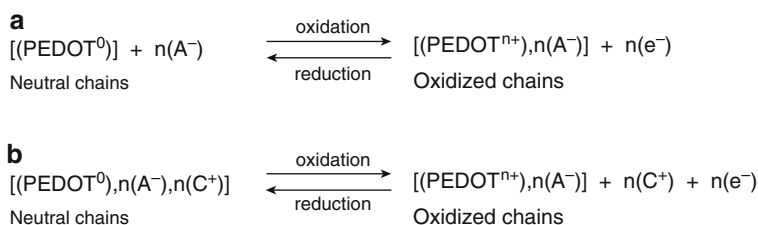


Fig. 11.4 (a) Redox process occurring in the case of mobile anions (A^-) and leading to a volume expansion during oxidation. (b) Redox process occurring in the case of immobile anions (A^-) and mobile cation (C^+), leading to a volume contraction during oxidation

to the short-circuited reference/counter-electrodes. One layer will be reduced (oxidized), whereas the second PEDOT layer will be oxidized (reduced), leading to an increase of volume on one side and conversely a shrinking of the other face. The net result is a bending movement. The direction of the bending movement clearly indicates if the mechanism is mainly governed by cation or anion. Using EMITFSI as electrolyte, the actuation direction corresponds to an increase in volume at the anode and a shrinking at the cathode. These observations indicate the incorporation of EMI^+ in the PEDOT layer in order to balance the negative charge of the nonmobile anion; after that, a positive charge on the PEDOT backbone has been removed. Of course at the anode, the positive charge created on the PEDOT backbone is balanced by TFSI^- , after the expulsion of EMI^+ . This mechanism is called the “nonmobile anion mechanism” or “cation-driven mechanism.” Using more classical electrolyte as LiClO_4 /propylene carbonate, a different mechanism is observed. The actuation direction indicates that a positive charge on the PEDOT backbone is balanced by the incorporation of ClO_4^- ; therefore the “mobile anion mechanism” or “anion driven mechanism” should be considered. Different solvents and salts have been tested as electrolyte, but finally the best actuation performances are obtained with LiClO_4 /propylene carbonate (PC) and EMITFSI. LiClO_4 /PC allows the largest bending at the highest speed compared with EMITFSI. However the main drawback of LiClO_4 /PC electrolyte is the solvent evaporation. For instance, conducting IPN actuator can be cycled only few hours before the bending deformation stops due to PC evaporation. Nevertheless after being immersed again for a few hours in LiClO_4 /PC solution, the actuator fully recovers its working capacity [65], indicating that the solvent evaporation is the main issue for long-time actuation. In order to prevent the evaporation process, EMITFSI has been used as electrolyte since it is a nonvolatile compound. EMITFSI-swollen PEO/PB actuator with a 10Hz square cycling can be operated for 3.5×10^6 times without any degradation and/or delamination in open air. Moreover it could be stored over a period of 6 months without particular precaution and started again thereafter without any sign of weakness [28]. These actuators have also been tested at -20°C and the bending time to display a 60° angular deformation is obtained after 5 min upon 3 V instead 5 s at 30°C . When decreasing the temperature to -30°C , a 60° deflection is observed after 10 min [36]. These results indicate that EMITFSI is not able to crystallize inside the matrix at -30°C , a temperature which is very low compared to that of the melting point (-8°C) of EMITFSI [29].

Robust C-IPN Actuator Devices

As mentioned earlier PEO/NBR IPNs exhibit better mechanical properties than PEO/PB IPNs as matrix for the actuator devices. As seen before the mechanical properties of IPN are mainly ruled by the presence of NBR network while the IPN and the PEO network have almost the same ionic conductivity around 1mS cm^{-1} . Nevertheless both the presence of PEDOT and EMITFSI on the mechanical

Table 11.3 Strain at break (%), tensile strength (MPa), and Young's modulus (MPa) of IPNs and conducting IPNs in dry state or swollen in EMITFSI ionic liquid (134 %)

Materials	Strain at break (%)	Stress at break (MPa)	Young's modulus (MPa)
PEO/NBR	138	1.2	1.2
PEO/NBR + EMITFSI (134 %)	41	0.36	1.02
PEO/NBR/PEDOT	28	5.6	40
PEO/NBR/PEDOT + EMITFSI (134 %)	15	2.8	43

properties needs to be taken into account for applications. The effects of PEDOT interpenetration and EMITFSI uptake on the mechanical properties of the PEO/NBR IPNs have been characterized by tensile strength experiments [30] (Table 11.3).

Swelling in EMITFSI leads to a decrease in the elongation at break and in tensile strength for both IPN and C-IPN. This behavior is assigned to the stretching of IPN chains during swelling leading to a material in a pre-stretched state. No EMITFSI plasticizing effect has been observed since no major change in the Young's modulus has been measured on swollen or non-swollen materials. Finally C-IPNs can be swollen with more than 100 wt% EMITFSI and remain stretchable up to 15 % demonstrating the good mechanical properties of this electroactive material. After EMITFSI uptake a strip of conducting IPN was subjected to an applied voltage of ± 2 V between the two faces of the actuator film. The material presented bending deformations that have been quantified by the calculation of the strain difference $\Delta\epsilon$ [72]. A maximum strain difference of 2.4 % has been measured in free displacement condition and the blocking force (zero displacement) can reach 30 mN. Linear mechanical response versus electrical stimulation or versus EMITFSI content is observed with free strain difference varying from about 0.4–2.4 % and the output force from 10 to 30mN. This result implies that more and more PEDOT is undergoing the redox process and then participates to the actuation as the applied voltage or the EMITFSI is increased. For potential higher than 2 V, free strain and blocking force reach a plateau value indicating that the two electroactive polymer layers have already been fully oxidized and reduced. Then increasing the applied potential over 2 V may increase only the actuation speed. Surprisingly as the EMITFSI uptake increases, neither the free strain nor the blocking force reaches a plateau value. These results seem to indicate that higher actuation responses could be obtained if EMITFSI uptake could be further increased higher than 134 wt% which is the value at saturation.

This material presents high actuation performances as well as high robustness in air and opens ways to further developments and real integration of conducting polymer-based actuators. A specific design of actuators as well as its integration in a first prototype of biomimetic vision system has been performed [69]. The fabrication has been carried out using a masking technique in order to prevent EDOT polymerization in the central part of the film (250 μm thick) which allows the fabrication on two independent actuators on the same material. Tracking tests were

performed using a vision system composed of a microcamera fixed on the central part of the film and a visual perception board from BVS Company. The visual perception board is connected to the microcamera and to the two independent actuators. The vision system position control was done by a closed loop system. During tests, the target is detected and tracked autonomously by the system to remain centered in the camera image just as in biologic vision. The system is able to produce a maximum angle movement of 20° with an angular speed of $4^\circ/\text{s}$. A video of this first visual system prototype can be downloaded at <https://www.youtube.com/watch?v=wjJkpKI8W4>.

However interesting is a bending actuator, probably more interesting would be an actuator endowed with a linear-actuating ability in air with displacement amplitude as high as possible because it would suit more applications in robotics. In order to develop fiber-like linear actuators working in air, still two interpenetrated PEDOT electrodes and one SPE made of PEO/PEO IPN are required. However the main drawback is that the two electrodes display an opposite volume variation during the redox process. Therefore actuators with linear deformations have been developed as hollow fibers according to a design proposed by Smela et al. [73]. The principle is the fabrication of an actuator with two nonequivalent ECP electrodes. One electrode, with a higher quantity of ECP, plays the role of counter electrode and then easily compensates the charges from the other (working) electrode without undergoing significant redox degree changes and thus no significant dimensional or physicochemical modification. The deformation of the working layer is not hindered by the opposite deformation of a counter electrode and can proceed freely. A linear strain of 3 % has been obtained for 1 mm length samples in the presence of LiTFSI/PC as electrolyte. The linear strain decreases to 1 % as the sample length is increased (30 mm) due to ohmic drop along the fiber. An isometric stress of 0.01 MPa (300 mN for a sample weight of 0.4 g) has been obtained. The response time is rather low since the distance between the inner and the outer electrode is quite important, higher than $500\text{ }\mu\text{m}$, and prevents fast ionic transport of electrolyte ions between the electrodes leading to a slow macroscopic response. Nevertheless to our best knowledge, these are the highest values obtained for a linear ECP actuator working in air [32].

High-Speed C-IPN Actuators

ECP-based actuator belongs to the class of ionic actuators due to the presence of solvent/ion when operated. Such actuators present slow responses since actuation mainly results from the redox process of the conducting polymer which is limited by ion diffusion. However, examples of ionic EAPs presenting high actuation frequency have been described. In order to increase the actuation speed, a decrease in the thickness of the actuators has been performed. Indeed since the actuation mechanism is dominated by mass transfer, the actuation is determined by the diffusion rates and distances [74]. Therefore high actuation speeds can be obtained by designing ideal characteristics of the SPE. On the one hand the SPE must exhibit

high conductivity in order to lead to high ion diffusion rate within the matrix. On the other hand, the diffusion distance can be minimized by decreasing the thickness of the SPE. In order to obtain very thin but resistant materials, SPEs combining the PEO network with either NBR or PTHF polymer have been done. The synthesis of thin film forced us to revise the synthetic route. For instance, PEO/PTHF IPNs were obtained via a one-shot in situ method in which the polymerization is carried out under a hot press using thin mold. Then the EDOT monomer is incorporated into the 10 μm thick PEO/PTHF IPNs, but in this case, by gas phase swelling under reduced pressure until a 200 % swelling rate of the film was reached. Next, as usual the samples were dipped into an aqueous solution of FeCl_3 for the oxidative polymerization. This procedure ensures the formation of 3–4 μm surface layers of interpenetrated PEDOT on a 12 μm thick actuator as measured by EDX. After EMITFSI incorporation (140 wt%), displacements were recorded at an applied voltage of ± 5 V at different frequencies. Such high voltage increases the strain rate but should be applied over a short period (<1 s) in order to avoid PEDOT degradation [12]. The strain of the PEO/PTHF/PEDOT actuator decreases as the frequency increases; however, when the frequency reaches 100 Hz, the tip displacement sharply increases with a resonance peak at 125 Hz corresponding to a total displacement of 400 μm at 1,000 μm of the metallic contacts. A similar behavior has been also observed using NBR instead of PTHF. A 90 μm thick PEO/NBR/PEDOT actuator shows a mechanical resonance up to 156 Hz with almost 4 % strain ($\Delta\epsilon$) for an applied potential of ± 5 V. The resonance peak occurs when the actuator is operated near the system's natural frequency, and the resonance frequency is dependent of the geometrical dimensions of the actuators [33]. In these studies resonance frequencies as high as 156 Hz could be reached which were hitherto considered unreachable for ionic actuators.

C-IPN-Based Microactuator

For the development of flapping-wing micro-robots that mimic insect, high-speed microactuator in open air must be created. Previously it was demonstrated that ionic actuators display fast actuation if the SPE is thin enough. However integrating electronic conducting polymer actuators into microsystems is a challenge, and difficulties inevitably arise when it is necessary to microsize these polymers. To address this issue different techniques have been considered and largely reviewed [75, 76]. The first limiting factor is the robustness of CPs and IPNs with respect to etching techniques. For the first attempts, 10 μm thickness of PEO/PTHF IPN matrix has been chosen with two symmetrical interpenetrated PEDOT layers of 3.5 μm thick. Patterning using photolithographic methods requires planar and motionless films. Thus actuators were fixed on a silicon substrate bearing a 5.5 μm PVA layer obtained from spin coating of a 300 g L^{-1} PVA solution. The Megaposit SPR 220 7.0 photoresist was found to be useful in the protection of the actuator prior to dry etching, thus presenting good resistance to the plasma.

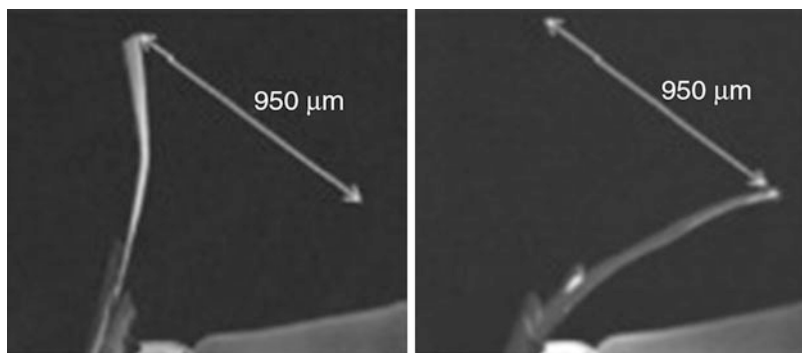


Fig. 11.5 SEM images of PEO/PTHF/PEDOT microactuator ($900 \times 300 \times 20 \mu\text{m}^3$) operating at 10^{-4} mTorr. *Left*: applied potential +2 V. *Right*: applied potential -2 V (From [77])

Dry etching of the conducting polymer was then performed by reactive ion etching (RIE) with O_2/CF_4 plasma at 300 W and 200 mT. It is believed that the degradation of PEO by RIE triggers the etching of PEDOT partner in the conducting IPN [77, 78]. Indeed in the absence of PEO, the PEDOT is hardly patterned. For instance, C-IPN without PEO partner was etched in the same conditions and no measurable etching was detected. This definitely confirms that PEO is the predominant factor in the etching process. The plasma produces a large quantity and variety of radicals that activate the decomposition of PEO which in turn produce oxygenated radicals as HO° which decompose PEDOT [34]. In this case the etching is done essentially by radical species produced directly inside the C-IPN, and the plasma plays a secondary role. It is therefore a process of “self-etching” [77].

This plasma was used to pattern conducting IPN microbeams ($900 \times 300 \times 12 \mu\text{m}^3$) before it was immersed in EMITFSI solution which leads to a final $20 \mu\text{m}$ thick actuator. The actuator was stimulated by a 4 V square input voltage peak to peak at 0.5 Hz in air but also within a scanning electronic microscope. Thanks to the nonvolatility of ionic liquid, actuation properties could be measured in low vacuum (10^{-4} mTorr). Large amplitude of $950 \mu\text{m}$ was observed corresponding to a strain of 1.1 %, a curvature of $1.045 \times 10^3 \text{ m}^{-1}$, and a bending angle of 63° . In our best knowledge, it was for the first time that an actuator was operated successfully in low vacuum. What has been done with PTHF polymer has been also translated to NBR. With this particular plasma etching method, microbeams with very promising amplitudes and frequencies were obtained (Fig. 11.5).

Conclusion

An original way to fabricate self-standing one-piece pseudo three-layer electroactive devices have been described. Indeed due to a particular synthetic method, an electronic conducting polymer (PEDOT) is symmetrically

interpenetrated in the two outer faces of an IPN matrix based on PEO and another nonconducting polymer (PB, NBR, PTHF, PEO), the ionic conductivity being ensured by an ionic liquid (EMITFSI). Thus delamination effects are ruled out by construction and the device is able to work in open air. Under low voltage bias ($\pm 2 - \pm 5$ V), the actuator can exhibit interesting curvatures due to anion or cation movements from one face to the symmetrical one due to oxidation/reduction process of the PEDOT layers. Actuators can undergo symmetrical bending movements from 0.05 to 156 Hz depending on the sample. Reactive ion etching (RIE) with O_2/CF_4 plasma has proven efficient patterning of these C-IPNs, and the subsequent successful integration of microactuators was performed with displacement as high as 950 μm .

Depending on the total amount of PEDOT in the C-IPNs, electrochromic (<0.3 wt%) or electroreflective ($\sim 1-2$ wt%) effects can be also observed with contrasts of $R = 35\%$ and 33% in the middle infrared range or in the visible range, respectively. Thus a very versatile synthetic pathway has been carried out to take advantage of these pseudo one-piece electroactive devices, and improvements in the performances of these devices are in progress.

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Itxaso Azcune, Aratz Genua, Alaitz Ruiz de Luzuriaga, and Ibon Odriozola

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Abstract

This chapter describes the different applications of Poly(ionic liquid)s in nanotechnology, including nanocomposites and nanodevices.

