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Jim Massy

**A Little Book about
BIG Chemistry**
The Story of
Man-Made Polymers

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Jim Massy

A Little Book about BIG Chemistry

The Story of Man-Made Polymers

 Springer

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The first essential in chemistry is that thou shouldst perform practical work and conduct experiments, for he who performs not practical work nor makes experiments will never attain to the least degree of mastery. But thou, O my son, do thou experiment so that thou mayest acquire knowledge.

Jābir ibn Hayyān (Geber); ca 721–815 AD
Probably from *The Discovery of Secrets*
attributed to Geber, 1892
(London: Geber Society)

For Bea

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I hope that remaining errors are minor ones and will not disturb the reader. In particular, some of the dates given in the headings of Chap. 12 are difficult to determine accurately and must be considered approximate.

Images

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Helvetica Chimica Acta for the extract from **Staudinger and Fritschi's paper** on p. 4.

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About the Author

Jim Massy worked mainly in industrial polymer research, with an emphasis on surface coatings and textile chemicals. Following an uninvited early retirement, he studied further at the University of East Anglia (UEA) and gained a Ph.D. in 1986. Thereafter he spent his time doing organic synthesis of varied types in pharmaceutical research and at the UEA until a more normal retirement age beckoned.

Acronyms and Initialisms

ABS	Acrylonitrile butadiene styrene
AIBN	Azo diisobutyronitrile
AZDN	Azo diisobutyronitrile
BR	Polybutadiene rubber
BUNA	Polybutadiene rubber (NA indicating sodium-catalysed)
BUNA (N)	Butadiene/acrylonitrile copolymer rubber (N for Nitrile, NA indicating sodium-catalysed)
BUNA (S)	Butadiene/styrene copolymer rubber (S for Styrene, NA indicating sodium-catalysed)
DNA	Deoxyribonucleic acid
HDPE	High density polyethylene
ICI	Imperial Chemical Industries
LDPE	Low density polyethylene
MF	Melamine formaldehyde
MW	Molecular weight
PAEK	Polyaryletherketone
PBAT	Poly(butylene adipate/terephthalate)
PBS	Poly(butylene succinate)
PEEK	Polyetheretherketone
PET	Poly(ethylene terephthalate), sometimes PETE
PF	Phenol formaldehyde
PLA	Poly(lactic acid)
PP	Polypropylene
PS	Polystyrene
PVC	Poly(vinyl chloride)
RNA	Ribonucleic acid
TDI	Tolylene diisocyanate
UF	Urea formaldehyde

Introduction

This little book is addressed to anyone keen to know how everyday plastic materials came to be discovered and the basic chemistry underlying them. It gives a broad view of man-made polymers, thermoplastic, thermosetting and elastomeric and includes examples of their use in unexpected fields such as water softening and protein synthesis.

Readers should preferably be familiar with organic chemical structures and know something about the chemistry of simple reactions such as esterification. Many will know much more and must forgive me if the treatment is sometimes too simplistic.

This book was first available in October 2013 as an electronic edition (eBook) from Apple's iBooks Store. It is now replaced by this print edition which has been revised and corrected as necessary.

For reference purposes there is a detailed list of Contents and Acronyms at the beginning of the book and a full Index at the end. Where there are several index entries, those page numbers in **bold type** refer to the principal text items. Also at the end of the book there are Suggestions for Further Reading, a Glossary and References.

The idea for the book arose from a talk which I gave to sixth formers at several UK schools. I always found there was more material than could be crammed into a 45 min session. In particular I was keen to show the chronological development of polymers over the years, but this was almost impossible in one session. Eventually I listed a time line of the major polymers with notes on each and offered it as a separate resource. That list is now presented in Chap. 12, The Chronology of Polymers.

The early chapters of the book have a high historical content, but later ones concentrate on more general aspects of polymers, such as factors affecting their physical properties (Chap. 7).

I have emphasized the chemical reactivity of polymers in Chap. 8, Chemical Properties of Polymers, because I feel that in this area lies a great deal of undiscovered territory and I would like to think that one day, readers, who find themselves in disciplines other than chemistry, might be stimulated to think of new uses

for polymers in their particular field. That has been the case in the past and will undoubtedly happen again.

Chapter 11, Ethical Issues, touches on several environmental questions many of which, unfortunately, are posed by the very success of man-made plastics.

Finally, on a personal note, I've enjoyed chemistry since I was a boy. I was able to indulge this passion at home, as well as at school, thanks to a tolerant parent and an uncle, himself a chemist, who supplied me with apparatus and chemicals. I hope that chemistry will provide readers with at least as much enjoyment as it did me, especially if they should find themselves involved with **BIG Chemistry!**

Norwich, UK
December 2016

Jim Massy

Chapter 1

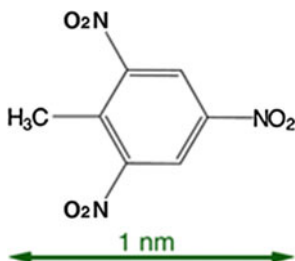
Big Molecules

A Little Book about BIG Chemistry—the Story of Man-Made Polymers, dips into a vast subject—the substance of many of the everyday articles in our lives. So far as it goes, it describes how these plastic articles came into being and some of the people who brought them into the world. It also delves into several fascinating aspects of their physical and chemical properties and highlights some of the problems arising out of their indisputable success. To start with though:

How Big Are Molecules of Plastics?

All common plastics are organic substances (carbon compounds) the molecules of which are very large. But how big are they compared to other common organic compounds such as glucose or the explosive TNT (trinitrotoluene)? Both of these are of similar size and could be regarded as small or medium-sized organic compounds.

Trinitrotoluene



Thus, TNT has a length of almost exactly 1 **nanometer** [1], that is a thousand millionth of a meter (I remember this because “nano” is a bit like “nine”, and a thousand millionth of a meter is ten to the minus **nine** meters).

That is our yardstick. However, **molecules of common plastics can be 1 micron (μm) in length**, that is a thousand times greater than TNT; although do please bear in mind that molecules of plastics are seldom stretched out in a straight line.

In terms of molecular weight, useful **plastics with values well above 100,000 are commonplace and some are several million**; by comparison, TNT is 227. But it has to be said that all common synthetic polymers comprise a mixture of molecules of various sizes. Hence, for these substances, any value of molecular weight that you read about will be an average.

Macromolecules—What Are They?

Now we’re going to look at how the idea of very large molecules, that is macromolecules, came about. The words ‘polymerization’ and ‘polymer’ were used as early as 1872 [2], but at that time they did not necessarily mean very large molecules. Often the nature of the products was quite vague, perhaps being thought to be colloidal particles made up of clumps of small molecules or else relatively small cyclic molecules made up of a few of the unit components. The word ‘macromolecule’, having the meaning of **a molecule of a covalently bonded compound of very high molecular weight**, was first coined in 1922 by a pioneer in this area of organic chemistry, a German chemist called Hermann Staudinger [3].

Extract from:

Staudinger, H. and Fritschi, J., *Helvetica Chimica Acta*, 5, 785-806 (1922)

Der Kautschuk ist danach ein sehr hochmolekularer Kohlenwasserstoff mit vielen Äthylenbindungen, und das chemische Verhalten entspricht auch völlig dieser Auffassung. Die Äthylenbindungen können teilweise oder ganz durch Anlagerung von Halogen, Halogenwasserstoff oder Schwefelchlorür bei der Vulkanisation abgesättigt werden, ohne dass sich die kolloidalen Eigenschaften ändern, also ohne dass die „**Makromolekel**“ zerfällt²⁾.

My translation of this paragraph is:

*Accordingly, rubber is a very high molecular weight hydrocarbon with many ethylene bonds, and its chemical behavior fully corresponds to this conception. The ethylene bonds can be partially or completely saturated through addition of halogens, hydrogen halides or sulfur chloride on vulcanization, without altering the colloidal properties or destroying the “**Macromolecule**”.*

We shall hear more about Staudinger later, but I thought it would be interesting at this stage to reproduce just a small part of the original paper in which the word ‘macromolecule’ appeared.

Understanding and Inventing New Materials

Let’s now look back and see what happened before Staudinger took the field in the early years of the 20th century.

Some people have called the 20th century the **Plastics Age** [4], because so many new materials were introduced then.

But how much basic understanding was needed for this to come about?

Which came first, understanding or inventing?

Interesting questions indeed! So to find answers, we have to look at what happened before the Plastics Age.

During the 19th century chemistry developed very rapidly. In my opinion its principal foundations were the Law of Constant Composition, and the prevailing obsession with purity. Those substances which could not be obtained pure were hardly in the realm of chemistry as it was then understood. Nevertheless, a number of useful new materials were discovered even though they were often neither pure nor of constant composition.

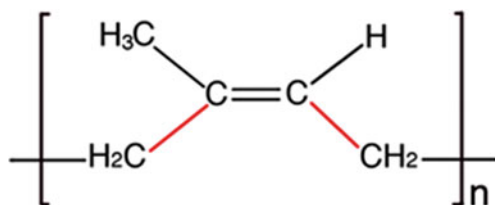
We’ll take a closer look at the three most successful of these: **rubber**, **cellulose** and the milk protein **casein** and see how they responded to man’s modification.

Chapter 2

Rubber in the 19th Century

Natives of Brazil had for centuries used rubber for footwear and other purposes, mainly obtaining it from the tree sap of *Hevea brasiliensis*. By the way, it's interesting to note that many other plants also contain rubber, for example certain species of the *Landolphia* plant found in the Congo region, and *Ficus elastica* widely distributed in Asia. However, these sources of rubber are not now exploited commercially on a large scale.

Here is the structure of a molecule of rubber, the chemical name for which is *cis*-1,4-polyisoprene:



cis 1,4-polyisoprene

It's worth taking a moment to emphasize some points about such polymer structures, as it is important to draw them correctly. In most cases they show exactly the unit of the polymer, so that it represents the total composition. The free bonds at each end of the structure will join the next unit. The letter "n" outside the brackets stands for the number of units in the polymer.

Returning to history, by the late 18th to early 19th century, supplies of South American rubber had reached North America and Europe and methods had been developed for coating fabrics (Mackintoshes), and to make rubber tubing, solid tires and many other articles. In England, Thomas Hancock made such items in the 1820s. They were very useful and practical just after manufacture, but ultimately they were seriously flawed by becoming soft and sticky in hot weather and hard and brittle in very cold weather. At that time many attempts were made to improve these

shortcomings but most failed. Because of this, most rubber businesses in the US, which had started with great hopes, collapsed. Clearly improvements were urgently needed. The discovery of the process which gave rise to the enduring and successful use of rubber worldwide, is one of great historical interest.

Nathaniel Hayward (1808–65) is correctly cited as the first person to use sulfur to improve rubber, and indeed US Patent 1060 dated 1838 was in his name, although assigned to Charles Goodyear (1800–60) [5]. Goodyear had already been obsessed with rubber and its improvement since 1834 and was interested in any new developments that came his way, and in fact Hayward worked with Goodyear for a time. Goodyear continued with a multitude of painstaking experiments until one day, the story goes, he accidentally dropped one of his samples on to a hot stove. It did not melt, as untreated rubber would have done, but instead it became tough and flexible. Goodyear was encouraged to continue. Further work confirmed that **heat** applied to a certain rubber, sulfur and white lead mixture gave this tough leather-like material. However, Goodyear struggled to reproduce such a product consistently and on a larger scale. Unfortunately, during this time, samples of his experimental materials were distributed widely for the purpose of obtaining financial support. Some reached Thomas Hancock in England, who suspected that they had sulfur in them. Hancock, who had more experience with rubber than anyone else in England, immediately saw the potential of this more durable rubber which he had previously thought was impossible to produce. So he secretly set about trying to duplicate it, applying himself with great energy and ultimately developing a process of his own based on rubber/sulfur mixtures. At the suggestion of a friend, he called it **vulcanization**. Hancock filed a provisional patent in England in November 1843, just a few weeks ahead of Goodyear's patent in the US [6]. This was to cause both parties seemingly endless legal disputes in the following years.