Keywords

Poly(ionic liquid)s • nanotechnology • nanoobjects • polyelectrolytes • nanoparticles • carbon nanotubes • graphene

Introduction

Due to their intriguing properties, poly(ionic liquid)s (PILs) have taken a relevant place among the classical polyelectrolytes, opening the way to new technological

I. Azcune • A. Genua • A. Ruiz de Luzuriaga • I. Odriozola (✉)
Materials Division, IK4-CIDETEC Research Centre, Donostia-San Sebastián, Spain
e-mail: iodriozola@cidetec.es

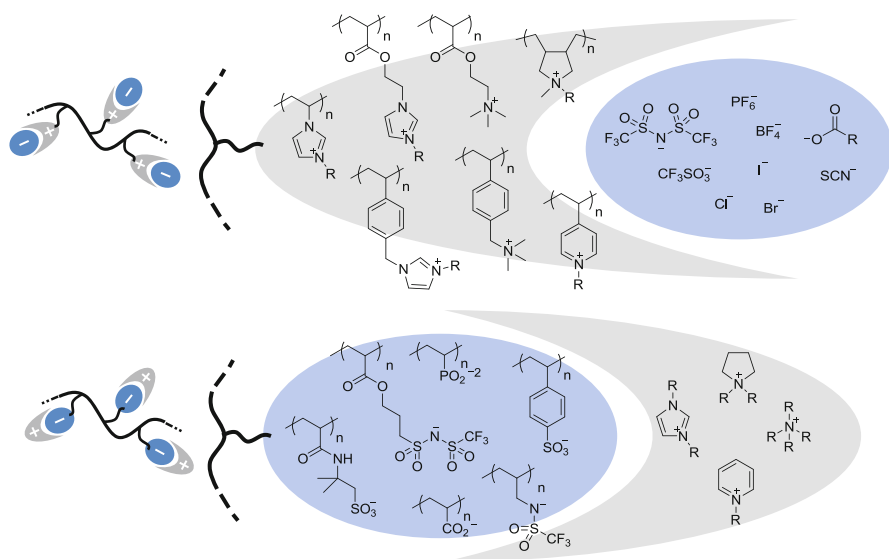


Fig. 12.1 Representative chemical structures of cationic (*top*) and anionic (*bottom*) PILs

applications and procedures in material science. Complete reviews on the synthesis, the physical properties and several applications of PILs have been recently released [1–6]. From the structural point of view, PILs can be considered as polymeric counterparts of ionic liquids (ILs), since they are constituted by IL monomers. The chemical structure of PILs is very broad, due to the variety of cations, anions and side groups available to construct them. Basically, PILs can be classified as being *cationic* or *anionic*, according to the ionic species which is incorporated in the polymeric backbone (Fig. 12.1). Although less investigated, *zwitterionic* PILs have also been reported in the scientific literature [7–10]. Common cations include imidazolium, tetraalkylammonium, pyrrolidinium and pyridinium. Anions can range from inorganics to organics, such as the widely used bis(trifluoromethylsulfonyl)imide (TFSI) (see Fig. 12.1).

Due to their unique structure, PILs retain the chemical versatility featured by IL monomers combined with the spatial controllability, the processability and the mechanical properties inherent of macromolecular materials. As happens with classical polymers, traditional and state-of-the-art polymerization techniques have been pursued for PIL synthesis, leading to both thermoplastic and thermoset materials. In this sense, PILs can also be classified as linear homopolymers, random or block copolymers and cross-linked networks.

Nevertheless, it is not mandatory to start with an IL monomer to construct a PIL. In many cases, either forced by technical or practical reasons, PILs are better prepared by a post-functionalization of a neutral polymer. Thus, there are two major approaches to prepare PILs:

- (a) *Polymerization of IL monomers*: IL monomers carrying a polymerizable chemical unit (typically styrene, acrylate or *N*-vinyl) are polymerized following different techniques, such as conventional radical polymerization, atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), ring opening polymerization (ROP), ring opening metathesis polymerization (ROMP), etc.
- (b) *Quaternization/post-functionalization of neutral polymer precursors*: neutral polymers, such as poly(4-vinylpyridine) or poly(vinylimidazole), are treated with electrophiles to form polyelectrolytes with a range of quaternization degrees. In addition, a subsequent anion exchange step can be considered a post functionalization of PILs.

The pioneering research on PILs has been acknowledged to Hoover in the early 70s [11–13], but it was not until Ohno's contribution in 2000 that PILs gained the attention of the research community [9, 14–22]. Ever since, PILs have been investigated as functional polymers for a wide range of technological applications such as solid ionic conductors, dispersants/stabilizers, absorbents or precursors of carbonaceous materials. In this chapter, the role of PILs in nanotechnology is reviewed, especially focusing on their combination with nanoobjects.

Use of PILs in Nanotechnology

PILs and Nanoobjects

The aim of this chapter is to highlight the different roles that PILs play in the field of nanotechnology, especially focusing on the possibilities that these polymers offer when combined with different nanoobjects. This research field has experienced an important growth in the last few years, as can be observed in Fig. 12.2.

The term nanomaterial or nanoobject refers to materials which present morphological features on the nanoscale (<100 nm), characterized with unique size- and shape-dependent physico-chemical properties [23–26]. They can be of different chemical nature (metals, oxides, carbonaceous or polymeric materials) and they can show a range of geometrical shapes (nanoparticles (NPs), nanotubes (NT), nanosheets, nanorods (NRs), nanorings, etc.). All of them have proven some potential in emerging technological fields of nanoscience, from electrochemistry to biotechnology [27]. However, the implementation of nanomaterials in such technologies involves challenges that still remain unsolved. For instance, full synthetic control over particle size and shape, as well as, strategies to transfer and disperse such nanoobjects into various solvents or polymeric matrices are especially demanding tasks for the development of high quality nanocomposites or blends.

One of the most challenging aspects of nanocomposite processing is rooted on the fact that nanoobjects prepared under certain conditions, are generally not dispersible in any other physico-chemical environment and tend to agglomerate.

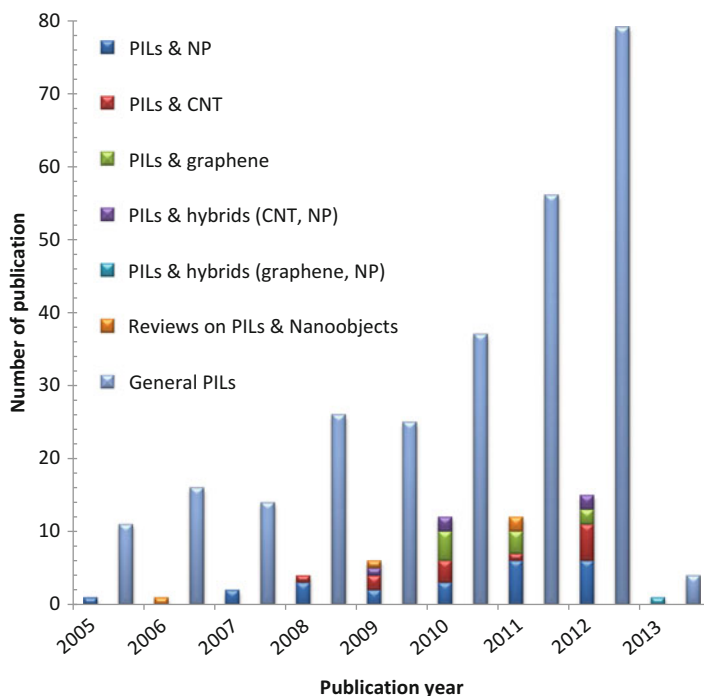


Fig. 12.2 Plot of the number of publications versus publication year obtained searching for “PIL & nanoobjects” and “PILs in general” (Specialized data concerning to “PIL & nanoobjects” was gathered from the ISI Web of Science by looking for two terms on the title of the publication, and then selected. Terms for PILs: “poly(IL),” “polymerized IL,” “IL polymer,” “IL derived,” “IL grafted,” “IL like,” “ionic poly*.” Terms for nanoobjects: “nano*,” “graphene.” Data for general publications on PILs was taken from Ref. [1])

Therefore the use of hydrophobic and hydrophilic dispersants and surface modifiers remains necessary to achieve successful preparation of nanocomposites. As an alternative to classical dispersion agents, such as thiols, amines, sulfonate surfactants or polyelectrolytes, PILs started to emerge soon after the potential of ILs was acknowledged in this field. The rapid swap of their physico-chemical properties by anion exchange entails that a given PIL soluble in certain solvent can precipitate right after combining with the new counter-ion. During the precipitation process, diverse nanoobjects can get trapped in the polymeric matrix and can be dissolved in a new dispersion media [28]. As we will see throughout this chapter, this strategy has been applied successfully for a variety of nanoobjects.

Independently to their ability for trapping nanoobjects, the polymeric counter-parts of imidazolium-based ILs are especially advantageous when it comes to dispersing carbonaceous nanomaterials. During the last decades single-wall carbon nanotubes (SWCNTs), multi-wall carbon nanotubes (MWCNTs) and graphene sheets have attracted much interest for their application in electrochemical devices, sensors and high strength composites, among others. Typically, these materials are

chemically treated with strong oxidant acids to favor their dispersibility in polar solvents and polymer matrices [29, 30]. However, this strategy disrupts long range conjugation networks, decreasing the electrical and mechanical properties of such carbonaceous nanomaterials. As an alternative, Aida and co-workers proved that imidazolium ILs are able to assemble CNTs by π - π interactions between the imidazolium ring and the surface of the CNT, favoring their dispersability [31]. The same or even enhanced physical attraction is observed between carbon nanoobjects and PILs. On the other hand, carbon nanomaterials have also been covalently functionalized with PILs following both “grafting from” [32] and “grafting to” [33] strategies. Covalently attached or physically adsorbed, PILs have provided well dispersed nanomaterials suitable to be employed in low-cost solution processing techniques such as spraying, drop-casting and dip- or spin-coating.

Another inherent property of PILs that makes them stick out from the classical polymers is their ability to act as compatibilizers. The clearest example is found when PILs are combined with IL electrolytes in electrochemical devices. Sometimes, ILs are combined with conventional polymers to obtain gel-type electrolytes, but those blends often suffer from phase-separation problems. The ionic character of PILs ensures full compatibility of the materials. Moreover, electrodes can be modified with PILs to enhance their wettability with ILs. As a matter of fact, a high performance supercapacitor was constructed by incorporating a PIL-modified reduced graphene oxide (RGO) electrode [34]. PIL/RGO shows good compatibility with the IL electrolyte, thereby increasing the effective electrode surface area accessible to ions. Besides, due to their high stability, PIL-coated CNTs can also be efficiently used to modify electrodes for direct electrochemistry and biosensing applications. Similarly, graphene has been shown ideal for biosensing applications due to their large specific area, excellent electrical conductivity and the ability to promote electron transfer reactions. Based on this, various redox proteins or enzymes have been coupled with PIL-functionalized graphene to construct modified electrodes applicable in direct electrochemistry, or in the production of third generation electrochemical biosensors [35, 36].

Apart from acting as dispersants or compatibilizers, PILs can also be used as non-covalent binders for other type of materials to construct functional hybrid materials and composites. For instance, PILs have been employed to attach conductive polymers such as polypyrrole (PPy), polyaniline (PANI) and poly (3,4-ethylenedioxythiophene) (PEDOT) over the surface of CNTs or RGO [37–39]. The PIL plays a dual role by increasing the solubility of these nanomaterials in organic solvents and proving effective anchoring sites to bond with polymer chains. Besides, PILs can replace water-soluble dispersants, typically employed to prepare colloidal dispersions of conductive polymers, avoiding any residual water that may damage the final electrochemical device.

Carbon nanomaterials are useful supports for metal NP due to their high surface area, electrical conductivity and chemical stability. This is important because naked NPs tend to aggregate to form bulk metal, resulting in a dramatic decrease of their catalytic activity. Therefore, it is convenient to immobilize the metallic NPs on

suitable supports, such as CNTs. As a matter of fact, hybrid systems composed of metallic NPs/PIL/CNT have been reported to show good electrocatalytic activity in fuel cells and potential application in advanced sensors [40–42]. Apart from keeping the structural integrity of the CNT, the PIL allows to obtain smaller size and more uniform distribution of NPs during the synthesis, which contributes to high catalytic activity and lower cost. The stabilization of metal NPs by imidazolium ILs is assisted by electrostatic factor and oxidative coordination of the *N*-heterocyclic cation to the low valence metal center. In the case of PILs, the stabilization can be enhanced by steric effects due to their polymeric character.

All this information is further developed in the coming sections devoted to carbonaceous, metal, metal oxides and miscellaneous systems which comprise various nanoobjects. Each of these sections starts with a short introduction to the nanomaterial, to provide the reader with the necessary background to understand the new opportunities that PILs have already offered to nanotechnology.

Carbonaceous Nanoobjects

Carbon Nanotubes (CNTs)

A CNT could be described as “a sheet of graphene rolled into a tube.” CNTs are comprised of continuous cylinders of graphene with opened or closed ends. When all the carbon atoms in the CNT except the ones in the end are bonded in a hexagonal lattice, then the CNTs are considered perfect CNTs. On the other hand, the fact of containing pentagons, heptagons and other kind of imperfections in the sidewalls entails defects in mass and inferior properties [43]. CNTs can be classified as SWCNTs, with diameters ranging from 1.0 to 1.4 nm (depending on the synthesis procedure), or MWCNTs, formed by 2–30 concentric graphitic layers with diameters that go from 10 to 50 nm [24, 44–47]. MWCNTs were accidentally discovered by Iijima [24] in 1991 as a by-product of the synthesis of fullerenes by the electric arc-discharge procedure. Two years later, SWCNTs were discovered [46], which are currently considered close to ideal CNTs. However, the former are still attractive from an industrial point of view, on account of their superior chemical stability and mechanical strength [48]. Since then, the number of research publications and patents regarding CNTs has increased considerably, as well as their production.

Due to their unique thermal, electrical and mechanical properties, CNTs are very interesting materials for a great variety of applications [49]. As an individual, CNTs may present some inherent properties such as a high aspect ratio, high tensile strength, low mass density, high heat conductivity, large surface area, and excellent electronic behavior. On the other hand, when a large amount of CNTs are combined, they can form different structures (ropes, fibers, papers, thin films, etc.) with their corresponding characteristic properties. Besides, since they can be modified by several methods, CNTs can be specifically designed and synthesized for each potential application [50]. They can be used as near-field microscope

probes [51, 52] owing to their high mechanical strength and the possibility of functionalizing them (they can be used for chemical force microscopy). They can act as very good field emitters [53] (presently employed for flat panel displays, for example). Thanks to their electrical conductance and its susceptibility to any variations in the chemical composition of the environment, CNTs can be utilized as chemical sensors [54–59] offering a higher sensitivity, selectivity, simplicity, smaller size devices, and the possibility to work at room temperature, in comparison with standard devices. Their morphology and size, their electronic properties, as well as their mechanical strength, make them excellent catalyst supporting materials [60–64]. Additionally, they can also be applied in electrodes (both, for optically transparent electrodes and for lithium ion batteries), for supercapacitors [65–67] (unmodified CNTs, metal/CNTs or polymer/CNT composites), as part of electronic components [68–77] (nanowires, transistors, switches), for biomedical applications [78–85], mechanical applications etc. CNTs also show great adsorption properties, making them interesting materials for future applications in, for example, gas storage (hydrogen [86–97] and others [98, 99]), gas separation [100–102] or adsorbents for preparing filters and membranes (for small molecules or for viruses and bacteria) [103–106].

Processing of CNTs is also something to be ameliorated in order to advance in their applications. Their low solubility and their proneness to agglomerate [107] limit the use of CNTs, since their mechanical and electric properties result seriously deteriorated. With the aim of solving this limitation, and taking advantage of the properties of CNTs for their many possible applications, several approaches have been pursued: (a) oxidizing them either with nitric or sulfuric acid [29, 30]. This technology considerably diminishes the intrinsic properties of CNTs by disrupting long range conjugation networks. (b) Covalent functionalization [25, 108, 109] of the CNTs. This technique changes their electronic structure and, thus, reduces their conductivity. (c) Non-covalent attachment of solubilizing units [110, 111] such as polymers, biomolecules, or ionic or nonionic surfactants. This is a procedure that improves the solubility of CNTs without changing their genuine properties.

Lately, ILs have been used to functionalize CNTs and make them dispersible in water and organic solvents. Aida and co-workers found, by chance, that grounding a set of CNTs into ILs they were somehow straighten out and gave a network structure. They explained this as a result of the π - π stacking interaction between the imidazolium ring and the surface of the CNT [112]. Taking this into consideration, this kind of ILs could be used for the modification of the surface of CNTs without altering the π -conjugated nanotube structure and using no solvent. The same group also found the possibility of synthesizing a new class of soft material, electroconductive and with stronger mechanical properties. These materials were formed by modifying a SWCNT with an imidazolium type PIL. Such composites, were named “bucky plastics” [113].

In the following paragraphs, the latest research contributions and new applications for these PIL/CNT hybrids are reviewed (Fig. 12.3).

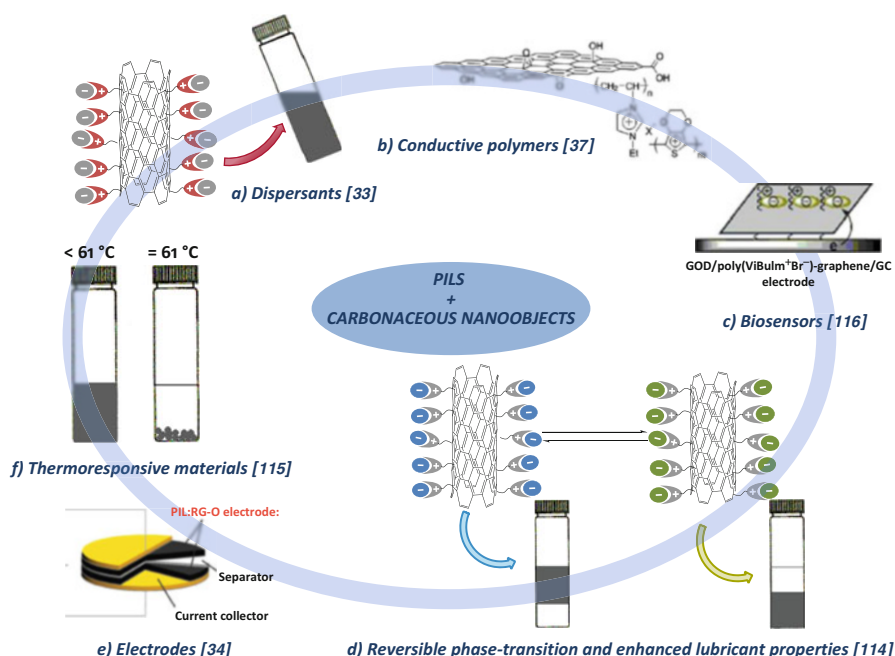


Fig. 12.3 Examples of applications of PIL-modified carbonaceous nanoobjects

Dispersants

Zheng and co-workers managed to disperse MWCNTs in water [114] by simply sonicating them in the presence of poly(1-glycidyl-3-methylimidazolium chloride). The dispersions were found to be better when sonication was carried out under acidic conditions. By using an imidazolium-based PIL, new interactions were introduced between the CNTs and the polymer, such as electrostatic repulsion and cation- π interactions, favoring the dispersion.