Charles Goodyear 1800 - 1860

Nevertheless, the vast improvement in properties brought about by vulcanization led to a rapid expansion of rubber usage, so that by the time Goodyear died in 1860, his material had been applied to nearly 500 uses, giving employment to 60,000 people [7].

An interesting example of an early use of vulcanized rubber was to make footballs, the first of which was manufactured in 1863, as illustrated here:



At that time neither the chemistry of rubber nor that of its vulcanization were understood. It was much later realized that what Goodyear and Hancock had done was to ‘crosslink’ the chains of rubber molecules with sulfur.

What Is Meant by Crosslinking?

A polymer without crosslinking (a linear polymer) can be shown as below



and this shows a crosslinked polymer, the black dots representing the points where the polymer chains are linked together by covalent bonds.



In the case of rubber, these dots would represent sulfur atoms linked to both chains by chemical reaction. About **3–4% of sulfur** is typically used.

More Extensive Crosslinking of Rubber

Then Thomas Hancock in the UK and Charles Goodyear and his brother Nelson in the USA, refined their experiments, examining more closely the products obtained from raw **rubber heated with much larger amounts of sulfur**. They obtained **hard solid materials** which did not have typical rubber elasticity. The process was included in Hancock's 1843 patent and Nelson Goodyear's of 1851. The new material was called Ebonite—after ebony, which some forms of it resembled—but alternative names were Vulcanite and 'hard rubber'. Because of the much larger amounts of sulfur used, it was a more highly crosslinked rubber than the flexible variety, typically containing **30–40% of sulfur**. It was useful for making articles such as pipe stems, fountain pens and even as a base into which porcelain teeth were embedded. Here is a picture of a set of artificial teeth in a Vulcanite base [8]:



Chapter 3

Cellulose and Casein in the 19th Century

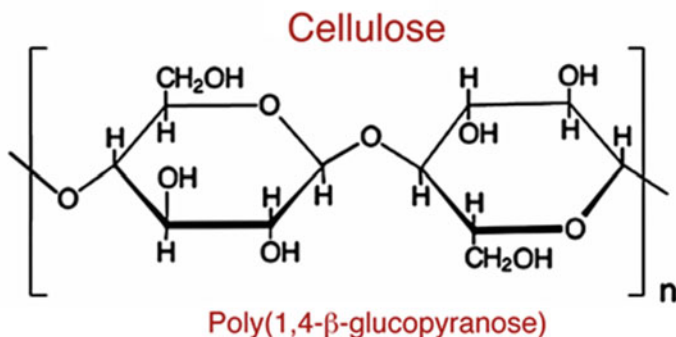
Now I want to turn to another natural polymer, cellulose, which was modified for practical use in the 19th century. The pure material was first isolated in 1838 by a brilliant French chemist, Anselme Payen [9], pictured here. He obtained it from wood as a white powder and gave it the name cellulose. Payen's analysis showed that it had the empirical formula $C_6H_{10}O_5$, and he pointed out its similarity to starch, but he did not know its chemical structure.



Anselme Payen 1795 - 1871

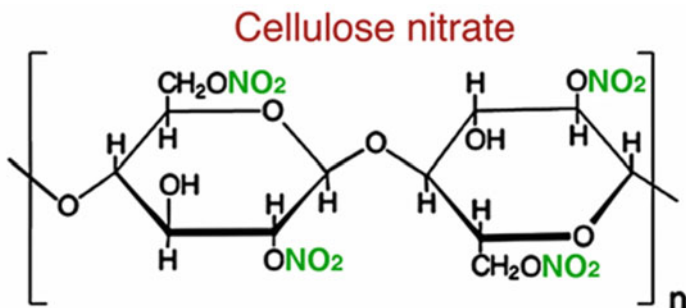
Cellulose

Here is the structure of cellulose as we know it today:



Poly(1,4- β -glucopyranose) is the formal name for cellulose. Typical values of 'n' are around 1500, giving a molecular weight of approximately 500,000. With such structures, there is a convention, particularly in carbohydrate chemistry, of using heavy lines for those ring bonds nearest the viewer. This gives a perspective effect; as though viewing the molecule at an angle, and enables one to show more clearly whether attached groups are above or below the plane of the ring.

At first, chemists investigating cellulose found it to be an intractable substance; it was insoluble in water and other solvents and when heated, it decomposed without melting. However, it was soon discovered that it could be reacted with a mixture of nitric and sulfuric acids forming a new product called **cellulose nitrate**, also known as nitrocellulose. This product could be dissolved easily, for example in ethyl acetate. Here is its structure:



The nitro groups are shown in green. Notice that not all of the hydroxyl groups have been nitrated—this is often done deliberately in order to get the desired properties. Cellulose nitrate is an extremely inflammable substance because the

nitrate groups decompose at high temperatures providing oxygen on the spot. This results in greatly accelerated combustion.

Its flammability may in fact have assisted its discovery. It has been said that around 1846 Christian Friedrich Schönbein [10], a German chemist who had become professor of chemistry in Basle, Switzerland, and was noted for his discovery of ozone, was working in the kitchen of his home, when he spilled a bottle of concentrated nitric acid on the table. He reached for the nearest cloth, his wife's cotton (cellulose) apron, and wiped it up. He hung the apron on the stove door to dry, and, as soon as it was dry, there was a flash as the apron exploded! The nitric acid had transformed it into cellulose nitrate, in a fibrous form. This became known as "gun cotton".

It was some years later that cellulose nitrate was used for producing molded artificial plastics. Such articles, which were made from a mixture of cellulose nitrate, camphor, oils and other ingredients, were shown at the 1862 Great Exhibition in London by Alexander Parkes [11]. All sorts of useful articles were displayed, such as buttons, combs, knife handles etc, most of which had previously been made out of metals, horn, ivory, tortoiseshell or shellac. The new material was called Parkesine and is generally regarded as the first artificial plastic material.



Alexander Parkes 1813 - 1890

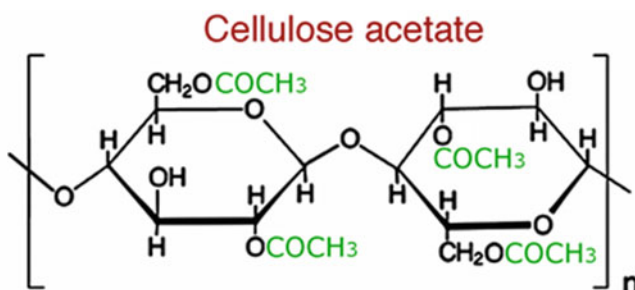
Unfortunately, however, the young Parkesine business was beset with financial and technical difficulties and soon collapsed, but the door had been opened for others and cellulose nitrate continued to be developed for many uses.

In the United States, two brothers, John and Isaiah Hyatt successfully manufactured a cellulose nitrate molding compound, naming it 'Celluloid' [12]. The Hyatts used camphor as solvent/plasticizer and patented such products in 1870 [13].

A similar product was independently made in England when Daniel Still, who had worked with Parkes, began a new enterprise in 1869. He called it Xylonite [11].

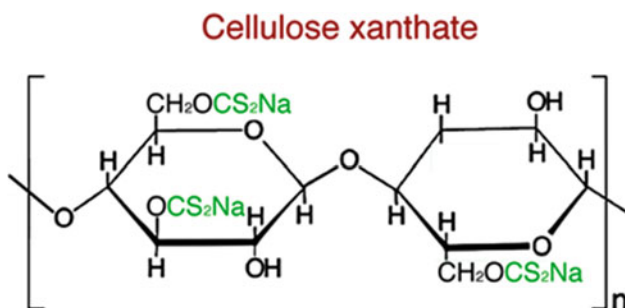
At the end of the 19th century, films of cellulose nitrate were used in the budding cinema industry. It was also found that fibers could be spun from solutions of the polymer and woven into textiles. Later on cellulose nitrate was used as an interlayer in safety glass, known by the name Triplex. However, one literally fatal shortcoming for many of these uses was the flammability of the new material. It proved to be far too dangerous as a film or textile fiber although its use in paints and varnishes, for example on Rolls Royce cars, in nail varnishes and in explosives, became very successful and continues today.

Meanwhile chemists eventually discovered that cellulose could be reacted with acetic anhydride to give **cellulose acetate**.



This product was in many respects similar to cellulose nitrate, but it was much less flammable. For this reason, in the cinema film industry, cellulose acetate was known as “safety” film. As with cellulose nitrate, not all the hydroxyl groups are generally esterified, in order to optimize properties.

Going back to the unmodified cellulose, in the course of time it was discovered that this material too could be dissolved under certain conditions. The most commercially important of these processes involved treating cellulose, in the form of wood pulp, with 18% sodium hydroxide solution followed by carbon disulfide, which reacted to form a solution of the water-soluble xanthate salt.



Xanthates are somewhat unusual chemical entities. They are also called dithiocarbonates, which may help us to understand where they come from.

On extruding a solution of sodium xanthate through a fine nozzle, into a coagulating solution, cellulose is regenerated as a fiber. That fiber is now called viscose and is still widely produced by the same method. Because of its hydroxyl groups, the fiber has an affinity for water, and clothing made from it is comfortable to wear, like cotton. After all, chemically, it has the same structure as cotton.

Alternatively, the same xanthate solution can be extruded as a transparent film well known as **Cellophane**.

Because carbon disulfide is highly inflammable, toxic and foul smelling, suitable alternative procedures to the xanthate method have long been sought. Rather surprisingly, cuprammonium salts have had some success as cellulose solvents since about the year 1900. Cuprammonium cellulose dope is extruded into a coagulating solution and drawn out into a fiber. The method is still used to a small extent today.

However, it wasn't until the 1980s that a commercial process was introduced using *N*-methylmorpholine *N*-oxide monohydrate, a solvent which, when heated above its melting point (73–76 °C), dissolves cellulose. Viscose fiber is formed on extruding the solution into water, and the solvent recovered. The fiber is known as Lyocell and also Tencel. Manufacture is said to be more environmentally friendly than the xanthate method and is now a major process worldwide.

Casein

One further development at the very end of the 19th century was the discovery that useful plastic materials could be made from casein, a protein present in milk, by treating it with formaldehyde [14].

This new material was apparently discovered by accident in the laboratory of the Bavarian chemist Adolf Spitteler in 1897, and was later marketed successfully under the names of Galalith and Erinoid, for making small articles such as buttons and costume jewellery. For these purposes it was remarkably successful. The new material could be molded and colored easily and the products were visually attractive. Furthermore, in Italy and the United States, casein-based fibers were marketed in the late 1930s under the names Lanital and Aralac, respectively.