With the same goal of preparing dispersions of CNTs, Ma and co-workers used poly(pyridinium salts) with various rigid aromatic moieties, for dispersing SWCNTs in dimethyl sulfoxide (DMSO) [115] via non-covalent coagulation, and studied the chemistry and morphology of the newly prepared composites.

Suh and co-workers also made use of non-covalent covering of CNTs [116] with PILs derived from 3-ethyl-1-vinylimidazolium bromide. This new composite showed good dispersibility in water. An anion exchange reaction with a more hydrophobic anion (TFSI) made the composite dispersible in different organic solvents (acetone, propylene carbonate, dimethyl formamide, tetrahydrofuran, *N*-methyl-pyrrolidone and nitromethane).

Gournis and co-workers functionalized MWCNTs with poly(4-vinylpyridine) (P4VP) which was further quaternized with bromoethane [33]. The use of a PIL for the formation of the composite instead of the P4VP polymer, lead to an enhanced dispersibility in water.

Lin and co-workers intended to enhance the photovoltaic performance of ILs based dye-sensitized solar cell (DSSC) by incorporating MWCNT to the 1-methyl-3-propylimidazolium iodide (PMII) IL solvent. Initial testing showed that pristine MWCNT in PMII tend to agglomerate. Therefore, MWCNT/poly(1-[(2-acryloyloxy)ethyl]-3-methyl-benzoimidazol-1-ium iodide) was fabricated through “grafting from” method using MWCNT-Br as initiator. The new composite showed good dispersion in PMII [32], thus, improving the photovoltaic performance of IL based DSSC.

Conductive Polymers

Conductive polymers are difficult to process because they are not soluble in common solvents and typically aqueous colloidal dispersants are used instead. However, the presence of residual water damages the integrity of the final electrochemical device. Therefore, strategies to obtain conductive polymers dispersions in organic solvents are required. PILs derived from 3-ethyl-1-vinylimidazolium salts have shown to be ideal as templates for the dispersion of conducting polymers [38, 39].

Suh and co-workers improved the dispersibility of SWCNTs in propylene carbonate by functionalizing them with poly(3-ethyl-1-vinylimidazolium TFSI). Then, they managed to polymerize (3,4-ethylenedioxy thiophene) (EDOT), a conducting polymer [117] in the obtained SWCNT/PIL dispersion, substituting the common water solvents.

On the other hand, Samuelson and co-workers reported the synthesis of a water-soluble CNT/conducting polymer composite via grafting from of poly(*N*-methylethynylpyridinium triflate) on SWCNTs [118]. These new composites were easily solubilized in water and showed a high electrical conductivity, making them interesting for the synthesis of nanocomposite films with highly selective permeability.

Biosensors

PIL-stabilized CNTs have been used in electrochemistry and biosensing due to their unique physical and electronic properties. More importantly, PILs are good matrices for redox protein immobilization on CNTs' surfaces since their bioactivity is not damaged.

Chen and co-workers developed a new biosensor based on CNTs functionalized with poly(3-ethyl-1-vinylimidazolium bromide) as promising composites for direct electrochemistry and biosensing of redox proteins [119]. The hybrid material was easily dispersed in water and showed improved electrocatalytic activity towards O₂ and H₂O₂, comparing to pristine CNTs and the mixture of IL monomer and CNTs. This PIL/CNTs composite was used to modify glassy carbon (GC) electrodes where, later, glucose oxidase (GOD) was immobilized. Following this procedure, a new biosensor was obtained, combining both, the great physico-chemical properties of CNTs and the good biocompatibility and unique ionic properties of PILs. The prepared biosensor (GOD/PIL/CNT/GC electrode) showed good analytical performance for glucose, good stability and selectivity.

CNTs have also been investigated as support for gas sensors, due to the fact that their electrical properties can be significantly altered by the existence of trace levels of gas analytes. Nevertheless, pure CNTs are not sensitive enough towards weak Lewis acids or bases (CO_2 , CH_4 , and H_2). For that reason they need to be functionalized in order to increase their sensitivity and enhance their selectivity. Jin and co-workers developed a very sensitive CO_2 sensor using poly(1-(4-vinylbenzyl)3-methylimidazolium tetrafluoroborate)-wrapped SWCNTs [120]. For this purpose, they just grinded the SWCNTs together with the PIL solution and then, sonicated the mixture. The suspension was then drop-deposited onto a patterned Si/SiO₂ electrode. The sensor had an excellent selectivity towards CO_2 , a low detection limit of 500 ppt and appeared to be resistant to the interference of relative humidity.

Lubricants

Hao and co-workers used poly(1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium hexafluorophosphate) modified MWCNTs for dispersing them in different solvents by just changing the anion of the PIL [121]. Besides, they could observe that this combined compounds improved the friction coefficient and the antiwear properties of base lubricant 1-methyl-3-butylimidazolium hexafluorophosphate. A possible explanation for this effect could be the above mentioned improved dispersibility as well as the “rigid CNT core-flexible PILs shell” structure that acts as a roller between two sliding surfaces.

Membrane Actuators

Ionic polymer/metal composites (IPMC) made of ionic membranes, metal electrodes and inner solutions, are very interesting materials for the synthesis of sensors and actuators for biomedical applications. The combination of PILs with MWCNTs gives IPMCs with higher ionic conductivity and enhanced mechanical and electrical properties. Ma and co-workers prepared poly(vinyl alcohol)/poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PVA/PAMPS) membranes strengthened with MWCNTs to be used as IPMC membranes and investigated their deformation behavior [122]. The thermal stability of these membranes seemed to improve by increasing the PAMPS content, as well as the water uptake, the ionic exchange capacity and the ionic conductivity.

Xie and co-workers also studied a combination of CNTs and ionic polymer to synthesize a new IPMC with enhanced properties [123]. They coated both sides of a MWCNT/poly(vinyl alcohol)/poly(sodium 4-styrenesulfonate-*co*-acrylic acid) (MWCNT/PVA/PSA) blend membrane with PSA-g-MWCNT-diaphragms. The so-formed structures presented good applicability as electrodes in substitution of the usual metal layers, due to their very attractive characteristics, such as lightweight, low cost, large mechanical output, and long life.

Graphene

Graphene can be considered as a two-dimensional nanostructure which is composed by a unique layer of carbon atoms in a hexagonal lattice [124]. Graphene is a new kind of nanomaterial which presents singular thermal, mechanical and

electronic properties that make it suitable for a large number of different applications [35, 36, 125–128]. Among these applications are electronic devices, ultrasensitive chemical sensors, nanocomposites and energy storage materials to mention a few.

Considering that graphite is formed by piled graphene sheets, one of the most straightforward and common techniques for synthesizing graphene in a large scale is the exfoliation of graphite (a low-cost and easily available material) in the liquid phase. Chemical reduction of exfoliated graphene oxide (GO) has also been a much employed technique for the synthesis of graphene sheets. The problem with graphene, as it happened with CNTs, is that they are prone to form aggregates. Thus, the challenge is always to obtain non-aggregated graphene sheets in order to keep their unique properties unchanged.

The above mentioned tendency to form agglomerates, may limit the broad field of applications [129, 130]. For this reason, several procedures have been investigated to achieve a good dispersion of graphene sheets either before or during their synthesis: pH-controlled reduction, stabilization by various polymeric surfactant or dispersants, or other covalent/non-covalent functionalizations, for example. At this point, ILs [131–135], and PILs have been considered as a good alternatives for such functionalization. Following this approach, a new kind of nanocomposites is obtained combining the advantages of graphene with those of PILs: hydrophobicity of graphene would not be a problem anymore and, in addition, its dispersibility could be tailored for different solvents by only changing the anion of the PIL.

These new graphene/PIL nanocomposites can be used for different applications (Fig. 12.3). Henceforward, applications for these hybrids are reviewed.

Dispersants

A good dispersion of graphene sheets would facilitate the use of inexpensive solution processing methods such as drop-casting, spraying, and dip- or spin-coating, to synthesize graphene-based materials. Suh and co-workers [136] synthesized phase transferable graphene sheets using poly(3-ethyl-1-vinylimidazolium) salts and taking advantage of their changeable solubility by a simple anion exchange.

Han and co-workers managed to disperse graphene sheets in 1-butyl-3-methylimidazolium hexafluorophosphate for the first time, with the aid of a poly(3-butyl-1-vinylimidazolium chloride) [137]. The PIL presented strong π - π interactions with graphene sheets and, in addition, good solubility in the chosen IL. These dispersions were very stable and enhanced the conductivity of the ILs in a significant way (may be due to the excellent electronic transport property of graphene sheets), making them interesting candidates for a large variety of possible applications (solar cells, lubricating materials, energy-storage, catalysis, etc.).

Conductive Polymers

When graphene is synthesized via a chemical exfoliation method, important quantities of RGO are obtained as a by-product. This RGO is similar to graphene, but has some oxygen groups and structural defects, and can be used for a wide variety of

applications. However, their conductivity may be limited due to the above mentioned defects. A good method for obtaining an improved charge transport within or between the RGO platelets could be hybridizing them with conducting polymers. In order to achieve this, it is absolutely necessary to have the RGO platelets well dispersed. Decoration of RGO with PILs offers a unique alternative to obtain good dispersabilities.

Suh and co-workers used poly(3-ethyl-1-vinylimidazolium) derived salts for modifying RGO platelets and stabilize their dispersions in organic solvents. Such functionalization provided the RGO surface with an effective linkage for further polymerization of PEDOT [37]. The obtained hybrid material has application in optoelectronic devices, especially when transparency, electrical conductivity and stability properties are needed.

Han and co-workers prepared stable water dispersions of a graphene/PANI composite thanks to a previous functionalization of graphene nanosheets with poly(3-butyl-1-vinylimidazolium) chloride/peroxydisulfate [138]. The chosen PIL based on chloride anions was first adsorbed on the surface of graphene sheets (PIL/G), stabilizing their dispersion in water. Then, the chloride anions were exchanged by a simple metathesis reaction with ammonium peroxydisulfate to give the peroxydisulfate-based PIL (PIL/G/S₂O₈), which would be able to initiate aniline's polymerization reaction. The so-fabricated graphene/PANI composite had a higher electrical conductivity than that of PANI and its aqueous dispersion could be used for microelectronics, energy storage, electromagnetic shielding devices, and anticorrosion coatings.

Biosensors

Graphene has a large specific area and excellent electrical conductivity, which makes it very attractive for biosensing applications, since it can enhance the performance of biosensors. Graphene, when used as an electrode material, has also the ability to favor the electron transfer reaction [126, 127]. Considering this fact, different electrodes have been made either for direct application in electrochemistry or for the fabrication of third generation electrochemical biosensors, just by coupling redox proteins or enzymes with graphene [35, 36].

For instance, Zhu and co-workers used poly(diallyldimethylammonium chloride) to modify graphene and help in its dispersion [36]. After functionalization, these PIL/graphene nanosheets were combined with an IL in order to synthesize a new nanocomposite with very good conductivity, biocompatibility and solubility. Such nanocomposite presented an increased redox protein loading capacity, what made it applicable for the fabrication of electrochemical biosensors. As a matter of fact, they were able to prepare a biosensor which presented a fast direct electron transfer of hemoglobin and a very good analytical performance in the determination of nitrite with a wide linear range and low detection limit.

Moreover, Song and co-workers [129] modified graphene with poly(3-butyl-1-vinyl imidazolium bromide) to create a new nanocomposite. The nanocomposite not only did not have the unwilling hydrophobicity of graphene, but also rendered a

positive charge in water solutions making it easier the immobilization of glucose oxidase afterwards through self-assembly under soft conditions. The synthesized electrode demonstrated to have a good electrocatalytic performance to glucose with high sensitivity, wide linear range and good stability.

Similarly, Zhao and co-workers [139] prepared a composite made of poly(3-ethyl-1-vinylimidazolium bromide) and graphene, to immobilize cytochrome c (Cyt c) on graphite electrode. The so constructed biosensor had a very good electrochemical activity for the detection of NO, showing a wide linear range and low limit of detection.

Electrodes

Suh and co-workers again, reported the fabrication of a high-performance supercapacitor based on poly(3-ethyl-1-vinylimidazolium TFSI)-modified RGO electrodes and an IL electrolyte 1-ethyl-3-methylimidazolium TFSI [34]. These hybrid materials were propitious for supercapacitor applications, since they ought to augment compatibility of RGO with ILs and the accessibility of IL electrolyte ions into the RGO electrodes.

Stimuli Responsive Materials

Antonietti and co-workers reported the synthesis of a thermo-responsive poly(tetrabutylphosphonium 4-styrenesulfonate) (PTPSS) which was used to modify graphene sheets [140, 141]. PTPSS shows the ability to produce stable water dispersions of graphene and, due to its thermal-responsive behavior offers the possibility of changing the dispersion state from exfoliated to stacked-agglomerated at a given temperature, depending on the concentration of the polymer and the ionic strength in the solution. Thus, this modified graphene could be used for sensing temperature and ionic strength in solution.

Metal and Metal-oxide Nanoobjects

Metal NPs have received considerable attention in the last years due to their unusual properties and promising applications in electronics, photonics and biochemical sensing and imaging. However, metal NPs are kinetically unstable with respect to agglomeration to the bulk metal and must therefore be stabilized by additives. PILs have demonstrated to be very appropriate for imparting such stabilization. PILs present a different set of solubility parameters compared to conventional polymers [142–144], and can be structurally tuned to influence metal-polymer or metal-counterion interactions. A number of imidazolium-based polymers have been reported as excellent stabilizers for metal NPs [143–148].

PILs have also been used as vehicles for the phase transfer of different nanoobjects such as metal NPs and NRs [28]. The phase transfer approach has been based on the anion exchange-induced precipitation of a cationic PIL in an aqueous dispersion of the corresponding nanoobject. It was observed

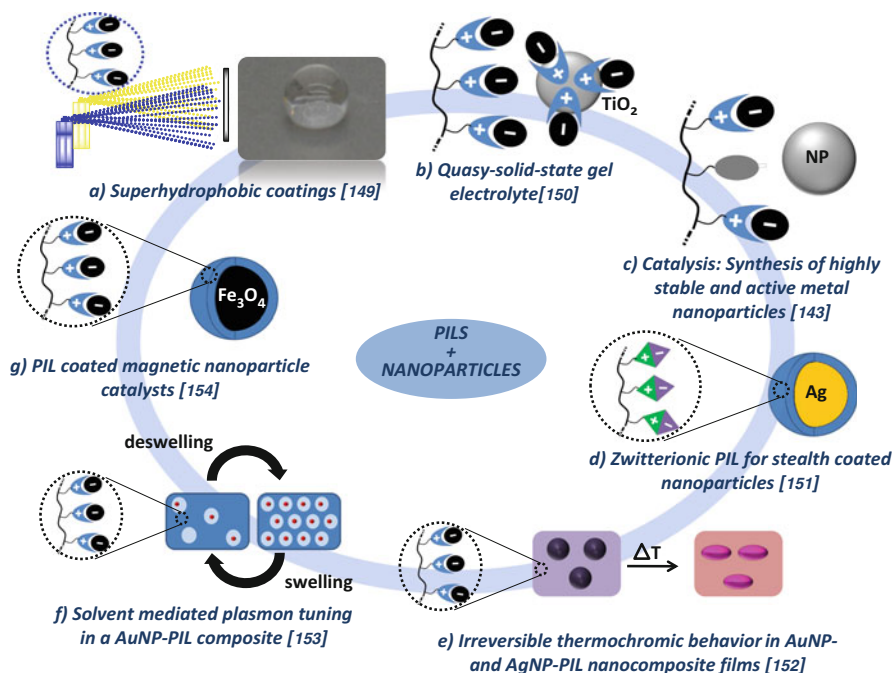


Fig. 12.4 Examples of applications of PIL modified metal and metal oxide NPs

experimentally that the PILs are able to trap quantitatively the nanoobjects during their precipitation forming PIL/nanoobject nanocomposites. Besides, due to the subsequent solubility of the PIL into organic solvents, stable dispersions of NRs or NPs could be obtained. Since the anion exchange process is reversible, it is possible to make the PIL hydrosoluble again, making again the nanoobject dispersible in water.