Worldwide production of casein plastics reached 10,000 tons in 1936, but after World War II, production declined in the face of newer plastics materials.

From a chemical viewpoint, formaldehyde acts as a crosslinking agent for casein, analogous to the crosslinking of rubber with sulfur, but this was still not fully understood at the time it was first introduced.

Into the 20th Century

So we see that by the turn of the 19th to 20th centuries rubber, cellulose and casein had become the starting points for most of the artificial plastics of that time. Although there had been quite extensive developments in these polymers, it was not generally understood that the materials owed their useful physical properties to the fact that they were of high molecular weight. Once that had been accepted, chemists began to realize that perhaps new products could be made wholly synthetically, and maybe with even better properties.

Chapter 4

Macromolecules in the 20th Century

Now we shall move into the 20th century and see how the idea of very large molecules **did** become accepted.



Hermann Staudinger
1881 - 1965

The main credit for this crucial new understanding, which led to the so-called Plastics Age, can be given to Hermann Staudinger [16], a German chemist we mentioned earlier.

Staudinger had many chemical interests and was the discoverer of ketenes which themselves have a tendency to polymerize. In 1920 he published a paper entitled "Concerning Polymerisation" which dealt with many types of polymers, some of which he claimed were of high molecular weight.

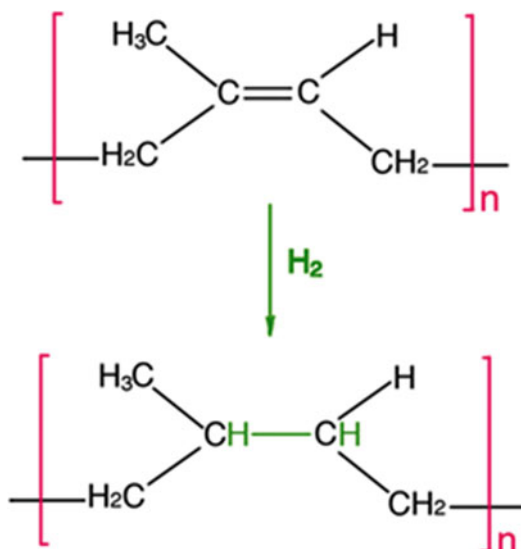
But many substances formed ring systems, not long chains. So although it was not easy to prove that high molecular weight products existed, Staudinger and a few other chemists firmly believed that they did. Critics held that indications of high molecular weight, such as little or no depression of freezing point, were actually caused by aggregation of small molecules into micelles or colloidal particles, held together by what were termed "partial valence bonds".

For example, unvulcanized rubber forms such colloidal solutions in benzene. At rubber concentrations of 2 or 3% the freezing point of benzene is unchanged (approx. 5.5 °C) and on increasing the concentration of rubber, such solutions become viscous. You remember we have seen that the unit of rubber contains a double bond. Well, some people thought at the time that interactions between the double bonds were the cause of this behavior.

Staudinger believed that if he could remove those double bonds and if the product then remained colloidal, his idea that rubber was intrinsically a material of high molecular weight would be strongly supported. There could be no other explanation in his view.

Staudinger succeeded in removing the double bonds by various means such as addition of hydrogen chloride or hydrogen [3]. The addition of hydrogen was achieved under extreme conditions using a platinum catalyst, hydrogen at 100 atmospheres pressure and a temperature of 270 °C.

Here is the scheme showing this transformation:



After work-up, the product was found to be a colorless, transparent, tough mass, lacking the fully elastic properties of rubber. The results of combustion analysis corresponded to C_5H_{10} . However, solutions in benzene still showed typical colloidal character: the freezing point was not depressed and the ultramicroscope revealed recognizable particles. Full hydrogenation was confirmed by treatment with a solution of bromine, which was not decolorized, unlike ordinary rubber solutions. According to the orthodox view, removal of the double bonds by hydrogenation should remove the possibility of aggregation, yielding a substance of low molecular weight which would depress the melting point of its solution in benzene.

But it didn't!

This, he argued, could only be explained by accepting that the rubber molecule was strongly bonded and of very high molecular weight. His critics disagreed; the orthodox scientific community doubted the existence of compounds with molecular weights above 5000, because they thought that such large covalently bound molecules would be too unstable.

Thus, in 1926 Heinrich Wieland, one of the leading organic chemists of his day, was said to have written to Staudinger [17]:

Dear Colleague,
drop the idea of large molecules; organic molecules
with a molecular weight higher than 5000 do not exist.

Purify your products, such as rubber, then they will crystallize
and prove to be low molecular compounds.

It took Staudinger and a few others, notably W.H. Carothers in the USA, many years of painstaking research before the majority of chemists were persuaded that macromolecules existed.

Staudinger was finally vindicated in 1953 with the award of the Nobel Prize in chemistry for his work on macromolecules [18].

Chapter 5

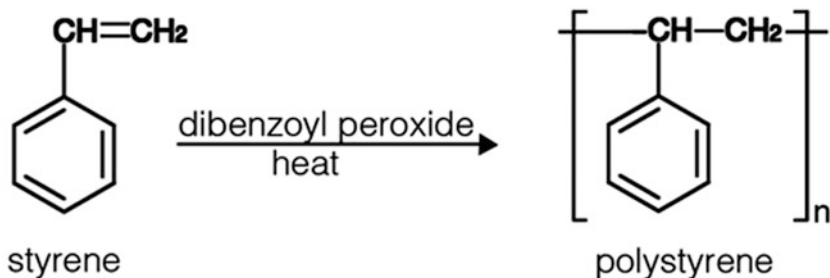
Thermoplastic and Thermosetting Polymers

Now I want to discuss two basic types of polymers. You probably know these types, at least by name. Thermoplastic and thermosetting. As the names imply, thermoplastic polymers soften and become plastic or rubbery when heated, whereas thermosetting types become “set”, that is they harden irreversibly when heated. Cellulose acetate and nitrate are examples of thermoplastic polymers and Ebonite, which is highly crosslinked rubber, is a typical thermoset polymer. Another thermoset is casein/formaldehyde. As we have seen, all these substances are derived from natural products, cellulose, rubber and, in this last case, the milk protein casein. Nature did the polymerization, man modified the polymers.