Therefore, by combining the properties of both PILs and NPs, a variety of materials for different applications can be obtained (Fig. 12.4). Some of them are listed below:

Coatings

Mainly inspired by nature, super- or ultra-hydrophobicity is currently the focus of a large amount of research owing to its scientific and technological importance. Industrial applications include self-cleaning surfaces (for windows and facade paints), anti-graffiti paints, coatings that prevent snow or ice from sticking to antennas, containers that are easier to clean and biomimetic and biocompatible surfaces [149]. Different methods have been developed to obtain biomimetic superhydrophobic surfaces, which generally rely on the creation of rough micro and nanostructured surfaces covered with low surface energy molecules [150–152].

Recently, Mecerreyes et al. [153] prepared superhydrophobic coatings (water contact angle $>150^\circ$) by simultaneous spraying of oppositively charged polyelectrolytes and NPs with a home-made spraying system. Poly(3-ethyl-1-vinylimidazolium TFSI) was successfully used as a fluorinated polyelectrolyte alternative to Nafion. For getting superhydrophobic thin films fumed silica NPs and clay NRs were introduced into the polyelectrolyte multilayer films.

Catalysis

One of the main issues when using homogeneous catalysts in industry is the difficulty for separating the catalyst from the reaction mixture, or separating the product from the catalyst continuously. Heterogeneous catalysts overcome this problem because of their facile separation and recycling [154, 155], but they show lower activity. A rational choice in order to obtain a highly active heterogeneous catalyst is immobilization of homogenous catalysts on a variety of insoluble support materials.

ILs have found unusually broad potential application in catalysis, due to their negligible vapor pressure, high thermal stability, and powerful solvation capability. They can be used either directly as a catalyst to accelerate the reaction kinetics or indirectly, as an alternative reaction media for many organic and inorganic substances. The freedom to choose the cation and anion and their tunable miscibility with organic compounds facilitate the recycling and reuse of IL catalysts. The potential of PILs as catalysts has not been fully explored yet. Some groups attempted to exploit PILs as heterogeneous catalysts to replace IL-grafted solid systems. At the moment, the potential of PILs in catalysis focuses on their use as a (co)catalyst, catalyst supports, or catalyst precursors. In this section, the role of PILs as a metal NP support and (co)catalyst will be analyzed.

Kou et al. [143] described the synthesis of highly stable and active Rh NPs as heterogeneous catalysts. The so-obtained Rh NPs were stabilized by poly(*N*-vinyl-2-pyrrolidone)-*co*-(1-vinyl-3-butylimidazolium chloride). They demonstrated that such NPs showed unprecedented lifetime and activity in arene hydrogenation. Later, Dyson et al. reported a new PIL-stabilized Pt NPs in ILs [156] as effective catalysts for selective hydrogenation of aromatic chloronitro compounds to aromatic chloramines.

An interesting application of PILs is their use as nanoreactors for the generation and immobilization of metal NPs that could act as catalysts [157]. Yuan et al. reported the synthesis of spherical polyelectrolyte brushes, by photo-emulsion polymerization with a solid polystyrene core onto which chains of vinylimidazolium-type PILs were densely grafted. The as-synthesized brush particles were employed to generate homogeneously embedded Au and Pd NP/PIL nanocomposite which efficiently catalyzed the reduction of 4-nitrophenol in the presence of sodium borohydride.

In a first article Dyson et al. developed highly stable Pd NPs, protected by an imidazolium-based PIL in a functionalized IL [158]. In their work, the NP/PIL/IL-based catalyst was synthesized all-in-one. Poly(3-(4-vinylbenzyl)-1-methylimidazolium TFSI) was dissolved in the IL. PdCl₂ reduction in PIL/IL was

carried out with NaBH_4 to obtain the NP/PIL/IL catalytic system. So far, the NP/PIL/IL system can be considered as an alternative for traditional precatalysts such as Pd/C due to its robust nature, water stability, and good activity. Besides to the high activity of the developed NP/PIL/IL catalytic system, the newly developed system required lower loadings of Pd (0.5–1.0 mol%) compared to classical Pd/C systems (2–5 mol%). Later, the same group [159] described the synthesis of Au NP catalysts based on a water soluble PIL. Once again, the role of the PIL in the stabilization of Au NPs was corroborated. They demonstrated catalytic activity of Au NPs in the reduction of *p*-nitrophenol and in the hydrogenation of cinnamaldehyde. In another approach, Dyson et al. [160], reported the application of PIL-stabilized Rh NPs for the hydrogenation of benzene and other arenes in greater detail. Moreover, PILs were evaluated in terms of composition and average molecular weight and compared with poly(*N*-vinyl-2-pyrrolidone) (PVP), a widely used protecting agent [161]. The NP catalysts protected by [poly(NVP-*co*-VBIMCl)] immobilized in ILs could withstand forcing reaction conditions, resulting in high reaction rates and high conversions.

Recently, Pourjavadi et al. [162] reported the synthesis of a new class of acid heterogeneous magnetic catalyst with high loading of homogeneous catalyst on the surface. To achieve that, magnetic NPs were coated with multilayers of PIL functionalized with sulfonic acid and used as catalysts for the chemoselective synthesis of 1,1-diacetyls. Also, the catalyst showed good activity for the deprotection reaction of acylals. One of the main advantages of the newly developed heterogeneous catalyst was that the catalyst could be easily recovered by an external magnet at the end of reaction.

Shang et al. [163] proposed a facile approach for the synthesis of PIL microspheres and their application as potential scaffolds for the immobilization of metal NPs for catalysis. The synthesis of such PIL microspheres was performed *via* emulsion polymerization techniques. In a second step, they carried out the anion exchange of PIL microspheres with a Pt precursor, followed by its reduction to produce PIL/Pt hybrid NPs. Finally, they demonstrated that PIL/Pt hybrid NPs showed better electrocatalytic activity toward the electrooxidation of methanol than pure Pt NPs.

Stimuli Responsive Materials

Considerable research attention has been focused recently on materials that change their structure and properties in response to external chemical and/or physical stimuli. These “smart” or “stimuli responsive” materials can be classified according to the stimuli they respond to, as: temperature, pH, ionic strength, light, electric and magnetic field.

Thermo-responsive materials are smart materials that undergo a transformation due to a change in temperature. Thermochromic, thermotropic, thermoelectric, and shape memory materials are primary examples of thermo-responsive smart systems. Irreversible thermochromic behavior was observed in Au and Ag/nanocomposite films developed by Mecerreyes and co-workers [164]. The authors reported the high temperature irreversible thermochromic behavior

of Au and Ag NR/PIL nanocomposites films, based on a change of the shape of the NR within these composites at elevated temperatures. The synthesis of these new materials was carried out by anion exchange of an imidazolium-based PIL solution containing Au and Ag NRs. It is well established that NRs exhibit two surface plasmon resonance modes. Both experimental and theoretical studies have shown that there is a linear dependence of the longitudinal plasmon wavelength of both Au and Ag NRs upon their length to diameter aspect ratio. Hence, a minor variation in the aspect ratio of the NRs induces distinct color changes. The effect of the temperature was studied in relation to the change on shape and, consequently, color of the Au or Ag NRs within the films. Mecerreyes and co-workers observed two visual thermochromic transitions for Au NRs and up to three for Ag NRs. Such NR/PIL nanocomposites open up new routes in the design of a new generation of irreversible thermochromic nanocomposites.

Another important field of application of PILs in nanotechnology is the design and synthesis of stimuli responsive matrices which permit an external control of the encapsulated nanoobjects. Firestone et al. developed a hierarchically ordered composite in which both structure and optical properties could be reversibly switched. They prepared PIL-containing Au NPs in a single step by UV irradiation of a metal ion precursor [165]. The encapsulated NPs did not leach from the matrix even after long exposure to several solvents. They demonstrated that by controlling the solvent exposure conditions, color tuning of the composite could be readily achieved due to different interaction of encapsulated Au NPs. These new materials could be suitable for use in applications where environmental responsiveness is required.

In order to benefit from the optical and electronic properties of quantum dots (QDs) in practical applications (polymer coating, sensors, optoelectronic devices, etc.), it is mandatory to preserve their size monodispersity [166–169]. Many electronic, optoelectronic, and optical devices require solid state QDs isolated from solutions. Therefore, incorporation of QDs into polymer matrix is an efficient method to enhance the functions of QDs. In this regard, Shen et al. [170] prepared fluorescent cadmium/tellurium/polyurethane (PU) composites in solution by the electrostatic interaction between positively charged imidazolium functionalized ionic PUs and negatively charged CdTe QDs.

Dye-sensitized Solar Cells

DSSCs are attracting both scientific and technological interest over the past decades due to their potential advantages of high-efficiency and low-cost [171, 172]. Overall photoelectric conversion efficiency up to 12 % of DSSCs has been achieved with liquid state electrolytes [173]. However, there are still some practical limitations, such as dye degradation, electrode corrosion, leakage and evaporation of organic liquid electrolytes, which restrict their applications. In this sense different procedures involving the use of PILs have been employed to overcome these drawbacks.

Yan et al. [174] reported the fabrication of high-performance quasi solid state DSSCs using PILs which doped with IL-tethered TiO₂ NPs as an electrolyte. IL-tethered TiO₂ NPs were prepared by tethering 1-methyl-3-[(triethoxysilyl)propyl]

imidazolium chloride to TiO_2 NPs. They demonstrated that the new IL-tethered NP/PIL hybrid electrolytes showed an overall power conversion efficiency of 5.67 % under simulated AM 1.5 solar spectrum irradiation at 50 mW cm^{-2} .

Later on, Chen et al. [175] reported “all solid” DSSCs with alkyloxy imidazolium iodide PIL/ SiO_2 nanocomposite electrolyte and triphenylamine-based metal free organic dyes. They demonstrated that the newly developed “all solid” solar cells attained high energy conversion efficiencies up to 2.7 % and 4.12 % under illumination intensities of 100 and 10 mW cm^{-2} .

Template

PILs have also received increasing attention in recent years due to their capacity to organize NPs in ordered structures with different topologies. Dyson et al. [176] described a facile preparation of various Au NPs, along with dendrimer-like NPs, using a PIL both as stabilizer and as template. Considering that different PILs could form different macromolecular structures by tuning of pH, anion, solvent etc., they demonstrated that the observed shape of the PIL is closely related to the derived Au NPs.

Miscellaneous

Zwitterionic PILs have also been employed for surface modification of NPs, aiming at providing stealthiness for biological applications (drug delivery, diagnostics, biosensing, etc.) [177]. The wrapping of NP core diminishes both, non-specific interactions and fouling properties of NPs against cells and proteins, as well as it enhances biocompatibility and colloidal stability. Poly(ethylene glycol) (PEG) is one of the most popular amphiphilic non-ionic modifier employed for this purpose, and super-hydrophilic zwitterionic polymers, such as poly(carboxybetaine), have emerged as promising alternatives. A recent review compares the pros and cons of PEG and zwitterionic PILs for creating stealth NPs [178]. The main advantages that these new PILs offer over PEG, are the high non-fouling properties and the enhanced stability in harsh conditions (e.g., freeze-drying, lyophilization). These advantages are attributed to the high hydration ability provided by electrostatic interactions and their high hydrophilicity.

Mixtures of Carbonaceous and Metallic Nanoobjects

CNTs are very useful for supporting noble-metal NPs, and metal-NP/CNT nanohybrids have many potential applications ranging from advanced sensors to highly efficient fuel cells [58, 179–186]. However, it is well known that for naked CNTs, there are insufficient binding sites for anchoring the precursors of metal ions or metal NPs, which usually leads to poor dispersion and large metal NPs, especially under high loading conditions [182, 187]. Several routes have been developed for the preparation of NP/CNT nanohybrids. It was reported that imidazolium-based ILs are excellent media for the preparation and stabilization of transition metal NPs with a narrow size distribution [188–190].

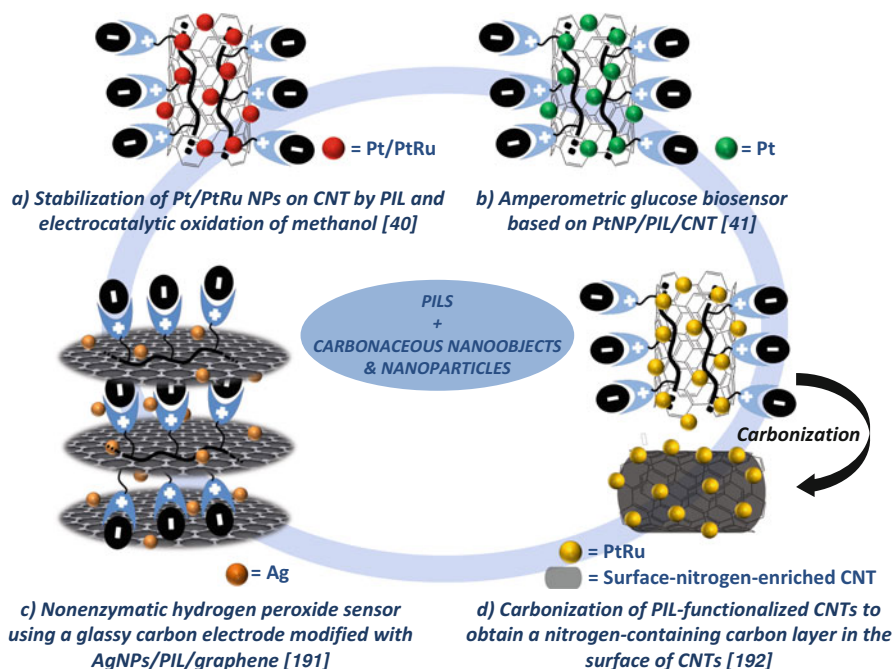


Fig. 12.5 Examples of applications of PIL modified NP/CNT nanohybrids

In the following paragraphs the use of these materials in the field of catalysis, biosensing and electrochemistry is reviewed (Fig. 12.5):

Catalysis

It is well known that high dispersion and small particle size of metal NPs on CNTs are desired for catalytic activity and low cost. However, metal NPs are prone to undergo agglomeration, which results in the rapid decay of their activity.

Recently, Chen et al. reported an alternative strategy to disperse both Pt and Pt/Ru NPs on CNTs covered with a PIL [40]. They polymerized 3-ethyl-1-vinylimidazolium tetrafluoroborate to obtain a film of PIL on the CNT surface, thus providing a large number of uniformly distributed surface functional groups on the CNTs where to anchor and grow metal NPs. These PIL-covered CNTs presented a distribution of positive charge in their surface, thus preventing their aggregation. In this case, the PIL served both as a stabilizer and anchoring site for metal NPs. As a result of the uniform distribution of the surface functional groups provided by the PIL, Pt and Pt/Ru NPs supported on such CNT/PIL hybrids presented a smaller particle size, better dispersion, and higher electrochemical surface area than those having CNTs without PIL modification. The same group also developed a new strategy for the stabilization of metal NPs supported on the CNTs using a film of PIL [191]. In a first step, Pt NPs were dispersed on 1-aminopyrene functionalized CNTs (AP/CNTs) [192]. In a second step, a PIL film was polymerized on the surface of

the Pt NPs/AP/CNTs nanohybrids. Thus, the long-term operation stability of Pt NPs/AP/CNTs electrocatalyst for methanol oxidation was improved by the effect of the thin PIL coating.

Recently, the same authors described one pot synthesis of highly dispersed Pd NPs on acetylenic PIL-functionalized CNTs for the electrocatalytic oxidation of glucose [193]. For the first time CNTs were functionalized with conductive PILs. CNTs were functionalized by polymerization of an acetylenic PIL catalyzed by PdCl_2 which was then reduced and dispersed on CNT in one pot. Finally, they demonstrated that the described Pd NP/PIL/CNT electrocatalyst showed better performance for the electrooxidation of glucose than a conventional Pd NP/CNT electrocatalyst.

In order to develop a new kind of composite materials, Chen et al. [194] also reported carbonization of PIL-functionalized CNTs as support for noble metal NPs. These newly developed nanohybrids successfully integrated the excellent properties of CNTs and unique electric, magnetic, optical, and catalytic properties of noble metal NPs. Surface modification of CNTs was achieved by radical polymerization of 3-ethyl-1-vinylimidazolium bromide. The so-obtained CNT/PIL material was then carbonized in a nitrogen atmosphere at 900 °C to obtain surface nitrogen enriched CNTs (SNE/CNTs). Finally, deposition of Pt/Ru on the SNE/CNTs was carried out via microwave assisted reduction process. Owing to the high surface area and uniform distribution of nitrogen atoms, the supported Pt/Ru NPs presented smaller size, better dispersion and higher electrochemical surface.

Biosensors

Because of their unique physical and electronic properties, CNTs have driven an impressive research effort in electrochemical biosensors [195]. At the same time, precious metal NPs have been widely employed in electrochemical biosensors because of their high ratio of surface atoms with free valences to the cluster of total atoms [196]. Consequently, electrodes modified with Pt NPs have been frequently used to design amperometric enzyme biosensors [197–200]. Some researchers have successfully constructed glucose biosensors using electrodes consisting of CNTs modified with Pt NPs and with GOD as the enzyme model [42, 196–201]. Nevertheless, in order to improve the analytical performance of the amperometric enzyme biosensors, it is still the challenge to highly disperse the metal NPs on the CNT surface.

Detecting the content of glucose in human blood is crucial to the diagnosis and management of diabetes mellitus, which is one of the worldwide health problems. Chen et al. [41] developed a new amperometric glucose biosensor based on Pt NPs/PIL/CNT nanocomposites. The CNTs were functionalized with a PIL through direct polymerization of 3-ethyl-1-vinylimidazolium tetrafluoroborate on CNTs, and then used as the support for the highly dispersed Pt NPs. They demonstrated that the presence of highly dispersed Pt NPs on the PIL/CNTs resulted in electrodes with an excellent electrocatalytic activity.

Guo et al. [202] developed ordered mesoporous carbons (OCMs) coated with PILs as electrode materials for electrochemical sensors and biosensors. OCMs were modified with 3-ethyl-1-vinylimidazolium tetrafluoroborate by in situ

polymerization. The presence of the PIL on the OCM surface provided sufficient binding site to anchor ultra-fine Pt NPs with high dispersion and small particle size. Finally, they concluded that the newly developed electrode could be employed as nonenzymatic H_2O_2 sensors.

Recently, Wang et al. [203] described a nonenzymatic sensor for H_2O_2 based on Ag NPs/PIL covered graphene. They demonstrated that the PIL plays a crucial role to obtain and stabilize individual graphene nanosheets and also serves as the anchoring point for the immobilization of metal NPs.

Lithium Ion Batteries

Considerable efforts have been made to utilize the unique properties of nanostructured carbon materials as energy materials, and tremendous progress has been achieved in developing high-performance energy conversion (e.g., solar cells and fuel cells) and storage (e.g., supercapacitors and batteries) devices [204–207]. A recent article [208] described the synthesis of Fe_2O_3 /nitrogen-doped hollow carbon spheres (NHCS) composite employed as anode material for a lithium-ion battery using PIL as carbon precursor and nitrogen source. PILs have attracted increasing attention for this application since the chemistry of PILs enables tuning the nitrogen content and wall thickness after combustion. In this paper, Fe_2O_3 functionalized porous NHCS were prepared by grafting a thin layer of PIL as carbon precursors onto silica particle surface followed by carbonization and template removal.

Conclusions and Future Prospects

In summary, PILs have shown considerable promise in a variety of nanotechnology applications. The role that PILs play in nanotechnology can be summarized as a functional layer that renders tailored dispersibility, compatibility, phase-transportability and functionality to active nanoobjects. Their compatibility with nanomaterials of high technological interest, such as CNTs, graphene and metallic NPs, and formation of high-valued nanocomposites considerably extend the range of technologies where PILs can be used. Throughout this chapter we have shown that PILs have been extensively investigated in electrochemical devices as electrode material. Smart-materials, such as irreversible thermoresponsive materials and superhydrophobic coatings have also been developed by combining them with active NPs. Even in the less explored biomedical field, PILs have shown promising potential that overcomes current existing limitations.

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Kari Vijayakrishna, Kasina Manojkumar, and Akella Sivaramakrishna

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Abstract

Due to their unique yet tunable properties, “ionic liquids” are widely used as solvent and/or catalysts in many organic reactions. From the past two decades, there are increasing literature reports on the usage of ionic liquids (ILs) even in the polymerization chemistry as solvent, cosolvent, initiator, catalyst, or metal-complexing ligand. IL-mediated polymerization offers faster rates, higher molecular weight polymers, good yields, easy separation of products, and recovery and reuse of catalyst over conventional organic solvent-mediated polymerization process. In this chapter, we discussed various ILs (literature reported)

K. Vijayakrishna (✉) • K. Manojkumar • A. Sivaramakrishna
Organic Chemistry Division, School of Advanced Sciences, VIT University, Vellore, India
e-mail: kari@vit.ac.in

that were employed as solvents and/or catalysts in different kinds of polymerization reactions and their advantages, influence on polymer properties, recovery, and polymerization kinetics.

Keywords

Ionic liquid • Ionic liquid as solvent • Ionic liquid as catalyst • Polymerization in ionic liquid • Enzymatic polymerization • Radical polymerization • ATRP • Reversible Addition Fragmentation Chain Transfer Technique (RAFT) • Ionic polymerization • Catalyst recycling

Introduction

Since, the past decades, ILs attracted considerable interest as alternate solvents over conventional organic solvents for a wide range of applications because of their versatile properties such as nonvolatility, nonflammability, high thermal and chemical stability, wide electrochemical window, moderate polarity, non-coordinating nature, non-toxicity, being environment friendly, and reusability. ILs have been reported in catalysis as – the catalyst, cocatalyst, and catalyst activator – the source of a new ligand for a catalytic metal center or just as a solvent medium for the reaction. As most of the ionic liquids are miscible in polar/nonpolar organic and inorganic solvents, catalysts (inorganic or organometallic compounds), monomers, and the polymers in appreciable amount, the significance in polymerization reactions is very high. ILs have been used extensively as solvents in different kinds of polymerization.

In this chapter we discuss various IL-mediated polymerization reactions such as radical polymerization, cationic polymerization, anion polymerization, coordination polymerization, condensation polymerization, and enzymatic polymerization. This chapter represents a summary from the most relevant results of the literature reports up to date. The final part of this chapter dealt about the study on IL-catalyzed polymerization reactions.

Radical Polymerization in ILs

For the first time, Rogers et al in 2002 used [BMIM][PF₆] as solvent for conventional free radical polymerization of MMA and styrene using Azobisisobutyronitrile (AIBN) initiator [1]. Polymers synthesized in IL media were of high molecular weight with high percentage conversion compared to the polymers synthesized in traditional organic solvents and bulk (Fig. 13.1). This observation could be attributed to the “diffusion control termination” because of high viscosity of ILs and solubility issue of monomers and resulting polymers in ILs [1]. The effect of ILs on MMA radical polymerization kinetics was studied through pulsed laser polymerization (PLP), and the study revealed an increase in propagation rate (k_p) and decrease in termination rate (k_t) with an increase in IL concentration (see Fig. 13.1) [2, 3]. For instance, relatively a double-fold increase of propagation

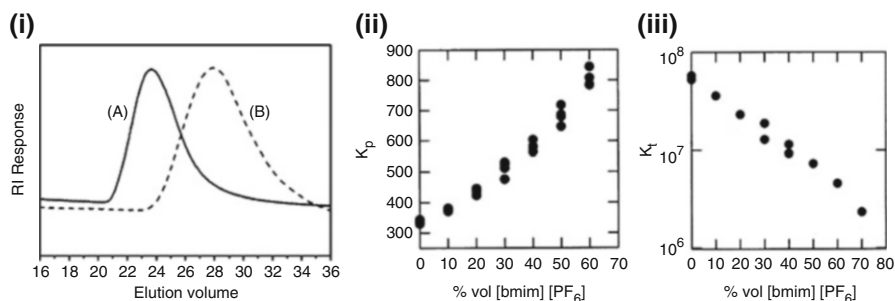


Fig. 13.1 (i). Size exclusion chromatography (SEC) traces of PMMA (A) polymerized using AIBN in [BMIM][PF₆] at 65 °C for 1 h (b) and polymerized using AIBN in benzene at 65 °C for 1 h [1]. (ii). Effect of ionic liquid concentration on propagation rate constant k_p (a) and termination rate constant k_t [2] (iii) of MMA in the radical polymerization at 25 °C [3]

constant in 50 volume % of [BMIM][PF₆] was observed for MMA polymerization when compared to bulk polymerization [2]. On the other hand, as ionic liquid concentration increased to 60 volume %, the rate of termination decreased by one order magnitude. It is also believed that the increase in k_p with IL concentration is due to the lowering of the activation energy of polymer propagation step [4]. The rate of polymerization was 79 % faster in [BMIM][PF₆], and molecular weight of Polymethyl methacrylate (PMMA) was five times more than that synthesized in organic solvent, benzene [5]. Polymers with enhanced propagation rate, high thermal stability, and low glass transition temperature were reported in free radical homopolymerization of AN in [BMIM][BF₄] [6]. Vygodskii research group employed a range of symmetric and asymmetric 1,3-dialkylimidazolium (**IL-I**), ammonium (**IL-II**), pyridinium (**IL-III**), and phosphonium (**IL-IV**) ILs with different alkyl groups and anions towards free radical polymerization of monomers like MMA, AN, and polymerizable tetrazoles (**M-10**). The alkyl chain length tethered to cation and the type of anion in IL had a pronounced effect over the molecular weight and properties of synthesized polymers. Imidazolium-based ILs exhibited significant results in polymer synthesis compared to the rest of ILs [7, 8]. ILs with NTf₂ anion were noticed to afford polymers with high molecular weight.

As in line with previously observed reports, for MMA radical polymerization with AIBN in [EMIM][EtSO₄] with increase in IL concentration in the system, an increase in k_p and decrease in k_t were noticed [9]. The propagation constant enhanced twofold in glycidyl methacrylate (GMA) polymerization and fourfold in MMA radical polymerization with ILs as solvent media. This is attributed to the decrease in activation energy by the replacement of monomeric species with IL (**IL-I**, **IL-II**, & **IL-III**) [10, 11]. Single-pulse pulsed laser polymerization in conjunction with electron paramagnetic resonance technique (SP-PLP-EPR) studies indicated that the termination rate for the free radical polymerization of PMMA in [EMIM][NTf₂] and [BMIM][BF₄] is relatively slow in comparison with bulk, which is in line with previous reports [12]. Synthesis of styrene and MMA block

copolymers by simple conventional radical polymerization was realized in 2002, by employing [BMIM][PF₆] as solvents [4]. ILs facilitated rapid homopolymerization of MMA at high temperatures and the resultant PMMA is insoluble in [BMIM][PF₆]. The temperature for the copolymerization of PST-PMMA was decreased in order to minimize the formation of new radicals from initiator residue and also extend the lifetime of growing polymeric radicals. The solubility and insolubility of styrene and polystyrene, respectively, in IL dispersion provide additional advantages facilitating “diffusion-controlled copolymerization.” The polymers were easily separated due to their poor solubility in IL (**IL-I**) [4].

Radical copolymerization of AN and St in [BMIM][BF₄] and [BMIM][PF₆] afforded high molecular weight P(AN-*co*-St) having bimodal distribution. The high viscosity of ILs and their poor solubility in PST are responsible for the above observation [13]. An intriguing “protected radical” mechanism was proposed in radical copolymerization of styrene and MMA with ILs as solvent media, where the polystyrene radicals are protected from radical termination and subsequently promoted the copolymerization with MMA. Interestingly, no traces of PMMA homopolymer were found after the reaction. The authors emphasized that the high viscosity and solubility of ILs (**IL-I**) was primarily attributed to the protected radical mechanism which is impossible to reproduce in traditional organic solvents [14]. In another report, imidazolium-based ILs enabled successful copolymerization of two monomers (**M-1d** & **M-3**) which strongly differ in polarity that provided amphiphilic copolymers [15]. ILs were also used as plasticizer in the in situ homopolymerization of MMA. The polymers synthesized in IL as plasticizer were found to show less mass loss and high thermal stability compared to the polymer made in dioctyl phthalate (DOP) plasticizer.

ILs (**IL-I**) also found applications as effective solvent for synthesis of carbon black-grafted polymers through conventional free radical polymerization. Carbon black retards the polymerization of monomers in organic solvents to an extent; but this retardation was reduced drastically in the presence of ILs. This is attributed to the high viscosity of ILs favoring stabilization and prolonging the lifetime of polymer radicals towards grafting over the carbon black surface. Also, the percentage of grafting was higher in ILs compared to organic solvents [16, 17]. In numerous occasions ILs were successfully employed as surfactant as well as solvent in radical dispersion polymerization.

ATRP is one of the widely used controlled polymerization techniques catalyzed by transition-metal complexes. The main drawbacks of this technique are solubility of catalyst in bulk or organic solvents, contamination of polymers with catalyst, and recyclability of catalyst. But, one or more of these drawbacks can be overcome with the application of ILs as solvents in ATRP polymerization. Copper (I)-mediated MMA atom transfer radical polymerization in [BMIM][PF₆] resulted in polymers with narrow polydispersity, well-defined architecture, and living characteristics [18]. After this first report of ATRP in ILs, several ILs (**IL-I**) of the kind [RMIM][PF₆] have been extensively used as solvent in transition-metal-mediated polymerization, organostibine-mediated controlled polymerization, and ATRP polymerization of different monomers (**M-1b**, **M1g**, **M1h**, **M-2**, & **M10**) such as MMA, acrylates, and acrylonitrile owing to its solubility towards catalyst and monomers [18–24].

The transition-metal catalysts employed in the polymerization were easily separated, reused, and recycled which could be attributed towards their solubility in ILs [18, 24].

The solubility of monomer in ILs is not a critical criterion here. For example, methacrylate, butyl acrylate, and hexyl acrylate are completely miscible, partially miscible, and immiscible in [BMIM][PF₆], respectively. But, this limited solubility minimizes the chance of side reactions in such heterogeneous polymerization system [25]. Similarly, the strategy involved in block copolymerization of MA and BA also clearly depends on the solubility of monomers in [BMIM][PF₆]. The block copolymers were synthesized in two different ways: first, PBA was synthesized through heterogeneous polymerization in [BMIM][PF₆] followed by in situ block copolymerization with MA and second, PMA was synthesized through homogeneous polymerization followed by in situ block polymerization with BA. The former strategy resulted in well-defined block copolymers even after addition of MA after complete conversion of BA, and no homopolymer traces of the latter were observed. But the polymerization in the second way resulted in block copolymers only at the addition of BA before 70 % conversion of MA. No block copolymer was formed when BA was added after complete conversion of MA. This remarkable difference in both strategies is solely attributed towards the solubility of monomers in IL [BMIM][PF₆] [26].

The solubility of monomers in IL varies with respect to the cationic and anionic substituents of IL towards the respective monomer. For example, MMA and MA are completely soluble in [BMIM][PF₆], and the resulting polymer separates out of IL after homogeneous polymerization leaving the catalyst inside IL thereby preventing the contamination of polymer with monomer and catalyst residues. In copper-mediated ATRP polymerization of MMA, [BMIM] with dibutyl phosphate anion served both as ligand and solvent compared to ILs (**IL-I**) with other anions such as halides (Br, Cl), chloroaluminates, and dodecyl sulfate which justifies the importance in choosing IL with particular cation and anion [27]. Thus by choosing appropriate IL, one can avoid the usage of external ligands to make ATRP much simpler.

It is observed that the polymerization rate constant increases with a decrease in the length of alkyl chains of IL anions (**IL-I**). These acid anions were found to chelate with transition-metal catalyst and thereby facilitated ATRP polymerization without use of any ligand which is an added advantage other than easy separation and use of catalyst [28]. *N*-butyl-*N*-methyl morpholinium tetrafluoroborate (**IL-V**) was also used as solvent for ATRP-mediated polymerization of MMA and contributed towards efficient separation and reuse of catalyst [29].

ILs were also used as solvents in reverse ATRP (RATRP) [30–34], as initiators for continuously activator generated ATRP (ICAR ATRP) [35], and as activators generated by electron transfer ATRP (AGET ATRP) [36–43]. ILs of the type 1-alkyl-3-methylimidazolium with different alkyl chains such as butyl, hexyl, octyl, and dodecyl and anions such as tetrafluoroborate and hexafluorophosphate (**IL-I**) were used extensively as solvents for RATRP polymerization [30–34]. It has been found that ILs with long alkyl chains (octyl, dodecyl)

were able to afford well-defined polymers and block copolymers with high polymerization rate constant compared to the ILs with short alkyl chains (butyl and hexyl).