We shall now look at examples of fully synthetic thermoplastic and thermosetting polymers manufactured in the 20th century.

Thermoplastic Polymers

One of the commonest of the thermoplastics is polystyrene. It is made by polymerizing styrene, the parent monomer, as shown in the following scheme:

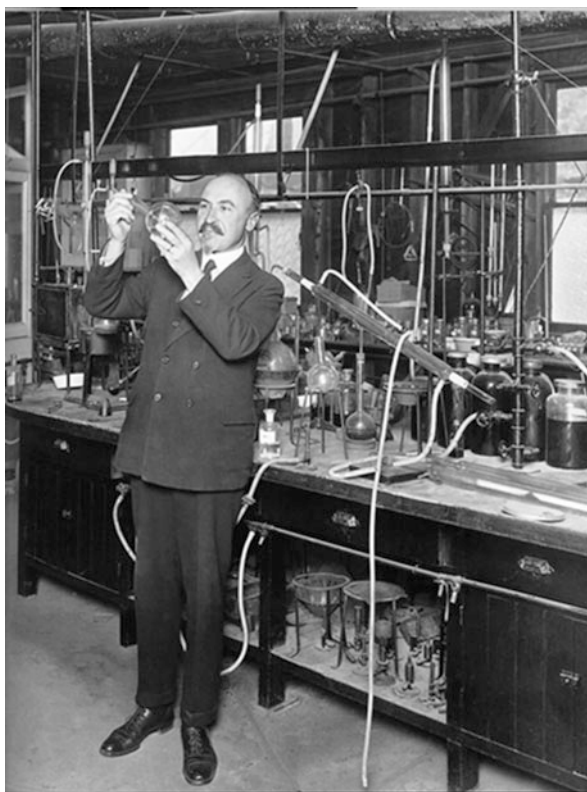


Styrene monomer is a clear, colorless volatile liquid with a strong smell. The polymer is a clear, colorless, odorless, strong solid material, which can be softened and molded by heat and becomes rigid again on cooling.

Polystyrene is a typical thermoplastic polymer. As we shall see, many polymers are made by opening up double bonds in this way and they are known as **addition polymers**—they may or may not be crosslinked. I might just add here that polymers produced by reactions which result in water being split out are sometimes called **condensation polymers**, examples of which are polyesters and polyamides (nylons). Like the addition polymers, they can be thermoplastic or thermosetting.

Thermosetting Polymers

As an example of a fully synthetic thermosetting polymer, let's look at the oldest of these: **phenol/formaldehyde resins**, developed by Leo Baekeland [19] in the early 1900s. Here is a picture of him in his laboratory:



Leo Baekeland 1863 - 1944

Baekeland came from Belgium and has a colorful history. He was an accomplished scientist with a Ph.D. from Ghent University. He married the Professor's daughter and got a job in the USA. Later he set up his own business there to make photographic papers and after a few years, sold it to Kodak for 750,000 dollars! He then embarked on finding a practical process for making molding resins from phenol and formaldehyde. He was eventually successful, and in 1909 he patented his process, naming the substance of the molded articles, **Bakelite**. It was the first fully synthetic polymer of any kind and did extremely well right from the start.

Functionality and Crosslinking

Now we have seen that there are these two types of polymers, but what is the underlying difference between thermoplastic polystyrene on the one hand and thermosetting phenol/formaldehyde on the other?

Why should phenol with formaldehyde give a thermosetting product, and styrene a thermoplastic one?

The answer is that thermoplastic polymers are made from compounds which can undergo **two** bond-forming reactions per molecule. However, if there are **more than two** bonding points per molecule, the resulting polymer can form a cross-linked network, i.e. it is thermosetting.

The number of bonding points of a substance is called its **functionality**.

Just to recap:

Two bonding points equals thermoplastic (linear molecules).

More than two bonding points equals thermosetting (network molecules).

Since styrene monomer (also known as vinylbenzene) has only two bonding points, the polymer is linear and thermoplastic.

On the other hand divinylbenzene has four bonding points and its polymer is a crosslinked, thermoset product.

Where two or more reactants have differing functionalities, the situation is slightly more complicated, the outcome depending critically on the amounts of each used and of course how far the reaction is taken. In the case of Baekeland's molding resins, the molecule of phenol used has three bonding points, two *ortho* and one *para*, where it can be reacted with formaldehyde, and the formaldehyde itself has two bonding points, yielding an overall bonding number greater than two. The system will be thermosetting provided more than one mol of formaldehyde per mol of phenol is used.

Heat of Polymerization

Many polymerization reactions, whether thermoplastic or thermosetting, are exothermic. This poses a number of problems in manufacturing, particularly on a large scale.

Take for example a stirred reaction vessel, either a laboratory glass flask or a large stainless steel industrial reactor. If styrene is heated in it with a polymerization initiator, such as benzoyl peroxide, but with no solvent, a succession of changes will occur. When the temperature reaches around 80 °C the benzoyl peroxide will start to dissociate into free radicals and polymerization will begin. As it proceeds, heat will be given out and the polymerization will become more rapid. The mixture will also become more viscous and at some point the stirrer will not be powerful enough to continue. However, unless the heat is removed, the reaction will continue, ever faster until decomposition sets in. Finally the whole system may even explode! For this reason, exothermic polymerizations are generally carried out in solution or with the monomer dispersed in water, the heat being removed by cooling the reaction vessel or by refluxing or both.