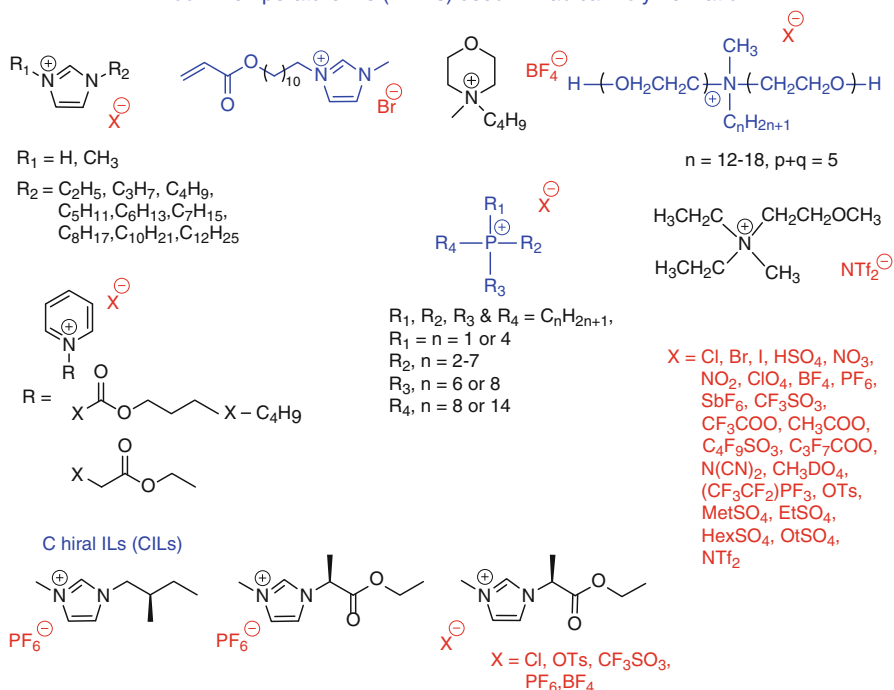
The immiscibility and miscibility of inorganic bases and ILs in organic solvents respectively motivated the researchers towards application of basic ILs (basic ILs) in polymerization process [36, 37]. 1-Butyl-3-methylimidazolium ILs with basic anions such as hydroxide, carbonate, bicarbonate, and phosphate were used as additives replacing inorganic bases such as NaOH, $\text{Fe}(\text{OH})_3$, and basic Al_2O_3 in AGET ATRP polymerization of MMA [39, 40]. Generally, AGET ATRP polymerization takes place in the presence of a reducing agent like vitamin C which reacts with higher oxidation state catalyst (deactivator) and generates lower oxidation state catalyst (activator) in situ. The main advantage of AGET ATRP over the conventional one is that the former reduces the amount of catalyst to be added and thus benefits the environment. Apart from being used as additives, ILs were also used as solvents for AGET ATRP-mediated polymerization of AN and MMA [38, 41–43]. The dependence of polymerization rate over alkyl chain length of ILs followed expected trend as discussed earlier, i.e., polymerization rate increased with increase in IL cation's alkyl chain length [38]. The biphasic ATRP polymerization of MMA catalyzed by an ionic liquid tethered to copper complex facilitating efficient separation and reusability of the catalyst resulting in well-defined polymers with narrow molecular weight distribution and low polydispersity index (PDI) (~ 1.2 – 1.4). The catalyst settled at the bottom of the reactor allowing an easier separation from the polymer solution, and the recycled catalyst exhibited good control and catalytic activity as fresh catalyst [44]. Achiral IL such as [BMIM][PF₆]-mediated ATRP produces atactic polymers, whereas chiral ILs (*see CILs* in Fig. 13.2 then remove the following figure) yield rise to well-defined polymers with specific tacticity [45–48].

The nitroxide mediated radical polymerization (NMP) polymerization of MA in [BMIM][PF₆] and [HMIM][PF₆] is observed to be faster compared to organic solvent, anisole. Surprisingly, the polymerization of MA took place both in bulk and IL without 4-oxo-TEMPO which may be due to spontaneous polymerization [49]. But, the attempt towards BPO/TEMPO- and TMPPAH-mediated NMP polymerization of MMA and styrene failed probably due to the slow degradation of TEMPO in IL. Instead, an uncontrolled polymerization of the monomers took place without any reactivation of monomeric chains [50]. With an attempt to overcome this drawback, it was tried to copolymerize MMA with small amount of styrene in [BMIM][NTf₂]. The copolymerization took place faster in IL within 2 h with high conversions compared to the organic solvent, dioxane [51].

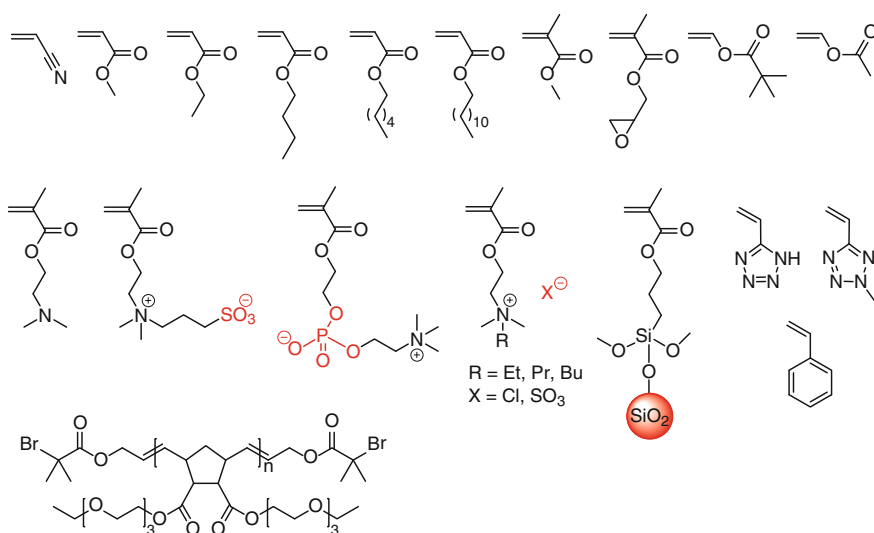
ILs of the kind 1-alkyl-3-methylimidazolium salts (**IL-I**) were reported as solvents for the first RAFT homopolymerization of MMA, MA, AA, and ST. The length of alkyl chains in ILs did not follow a particular trend over the polymerization kinetics which is contrary to the ATRP polymerization and free radical polymerization. Interestingly, there was a clear difference between the theoretical and the observed molecular weight which could be attributed to the poor solubility of RAFT agent in IL. All the monomers gave high conversions with linear increase

a

Room Temperature ILs (RTILs) used in Radical Polymerization

**b**

Monomers polymerized in ILs

**Fig. 13.2** List of ILs used in radical polymerization (a) of a different kind of monomers (b)

in molecular weight except styrene due to the insolubility of PST in IL, whose conversions are less than 2 % [52, 53]. But, pyridinium-based ILs (**IL-IV**) when used for the homopolymerization of ST, afforded more than 80 % conversion after 10 h. In coincidence with the previous observations in free radical polymerization, the IL with more viscosity exhibited high polymerization rate and slightly higher compared to toluene. Initially, the reaction mixture was clear and homogeneous and eventually turned cloudy with the progress of polymerization indicating a precipitation/heterogeneous polymerization. Though there was a lot of debate on trapped radical mechanism in such kind of heterogeneous free radical polymerization system, the authors stated that no such mechanism took place in controlled RAFT homopolymerization of ST. The constant rate of propagation and rate of termination throughout the experiment supports their statement [54].

When ILs with different anions were employed in RAFT homopolymerization of MMA, ILs with EtSO₄ and BF₄ anions resulted in heterogeneous polymerization with low conversions and low molecular weight polymers, and on the other hand, ILs with NTf₂ and PF₆ anion successfully afforded solution-type polymerization with high conversion and good control over molecular weight distribution. Room temperature ionic liquid (RTIL) tethered chain transfer agent (CTA) gave better results than literature CTAs due to their difference in solubility in ILs [55]. The same research group has explained the evidence for the difference in polymerization rate and solubility of monomers in different ILs (**IL-I**) through rotating frame nuclear overhauser effect spectroscopy (ROESY) technique. The protons of CTA and IL were labeled, and the effect of polar and nonpolar domain of ILs over the growing polymeric chain was studied. These investigations revealed that viscosity is not the only factor but also the solvation environment of the monomeric species and the type of IL employed plays a major role in the polymerization kinetics. The continued solubility of growing reactive species in IL depends upon the domains of IL which could rearrange around them. For example, the growing RAFT end-capped MMA chain in [BMIM][BF₄] separates out of IL after reaching a certain length leaving the monomer residues and unreacted initiator which further undergoes uncontrolled polymerization affording high molecular weight and multimodal molecular weight distribution curve [56]. ILs were also used as porogen in composition with organic solvent facilitating high column efficiency and high permeability which are the major challenges in synthesis of molecularly imprinted polymers (MIPs) [57].

The reactivity ratios depend on the monomers being polymerized, polymerization temperature, initiation, and solvent. These reactivity ratios could be tuned by changing the initiation mechanism from radical to charge transfer (CT) [58]. The reactivity of monomers was found to be enhanced in CT polymerization mediated by ILs as solvents compared to conventional free radical polymerization [59, 60].

As a general observation, when radical polymerization was carried out in ILs, higher molecular weight polymers with remarkably faster reaction rates in good conversions were noticed over conventional solvents. An increase in K_p/K_t with an increase in IL concentration is another advantage in IL-mediated radical polymerization. Block copolymer can be achieved by simple conventional radical

polymerization in IL. In IL-mediated ATRP, not only the isolation of the products is easy but also the recovery and reuse of catalysts is possible. It is also interesting to observe that the disproportionation of Cu(0) is highly favored in IL-mediated ATRP.

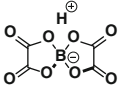
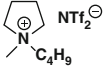
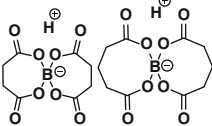
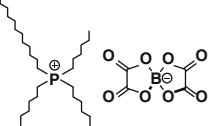
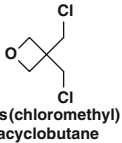
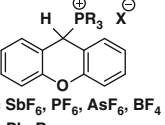
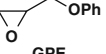
Ionic Polymerization in ILs

Cationic Polymerization in ILs

Cationic living polymerization of styrene was achieved in ionic liquid *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide, [BMPyr][NTf₂], which acted as a strong proton donor catalyzed by bis(oxalato) boric acid (HBOB) [61]. The cationic polymerization in ionic liquid strongly depends on the nature of anion. It was observed that organoborate acid-catalyzed styrene polymerization progressed smoothly in ILs with NTf₂ anion, irrespective of the cation, but when counter anion in the IL changed from NTf₂, no polymerization was observed. This clearly indicates the importance of the weakly basic counter anion such as NTf₂ in this cationic polymerization. Relatively higher basic counter anions in ILs completely deprotonate the borate catalyst thus preventing the polymerization of monomers through protonation [62]. Cationic styrene polymerization carried out in neutral ionic liquid [MIM][PF₆] with RCl/TiCl₄ provided good conversions, but with less control over molecular weight and PDI [63]. Kubisa et al demonstrated that C–Cl bond in phenylethyl chloride can be ionized in ILs in the absence of any co-initiator, to be used for styrene polymerization [63]. They observed an increase in the ionization of C–Cl bond in IL/SO₂ with more efficacy. However, in none of these cases, ionization is not sufficient enough to obtain controlled styrene polymerization [64]. It was observed that styrene polymerization initiated by AlCl₃ in [BMIM][PF₆] produced higher molecular weights PS in quantitative conversions in comparison with other solvent systems DCM, scCO₂, or [BMIM][PF₆] + scCO₂ that resulted in oligomers [65]. Very recently, vinyl ethers were polymerized via controlled manner in the absence of any Lewis acid catalyst, by in situ generation of vinyl ether–hydrogen halide adduct through simple mixing of CF₃SO₃H and Bu₄Ni to vinyl ether monomer. It was shown that these vinyl ether–hydrogen halide adducts act as cationogens for living cationic polymerization catalyzed by metallic Lewis acids [66].

There are an increasing number of reports on cationic ring-opening polymerization of a different kind of monomers in ionic liquids (Table 13.1). [BMIM][BF₄]-mediated cationic ring-opening polymerization of 3-ethyl-3-hydroxymethyloxetane (EOX) afforded low molecular weight polymers with high conversions. The intramolecular hydrogen bonding which is believed to be the limiting factor for lower molecular weights was not influenced by relatively polar ILs at higher temperatures in order to get the higher molecular weight polymers [67]. These limitations were also visible in the cationic ring-opening polymerization of 3,3-bis(chloromethyl)oxacyclobutane in ILs [68]. Rare-earth metal triflates in ILs were used as an effective reusable catalyst at least for three cycles in the synthesis of poly(ϵ -caprolactone) (PCL) by ring-opening polymerization of lactones without significant loss of catalyst activity [69].

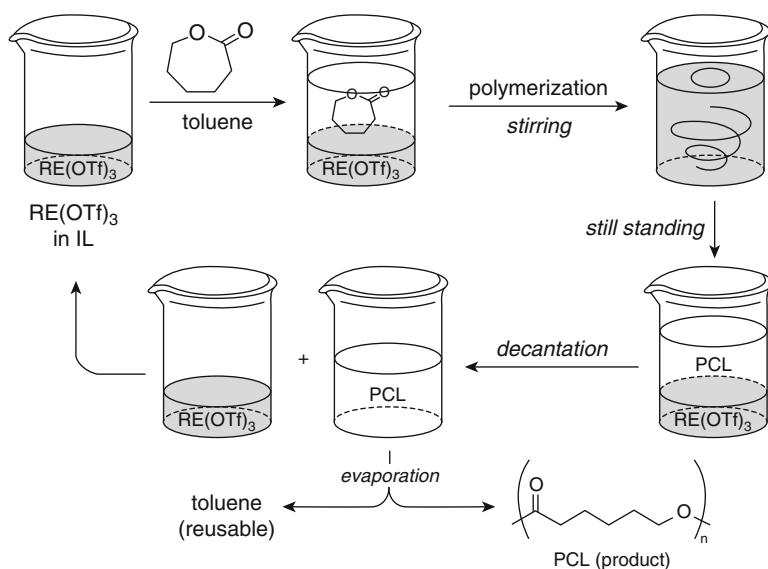
Table 13.1 List of catalysts and ionic liquids used in the cationic polymerization

Catalyst	IL	Monomers	References
		Styrene (living polymerization)	[61]
		Styrene (living polymerization)	[62]
	Neutral IL [BMIM] [PF ₆]	Styrene polymerization good conversions but less control over M _n and PDI	[63, 64]
	[BMIM][PF ₆]/SO ₂		
AlCl ₃	[BMIM][PF ₆] DCM [BMIM][PF ₆]/scCO ₂	Styrene	[65]
No catalyst	CF ₃ SO ₃ H and Bu ₄ NI to vinyl ether monomer	Vinyl ether polymerization by in situ generation of VE–hydrogen halide adduct	[66]
BF ₃ ·Et ₂ O	Neutral IL [BMIM] [BF ₄]		[67]
BF ₃ ·Et ₂ O	[BMIM][PF ₆] and [BMIM][BF ₄]	 3,3-bis(chloromethyl) oxacyclobutane	[68]
–	 X = SbF ₆ , PF ₆ , AsF ₆ , BF ₄ R = Ph, Bu PILs as activator	 GPE	[72]
Double metal cyanide	[RMIM]X R = ethyl, butyl, hexyl X = Cl, BF ₄ , PF ₆		[70]

(continued)

Table 13.1 (continued)

Catalyst	IL	Monomers	References
Sc(OTf) ₃	[BMIM][BF ₄]		[71]

**Fig. 13.3** Schematic ROP of CL using reusable $\text{RE}(\text{OTf})_3$ in an IL [69]

After completion of the reaction, the metal catalyst which is soluble in ILs will settle down at the bottom which can easily be separated from a polymer by simple decantation and reused for further polymerization reactions as shown in Fig. 13.3.

ROP of propene oxide and cyclohexene was carried out successfully in imidazolium-based ILs catalyzed by double metal cyanide and recyclable scandium triflate, respectively [70, 71]. ROP of ϵ -caprolactone catalyzed by polymer-anchored scandium triflate showed living nature, and the authors observed acceleration in polymerization when they used [EMIM][PF₆] and [BMIM][PF₆] ionic liquids over toluene [72]. The solubility of polysaccharides (such as cellulose, chitosan, chitin, starch, etc.) in ILs [73] was exploited to prepare a variety of polysaccharide-grafted polymers.

Anionic Polymerization in ILs

1,3-Dialkyl-substituted imidazolium-based ILs are vulnerable in basic conditions due to the presence of acidic proton at second position of imidazolium ring.

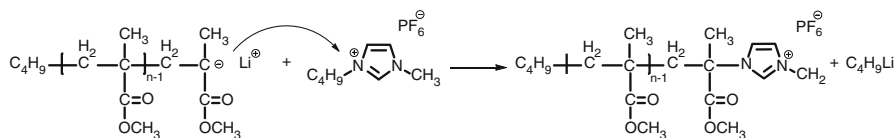


Fig. 13.4 Chain transfer to imidazolium ionic liquid in anionic polymerization of MMA

When anionic polymerization reactions were carried out in imidazolium-based ionic liquids, either initiator deactivation or chain transfer to imidazolium ring of the ionic liquid was also observed. For instance, when MMA was polymerized in [BMIM][PF₆] using alkyl lithium (anionic initiator), very poor yields (1–9 %) were observed due to decomposition of the anionic initiator [74]. Kubisa et al noticed the presence of ILs as chain ends when MMA was polymerized in [RMIM][PF₆] or [RMIM][BF₄] initiated by BuLi [75]. The chain transfer to imidazolium-based ILs in anionic polymerization is shown in Fig. 13.4. These studies suggest that imidazolium-based ILs are not suitable solvents for controlled anionic polymerization.

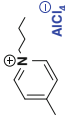
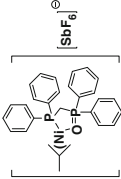
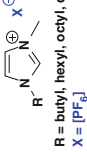
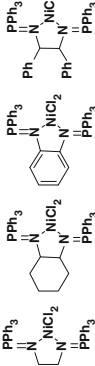
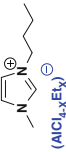
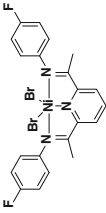
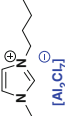
Sodium salt of hydroxylated imidazolium IL at second position initiated the anionic ring-opening polymerization of ethylene oxide that produced polyethylene oxide with degree of polymerization (DP) around 30 without any side reactions [76]. Under relatively mild reaction conditions, anionic polymerization of styrene in phosphonium-based IL was reported. Upon addition of imidazolium-based zwitterion, fourfold increase in yields was noticed with decrease in molecular weight with slightly higher PDI values [77].

ILs of the types [BMIM][PF₆] and [BMIM][NTf₂] were used as reaction medium for the ring-opening polymerization of g-benzyl-L-glutamate-*N*-carboxyanhydride (BLG-NCA) initiated by butylamine. When compared with common organic solvents, the polymer obtained in ILs showed same molecular weight and PDI values except small decrease in yields; this is due to heterogenized reactions in ILs [78]. But the group transfer polymerization of MMA carried out at ambient temperatures in ionic liquids gave relatively good yields with or without catalyst [79].

Transition-Metal-Catalyzed Polymerization in ILs

The poor solubility of highly active transition-metal complexes in organic solvents can be overcome by choosing appropriate ionic liquids with relatively non-coordinating counter anions such as NTf₂, PF₆, etc (Table 13.2). The first report on ILs in the homogeneous oligomerization [80] and polymerization reactions [81, 82] appeared in 1990. Later several research groups successfully carried out the oligomerization (ethylene and higher olefins) [83–92] and polymerization reactions in ILs [92, 91, 93–99]. The major concern in the homogeneous polymerization is the recovery of costly catalyst system. IL-based biphasic reactions facilitate the easy separation of catalyst system for further usage. Better results were observed in 2001 by

Table 13.2 Different transition-metal complex and ILs used for oligomerization and polymerization reactions

Catalyst	Ionic liquid	Type of reaction	References
	 Buffered with weak organic bases	Dimerization of 1-butene	[83]
	 R = butyl, hexyl, octyl, decyl X = [PF ₆]	Ethylene to higher α -olefins	[86, 87]
 R = Me, <i>i</i> -Pr R' = <i>n</i> -Pr, <i>i</i> -Pr, <i>n</i> -Bu	Buffered melt [BMIM]Cl, AlCl ₃ , and <i>N</i> -methylpyrrole (0.45:0.55:0.1 molar ratio)	Oligomerization of propene and 1-butene	[88]
	 (AlCl ₃ ·Et ₃ X)	Ethylene oligomerization	[89]
	Buffered with triarylphosphines  [Al ₂ Cl ₇]	Propene dimerization	[91]

(continued)

Table 13.2 (continued)

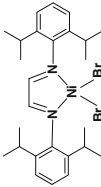
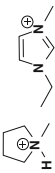
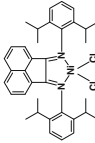
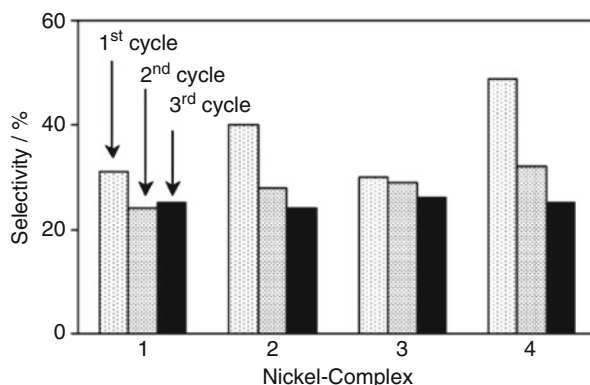
Catalyst	Ionic liquid	Type of reaction	References
	 Buffered chloroaluminate ILs	Oligomerization and ethylene polymerization	[92]
	Chloroaluminate ILs	Ethylene polymerization	[82]
	Organochloroaluminate ILs [BMIM][Cl-AlCl ₃ ·[EtAlCl ₂]] 1:1:0.32, X(Al) = 0.57) and toluene (cosolvent)	Ethylene polymerization	[93]
	[BMIM][AlCl ₄]	Ethylene polymerization	[95]

Fig. 13.5 Effect of selectivity in C4 upon repeating cycles in organochloroaluminate IL biphasic oligomerization of ethylene with four Ni complexes 1–4 (see Table 13.2) [89]



Wasserscheid et al in biphasic oligomerization of ethylene to higher olefins with cationic nickel complexes in ILs of the type $[R\text{MIM}][\text{PF}_6]$. The reactivity and selectivity in ILs were noticed to be better compared to conventional organic solvents [86–88].

It was observed that propene and 1-butene dimerizations with Ni(II) heterocyclic complexes were inactive or sparingly active in toluene. Upon changing the solvent to imidazolium-based ionic liquids, the same catalyst system showed considerable activity towards dimerization of propene and 1-butene. The catalyst inability towards oligomerization of propene and butene in toluene was attributed to rapid decomposition of Ni(II) complex via reductive elimination. But such decomposition was not observed in imidazolium-based ILs [88]. Biphasic ethylene oligomerization was carried out with Ni(II)–diiminophosphorane complexes in organochloroaluminate IL. The recovered catalyst system in repeated recycling showed an increase in activity with the expense of its selectivity (Fig. 13.5). This decrease in selectivity was attributed to the formation of a more active and new kind of Ni complexes due to ligand displacement of diiminophosphoranes with chloroaluminates [93].

Recently, it has been reported that buffered chloroaluminate ILs can activate Ni catalysts in the biphasic dimerization of propene with 84 % selectivity [98, 97]. IL-mediated biphasic ethylene polymerization was carried out successfully with 1,4-bis(2,6-diisopropylphenyl) acenaphthenediiminonickel(II) dichloride (catalyst) in $[\text{BMIM}]$ organoaluminate (solvent as well as cocatalyst) and toluene at mild polymerization conditions such as 1,050 mbar pressure and temperature between -10°C and $+10^\circ\text{C}$. For further reuse, the recycled catalyst needed addition of fresh cocatalyst trimethylaluminum (TMA) that leads to the formation of multiple active sites and eventually restricted the single-site polymerization process [93].

It was even demonstrated that ethylene polymerization can be successfully carried out in ionic liquid (imidazolium-based or pyridinium-based) hexane biphasic system using metallocene catalyst Cp_2TiCl_2 activated by alkylaluminum compounds such as MAO, Et_2AlCl EtAlCl_2 , or Et_3Al [96, 95]. By selecting suitable solvent and buffer, the same Ni catalyst (which was used for ethylene dimerization) was effective in producing 38 % polyethylene with M_n of 140 Kg/mol. Recently, ethylene polymerization was carried out homogeneously in ionic liquid and an

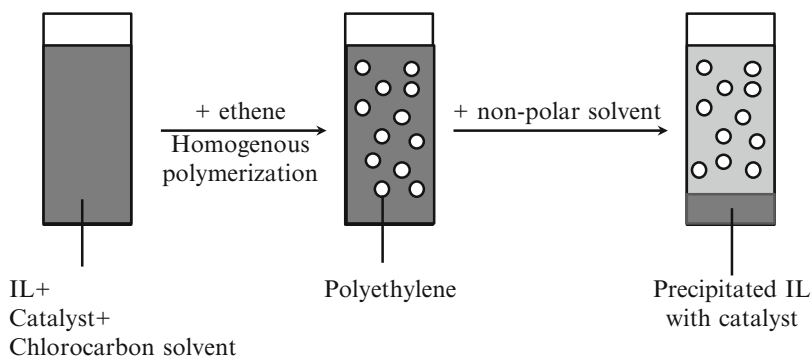


Fig. 13.6 Homogeneous IL-based ethylene polymerization reactions and subsequent catalyst recovery by precipitation [92]

appropriate organic solvent. After completion of the reaction, addition of nonpolar solvent to the polymerization mixture facilitates the precipitation of ionic liquid with catalyst at the bottom by leaving the polymer and organic solvent above as shown in Fig. 13.6 [92]. This is a very effective way of recovering the catalyst system using ionic liquid-based homogeneous polymerization.

Our attempts to polymerize 1-hexene with non-metallocene catalysts [100, 101] in [BMIM][BF₄] and [BMIM][PF₆] did not afford any polymer (unpublished results). Even the absence of literature reports on higher α -olefin polymerization in ILs suggests that ILs are not suitable solvents for α -olefin polymerization.

Poly(phenylacetylene) was prepared in high yields with high *cis* percentage (95–100 %) by Rh(I)/triethylamine catalyst system in [BMIM][BF₄] and [BPy][BF₄]. The recovered catalyst system in IL was effective for further use without any significant loss in activity [97]. An increase in molecular weights and yields was reported when Pd-catalyzed copolymerization of styrene and CO was carried out in [HPy][NTf₂]/methanol in comparison with methanol-mediated polymerization. The catalyst productivity in [HPy][NTf₂] was comparable to that of highly polar non-coordinating solvent trifluoroethanol [99, 98] (Table 13.2).

Compared to anionic polymerization, cationic polymerizations in IL media are more feasible. This is because under basic conditions imidazolium-based ILs are less stable and it leads to deactivation of the initiator and/or chain transfer to IL. An increase in catalyst activity was observed in some IL-mediated cationic polymerization. Though the mechanism is not clearly known, it is believed that the ILs can stabilize the charged intermediates. This can be attributed to the moderately polar and non-coordinating nature of ILs.

Polycondensation in ILs

In general, polycondensation processes require harsh conditions such as high temperatures and vacuum conditions for long reaction periods using protic acid or

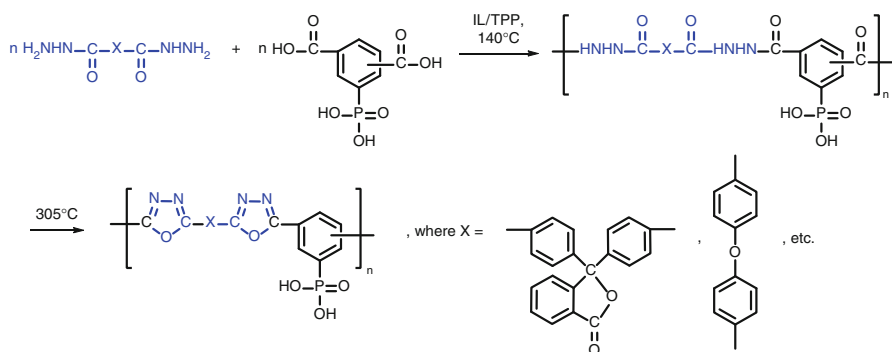


Fig. 13.7 Synthesis of various phosphonated PODs in ILs [107]

organometallic catalysts. These harsh reaction conditions not only pose environmental problems but also lead to side reactions resulting in polymers with undesired molar masses with varying microstructures. So there is a great demand for the replacement of toxic reagents and volatile solvents; ILs are being found as an efficient replacement for organic solvents owing to their unique properties like nonvolatile, thermally stable, nonflammable, and chemically inert. For the first time in 2002, different 1,3-dialkyl imidazolium-based ILs were used as reaction media successfully for the synthesis of high molecular weight aromatic polyamides and polyimides in the absence of any added catalyst [102, 103]. Synthesis of high molecular weight polyimides with quantitative conversions was realized in ILs/triphenyl phosphite (TPP) by direct polycondensation of different monomers such as diacids and diamides [104].

The addition of 40 % zwitterion IL ($\text{C}_4\text{MIM}^+\text{Br}^-$) improved the solubility of the monomers such as aromatic amines and di-anhydrides into 1,3-dialkyl imidazolium ILs, and eventually their polycondensation resulted in high molecular weight polyimides [105]. Poly(1,3,4-oxadiazole)s (PODs) and phosphonic acid-functionalized PODs were prepared in [PMIM]Br/TPP by direct polycondensation of corresponding dicarboxylic acids and their dihydrazides [106, 107] (Fig. 13.7).

Macroporous polyureas were prepared by polycondensation reaction at the interface of hexane and IL. FT-IR studies suggest the surface interactions between ILs and polyurea, which are responsible for the formation of macroporous polyureas [108]. The direct polycondensation of glycolic acid in imidazolium-based ILs at $200\text{--}240^\circ\text{C}$ afforded only poly(glycolic acid) (PGA) oligomers due to evaporation of glycolic acid at this temperature. Even the post polycondensation could produce PGA of only a maximum of 45 DP. Here, the solubility of PGA in IL is the limiting factor for higher molar mass. Another drawback observed in this kind of polyesterification in ILs is the less activity of $\text{Zn}(\text{OAc})_2$, and authors explained this as a consequence of its preferential interaction with ILs over acidic end groups [109] (Fig. 13.8).

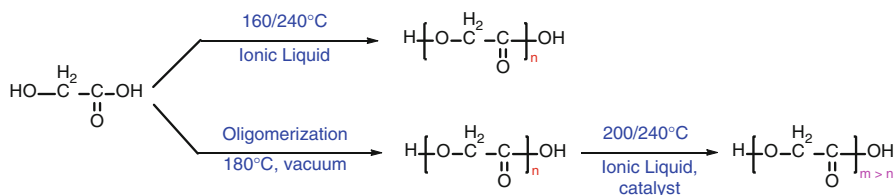


Fig. 13.8 Polycondensation of glycolic acid in ILs [109]

In another aliphatic polyester synthesis (from diols and diacids) in ionic liquid [HMIM]PF₆ catalyzed by SnCl₂, same kind of catalyst deactivation was noticed, with lower molecular weights ($M_w < 1.8 \times 10^4$) as that of catalyst-free bulk polymerization [110]. An increase in molecular weights of polyesters was noticed upon changing the counter anion from PF₆ to NTf₂ in the ionic liquid. The mechanism of this metal activation/deactivation in ILs was explained based on hard and soft acid-base principle [111]. It is believed that Sn⁺² which is a hard acid will totally fluorinate to give metal fluoride complex in IL with PF₆ counter anion and become inactive for the polymerization. But such a fluoride complexation is unlikely in NTf₂ (due to strong covalent bonded C–Fs); this may be the reason why Sn⁺² is catalytically active and provided relatively higher molecular weight polyesters in NTf₂-based ILs [110].

In IL-mediated polyphenol synthesis, the nature of ionic liquid largely influenced the outcome of the polymer. When hydrophilic ILs ([HMIM][Cl] and [HMIM][Br]) were employed as solvents, they produced low molecular weight polyphenols with low PDI. On the other hand, relatively higher molecular weight polyphenols with very high PDI were noticed in hydrophobic ILs ([HMIM][BF₄] and [HMIM][CF₃SO₃]). Depending upon the type of ILs (hydrophilic or hydrophobic), the interaction between imidazolium ring in ILs and phenol monomer varies thus affecting the molecular weight of the polymer (Fig. 13.9) [112].

Higher molar mass polyethers were prepared using BAILs [BBSIm][NTf₂] and [OBSIm][NTf₂] by polycondensation of aliphatic diols at relatively lower temperatures 130 °C [113]. Recently high-performance polyetheretherketone (PEEK) was prepared in [BMIM][NTf₂]/K₂CO₃ by polycondensation between hydroquinone and 4,4'-dihalobenzophenones at temperature around 320 °C, and the obtained PEEK showed properties same as that of PEEK synthesized in commercially used solvent diphenylsulfone under identical conditions. The major advantage of using ILs over commercial diphenylsulfone as a solvent in this polycondensation is due to the absence of solvent occlusion and the ease of polymer recovery [114].

Because of their higher thermal stability and nonvolatile nature, ILs are supposed to be the ideal media for the polycondensation. The increasing number of reports in this field indicates that ILs are promising solvents in the polycondensation over conventional solvents.