Reaction of Phenol with Formaldehyde

Thermosetting polymers, such as those based on phenol and formaldehyde, have to be made in such a way that the reaction proceeds as far as possible, without any significant crosslinking. Taken too far, the reaction mixture forms a gel which cannot be properly stirred. So the intermediate products are reacted to a point before gelation, and later converted to fully crosslinked plastic materials by the end user. These intermediates are called **PF resins**.

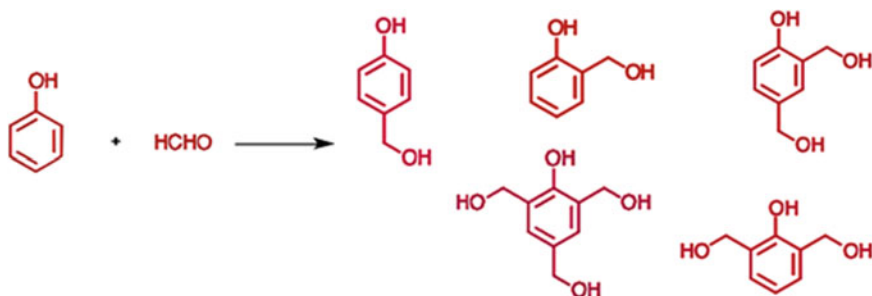
They are of two types, those reacted under alkaline conditions with an excess of formaldehyde (known as **resoles** or resols) and those reacted under acid conditions with a molar deficiency of formaldehyde, for example 1 mol of phenol to 0.9 mol of formaldehyde (known as **novolaks** or novolacs).

PF Reaction Under Alkaline Conditions

On the next pages we can see what reactions are taking place during the first stage of a reaction under alkaline conditions.

Phenol as a solid or concentrated aqueous solution is mixed with aqueous 40% formaldehyde (commonly called formalin) under alkaline conditions and heated under reflux with stirring. Adequate cooling is necessary to control the exothermic reaction (see above, on this page).

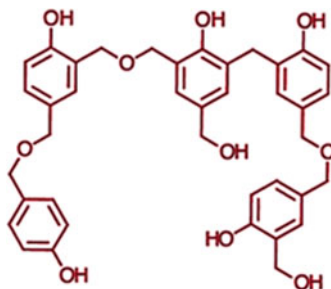
In the first stage, there is a gradual build-up of all the various possible reaction products. At the start, simple molecules containing one phenolic ring will be formed. Here are all the five possible monocyclic structures with 1, 2 or 3 hydroxymethyl groups attached to phenol:



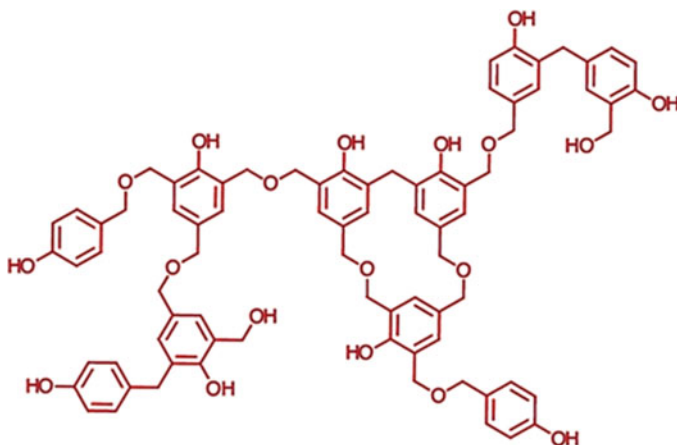
Compounds containing two phenolic rings are then formed by reactions between these monophenolic compounds as well as their reaction with further phenol. The inter-cycle linkages are mainly dimethylene ether groups, but simple methylene groups may also be present at this stage. Here are examples to illustrate the two types of linkage:



Reactions will of course continue, building up larger and larger molecules such as this:



and this:



So you can see that, unlike a simple organic reaction of the type $A + B$ giving AB , when polyfunctional chemicals are reacted together, there can be an endless number of products.

The reaction is stopped when the mixture becomes viscous. It is then neutralized, concentrated, poured out of the reaction vessel and cooled. The product is a resol. As you can see, this behavior is quite different to that of the polystyrene polymerization described on p. 19.

In the second stage, the product, containing compounds like the ones shown above and even more complex ones, is mixed with fillers and other additives and molded under heat and pressure to give the final article—say, for example, a part of a light switch. The molded product will have become fully reacted, highly cross-linked and will be composed of an infinite 3-dimensional network of atoms joined by covalent bonds. It is important to understand that the formation of this network is dependent on the ability of phenol to react at three places on the ring, two *ortho* and one *para*. For example, if you reacted formaldehyde with *para*-cresol, that is 4-methylphenol, (two bonding points) you would not get a thermosetting product. With *meta*-cresol, 3-methylphenol, (three bonding points) you would.

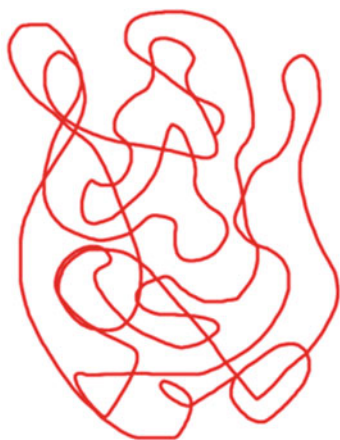
PF Reaction Under Acid Conditions

Under acid conditions the bonding between phenol molecules consists almost if not entirely of methylene bridges—methylene ethers are not stable under these conditions. Oxalic acid is often used as the catalyst. As mentioned above, the molar ratio of phenol to formaldehyde must be $1: <1$ otherwise the mixture will very readily gel. However, with the right ratio, a solid clear resin will be obtained after