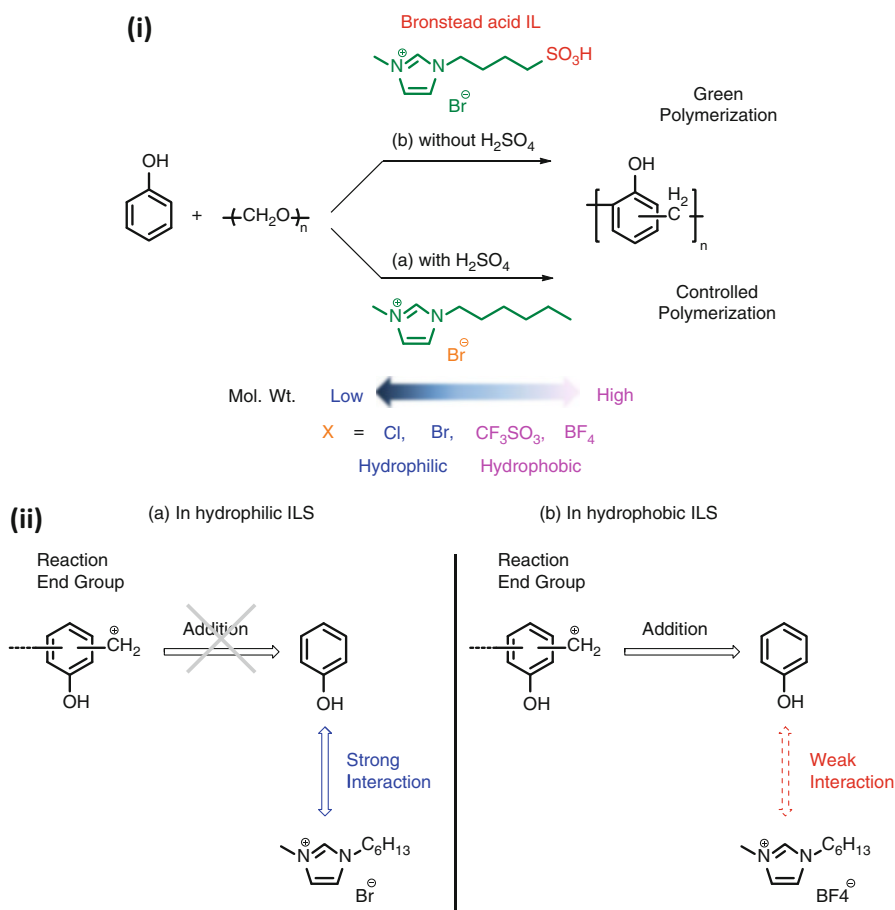


Fig. 13.9 Polymerization of phenol in (a) hydrophilic, hydrophobic, and (b) Bronstead acid ILS (ii). Interaction of phenol with (a) hydrophilic IL [HMIM][Br] and (b) hydrophobic IL [HMIM][BF_4] [112]

Enzymatic Polymerization in ILS

The crucial advantage of enzymatic catalysis is its inherent chiral discrimination ability and to proceed at milder conditions in the absence of any metal or organometallic compound. Enzymatic catalysis in ionic liquids – as an alternative for organic solvent – has gained considerable attention of the researchers [115, 116]. There are plenty of reports on the enzymatic polymerization in organic solvents [117, 118]. It is observed that enzymes are more stable in ILs than in conventional organic solvents where their decomposition was noticed [119–121]. There is limited number of reports on enzymatic polymerization reactions in IL medium. In general, lipases immobilized on porous polymer beads were used as catalysts in IL-mediated polymerization

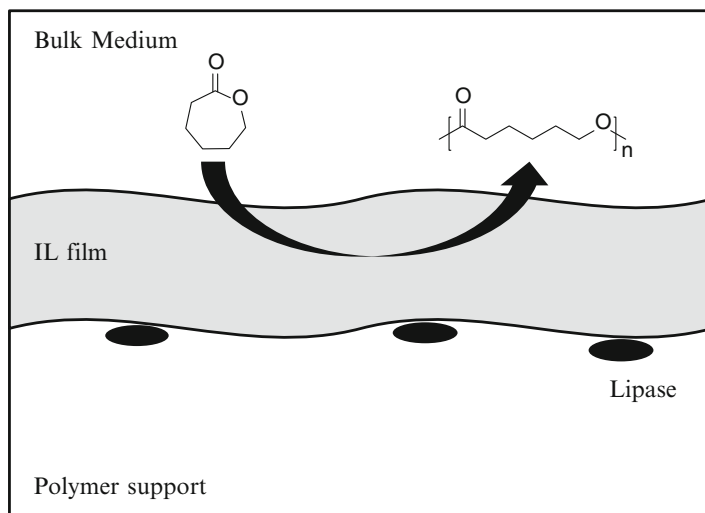


Fig. 13.10 Schematic representation of IL-coated lipase particles for lactide polymerization in solvent-free conditions [132]

reactions. So far these enzymatic polymerization reactions in IL medium were restricted largely towards polyester synthesis either by ring-opening polymerization (ROP) of lactones or by polycondensation of hydroxy acids [122–133]. In most of these polymerization reactions, lipase B from *Candida antarctica* (Novozyme 435) in imidazolium-based ILs (of the kind [RMIM] where R = alkyl group) with PF₆ as counter anion was used as solvent. Less monomer conversions and lower molecular weights were observed when ROP of ϵ -caprolactone was carried out with Novozyme 435 in ILs such as [BMIM][PF₆], [BMIM][BF₄], and [BMIM][NTf₂] over toluene. Apparently this is due to the limited miscibility of the polymer in ILs [122].

IL-coated enzymes showed higher catalytic activity than that of IL-mediated reactions. [BMIM][PF₆]-coated Novozyme 435 was very effective in synthesizing high molecular weight ($M_w = 182 \text{ k g/mol}$) poly(1,4-dioxan-2-one) (PPDO) [130]. When enzymes are coated with ILs, they protect from bound water, and in the presence of bound water, activation and propagation reactions will be more feasible (Fig. 13.10) [130].

Apart from polyester synthesis, the other kinds of polymerization reactions under this category are soybean peroxidase-catalyzed polymerization of phenols in [BMIM][BF₄]/[BMPy][BF₄] [134] and horseradish peroxidase-catalyzed aniline polymerization using anionic surfactant sodium dodecylbenzenesulfonate (SDBS) in [BMIM][NTf₂] [135]. It was observed that the deactivation of horseradish peroxidase by SDBS was minimized in the presence of ionic liquid [BMIM][OTf] [135].

Long reaction time and lower molecular weights are major disadvantages that were noticed in this type of polymerization reactions. Through the chiral discrimination capacity, enzymes facilitate the synthesis of chiral polymers from racemic monomer, but this advantage could not be explored further due to abovementioned limitations.

Ionic Liquids as Catalysts for Polymerization

As discussed earlier in this chapter, ionic liquids have been extensively used as solvents in different kinds of polymerization. Recently, researchers are finding applications of ionic liquids as catalysts in ring-opening polymerization, photopolymerization, ATRP polymerization, and proton-mediated polymerization.

Acidic and basic ILs were employed as an effective and reusable catalyst in some polymerization reactions. The acidic ionic liquids can be Lewis acid ionic liquids (LAILs), Bronsted acid ionic liquids (BAILs) (e.g., see IL-1 to IL-12 in Fig. 13.8), or Bronsted-Lewis acid ionic liquids (BA-LA ILs) (IL-13 in Fig 13.8). In Bronsted acid ionic liquids (BAILs), the Bronsted acid group can be introduced at cationic part, at anionic part, or at both cationic and anionic parts of the ionic liquid as shown in Fig. 13.11.

The catalytic activity of acidic ILs such as pyrrolidinium bisulfate [H-NMP][HSO₄], pyrrolidinium chloride [H-NMP][Cl], and morpholinium bisulfate [H-Mor][HSO₄] for the ring-opening polymerization of ϵ -caprolactones in toluene with benzyl alcohol as initiator was investigated recently [136]. A decrease in inherent viscosity with progress in reaction time was observed which was attributed to the increase in intramolecular transesterification. Pyrrolidinium chloride [H-NMP][Cl] was successful in catalyzing starch-grafted-PCL copolymerization; but pyrrolidinium bisulfate [H-NMP][HSO₄] and morpholinium bisulfate [H-Mor][HSO₄] could not catalyze the same, as starch gets easily hydrolyzed by the two ILs.

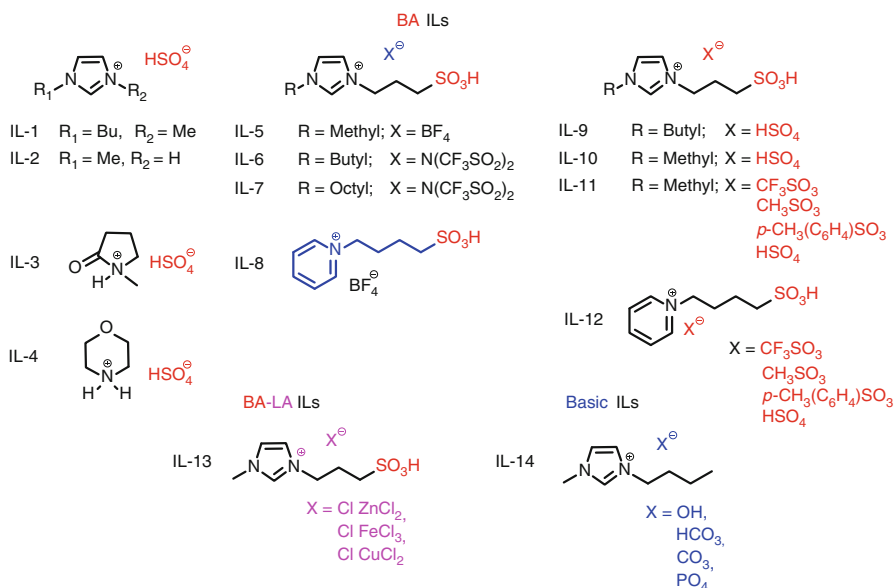


Fig. 13.11 List of acid and basic ILs used as catalyst in polymerization reactions

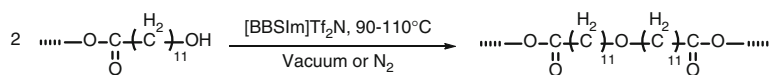
The direct polyesterification of 12-hydroxydodecanoic acid in Bronsted acid ionic liquids that acted as media as well as catalyst afforded high molar mass polyesters with M_n up to 50,000 g/mol in good yields (around 90 %) at atmospheric pressure and moderate temperatures (90–130 °C) which are milder conditions as compared with conventional ones (>200 °C, low pressure) [137]. The advantages of BAIL-catalyzed polyesterification which are worth mentioning include mild conditions, short reaction periods, good yields, and high molar mass. The effective polyesterification is largely influenced by cationic and anionic parts of the BAILs. The BAIL [BBSIm][NTf₂] exhibited high activity; within 5 min, M_w reached close to 35 k g/mol, but during prolonged reaction time, side reactions such as etherification of OH end groups and degradation (acid-catalyzed ester and ether scissions) were reported [137, 138] (Fig. 13.12).

Other BAILs, namely, [BBSIm][NTf₂] and [OBSIm][NTf₂], were effective in catalyzing the polyetherification of aliphatic diols with $n = 7$ –12 methylene units at around 130 °C [113]. ¹H NMR studies revealed that the OH groups underwent H⁺-catalyzed dehydration followed by carbocation migration to give double bonds at α , β , and γ position to the original OH group. Further, these double bonds at γ and/or δ position got hydroaminated by NHTf₂ in acidic conditions. But these two BAILs were not effective in polyetherification of 1,4-butanediol and 1,6-hexanediol; instead it resulted in cyclic ethers such as tetrahydrofuran and oxapene, respectively [113] (Fig. 13.13).

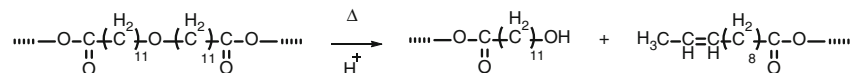
Sulfonic acid-functionalized BAILs are effective in copolymerization of L-lactic acid and ϵ -caprolactones [139]. These BAILs could be easily separable by phase separation and recyclable for a minimum of four times without any decrease in catalytic efficiency. Controlled kinetic studies revealed that the copolymerization is a combination of polycondensation and simultaneous transesterification immediately after fast ring-opening polymerization of ϵ -caprolactone.

Polyphenols were synthesized using BAILs without any other additives. In this process they have isolated the polyphenol and recovered the catalyst BAIL by simple reprecipitation in water and filtration. This is a complete green

i. Etherification



ii. Ester scission



iii. Ether scission

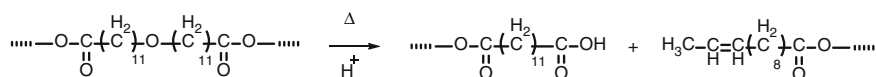


Fig. 13.12 Two different side reactions, namely, (i) etherification, (ii) dehydration reactions in [BBSIm][NTf₂]-catalyzed polyesterification of 12-hydroxydodecanoic acid and (iii) is ether scission

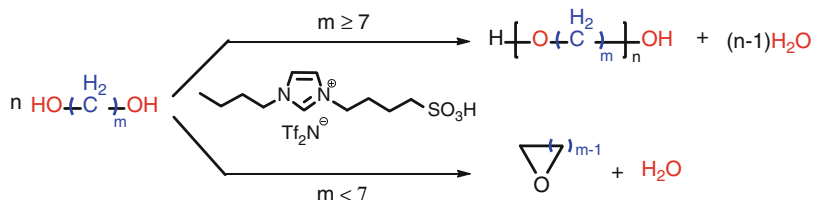


Fig. 13.13 Polyetherification of aliphatic diols using in BAILs

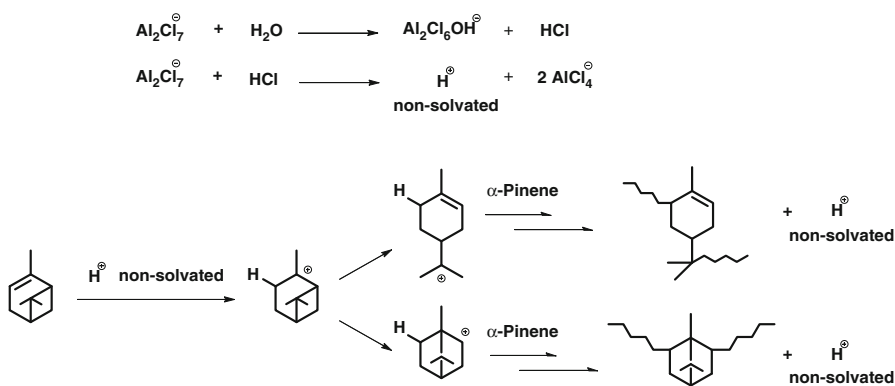


Fig. 13.14 Mechanism of α -pinene polymerization with LAILs

polymerization process free from any organic solvents and free acid [112]. Lewis acid ionic liquids (LAILs) of the type $[\text{EtOCOCH}_2\text{-mim}][\text{Cl-AlCl}_3]$ in combination of SbCl_3 (cocatalyst) were used in the polymerization of α -pinene in toluene solvent [140, 141]. As compared with commonly employed catalyst AlCl_3 , these LAILs are more effective in polymerizing α -pinene, and also in the latter case, the polymer separation is easy, and the catalyst can be effectively reused for several cycles. It was noticed that trace amounts of water was required for generation of activated proton which is responsible for higher catalytic activity (Fig. 13.14). The polymerization α -pinene with $[\text{EtOCOCH}_2\text{-mim}][\text{Cl-CuCl}_2]$ could not proceed due to its inability to give activated proton that supports the proposed mechanism.

Bronsted-Lewis acid ILs (BA-LA ILs) are also reported to be effective catalysts in dimerization of fatty acid methyl esters [142]. Basic ILs (see IL-14 in Fig. 13.8) such as $[\text{Bmim}][\text{OH}]$, $[\text{Bmim}][\text{PO}_4]$, $[\text{Bmim}][\text{CO}_3]$, and $[\text{Bmim}][\text{HCO}_3]$ were used as ligand and catalyst in iron-mediated AGET atom transfer radical polymerization [39]. The catalytic activity of $(\text{BMIm})_2(\text{DMIm})\text{PW}_{12}\text{O}_{40}$ was investigated for photopolymerization of styrene, methyl methacrylate, butyl methacrylate, and vinyl acetate in the absence of any additional co-initiators. And it was reported to be efficient recovery and reusability of catalyst [143]. Xanthenyl phosphonium salts were used as

thermo-latent initiator in the bulk polymerization of glycidyl phenyl ether that afforded polymer with a maximum M_n of 3,400 in quantitative conversions [144].

Hydroxylated imidazolium-based ILs were used as initiators with trifluoromethanesulfonic acid in cationic ring-opening polymerization of LA to synthesize medium molecular weight PLA with IL end groups. These IL functionalized polylactides were further used to stabilize the carbon nanotube suspensions. The strong interactions between IL part of PLA and carbon nanotube surfaces are the key in the stabilization of its suspension, and this interactions were noticed through SEM images [145]. ILs were also used as ligands towards metal complexes (catalysts) for polymerization reactions such as ATRP [44].

In polymerization reactions, when compared with traditional catalysts, some ILs showed better catalytic performance and recyclability. The adjustable acidity/basicity to desired level, the easier separation and isolation of polymer solution from catalyst, and the recyclability and reusability of catalyst are the predominant advantages of ILs over other commercial catalysts/ligands.

Conclusion

In general, higher molecular weight polymers with remarkably faster reaction rates in good conversions were noticed in IL-mediated radical polymerization reactions over conventional solvents. When polymerization is carried out in ILs, the observed advantages are increase in K_p/K_t with an increase in IL concentration (in radical polymerization), block copolymer synthesis by simple conventional radical polymerization, easy isolation of the products, and recovery and reuse of catalysts (ATRP, RAFT, Z-N system, etc.). It is also interesting to observe that the disproportionation of Cu(0) is highly favored in IL-mediated ATRP. Radical polymerization in ILs is very promising towards the commercialization of some of these techniques for the production of commodity polymers (homo- and block copolymers) in living manner.

Compared to anionic polymerization, cationic polymerizations in IL media are more feasible. This is because under basic conditions imidazolium-based ILs are less stable and it leads to deactivation of the initiator and/or chain transfer to IL. An increase in catalyst activity was observed in some IL-mediated cationic polymerization. Though the mechanism is not clearly known, it is believed that the ILs can stabilize the charged intermediates. This can be attributed to the moderately polar and non-coordinating nature of ILs.

Because of their higher thermal stability and nonvolatile nature, ILs are supposed to be the ideal media for the polycondensation. Though there are increasing reports in this field, much more is anticipated. Compared to other processes, the IL-mediated enzymatic polymerization suffers from the disadvantages such as long reaction time and lower molecular weights. Through the chiral discrimination capacity, enzymes facilitate the synthesis of chiral polymers from racemic monomer, but this advantage could not be explored further due to abovementioned limitations.

By selective choice of cationic and counter anionic part of ILs, the polymerization kinetics and the polymer properties can be tuned. There are more added advantages with positive impact on the environment when ILs are used as solvents in polymerization process. This is a promising research area that can be explored further for the better generation of tomorrow.

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