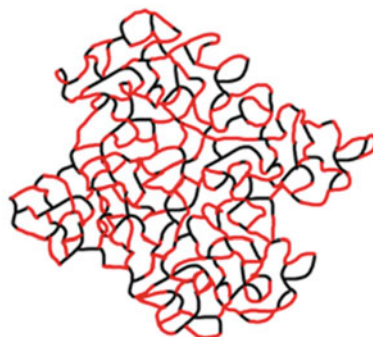
evaporating volatiles (mostly water, if the source of formaldehyde is formalin). This resin is a novolak and at this stage it is an example of a low molecular weight thermoplastic i.e. it can be melted and re-solidified without significant chemical change. The term **prepolymer** is often used to describe such intermediate products. Of course the novolak needs some more formaldehyde in order to form a thermoset and for this, hexamine is the most usual source. Hexamine (in full hexamethylene tetramine) is a solid, easily obtained from formaldehyde and ammonia. The novolak crosslinked with hexamine contains some dimethylene amine bridges between the phenolic rings: $-\text{CH}_2\text{NHCH}_2-$.

Thermoplastics and Thermosets Compared

As we saw earlier with rubber (p. 7), it is sometimes instructive to show polymer chains as lines, without individual atoms. Shown here are similar imagined possible structures of a thermoplastic polymer and a fully crosslinked thermosetting one.



Overlapping, but not crosslinked
eg polystyrene



Tightly crosslinked
eg PF resin

Thermoplastics of high molecular weight are suitable for making molded products, fibers, films) (including paints) and adhesives. Thermosets find application in similar fields, but are not generally useful as fibers.

In the case of thermosetting polymers, we have seen that there are two stages. After the first stage the reaction product is still thermoplastic, and is a mixture of compounds of comparatively low average molecular weight. At this point it may be sold by a resin manufacturer. The second stage is carried out at the point of use; perhaps a firm using paints, or making moldings or laminates, or a private individual using a two-part epoxy resin such as Araldite to stick something together.

An interesting example of a two-stage polymer system is that of so-called ‘thermosetting acrylics’. The first stages consist of polymerizing a monomer mixture which includes acrylamide at a level of about 10%—the other monomers being combinations of styrene, ethyl acrylate, methyl methacrylate and acrylic acid. In the same reaction vessel this copolymer is then reacted with formaldehyde, forming *N*-hydroxymethyl groups attached to the acrylamide nitrogen. These operations are carried out in solution. After intensive mixing with pigments and other additives, the resulting paint is used as a coating for domestic appliances. The second stage is to crosslink the coating, which is done in an oven for 30 min at 180 °C.

What is Meant by the Term ‘Elastomer’?

It’s convenient to classify polymers as thermoplastic or thermosetting, and the understanding of polymers in this way is perfectly correct up to a point. However, we do need to clarify the position of the various kinds of rubber. We’ll use the term **“elastomer” meaning any polymer which has rubber-like properties at ambient temperatures**. Temperature is the key. Many hard thermoplastics become rubbery on heating. Elastomers on the other hand, when cooled sufficiently, become hard solids.

A characteristic of polymers, both thermoplastics and elastomers, is their **glass transition temperature T_g** . Polymers with a value of T_g well above room temperature will be glassy and brittle; those with a T_g near to room temperature, will be less rigid and tougher. Elastomers, however, have a T_g well below room temperature.

If we consider thermoset polymers in relation to T_g , we find that as the extent of crosslinking increases, so does the T_g . However, take note that the factors which affect physical properties are complex. A little more discussion on this topic is to be found in Chap. 7.

Chapter 6

The Burgeoning of Modern Plastics

We have seen how the true nature of polymers only became properly understood in the early 20th century and we have looked at the differences between thermosetting and thermoplastic polymers and elastomers.

As the 20th century progressed, numerous new polymers, both thermosetting, thermoplastic and elastomeric, were invented and developed for a very great range of uses—far more extensive than those uses for which the man-modified polymers such as cellulose acetate were suited. Some of these uses were very unexpected, e.g. polymers as water treatment agents, oil additives, for solid phase synthesis of biopolymers, or as non-stick coatings, to mention just a few.

However, the three most striking things about the modern polymers were their **colossal strength**, their **relative cheapness** and their **availability on a vast scale**. Just as cellulose acetate and casein polymers were often successful in replacing fully natural polymers such as silk, ivory or horn, so the modern fully synthetic polymers challenged the older semi-synthetic ones, greatly enlarging their scope and totally replacing them in all sorts of applications.

The most conspicuous success of the 20th century polymers was in large volume areas such as molded articles—ranging from buttons to boats—films (particularly the ubiquitous plastic bags), fibers, laminates, adhesives and surface coatings, all of which required plastics on a staggering scale. Thus, although reports vary, annual production of plastics worldwide is soon expected to reach 300 million tonnes!

As a consequence of this success, mankind is now faced with an urgent problem about how to dispose of plastics after use, especially those used for packaging. This question is addressed in Chap. 11.

Chapter 7

Physical Properties of Polymers

The success of the major bulk polymers depends on their price, their physical properties and their durability. Of these, physical properties, such as tensile strength and impact resistance, are of primary importance—but what determines these properties? To an extent they are governed by the chemical structure of the polymer—polyethylene is flexible; polystyrene is hard and inclined to be brittle; polymers of high molecular weight are stronger than low molecular weight ones. But there are four other factors which have a profound effect on the physical properties of polymers:



Crystallinity

Crystallinity in this context means ordered regions, i.e. when polymer chains are aligned with each other. In this sense, many polymers are crystalline to a greater or lesser extent. **Crystalline regions improve the strength** and are formed when chains are folded back on each other in a regular manner or grow radially from fixed points.

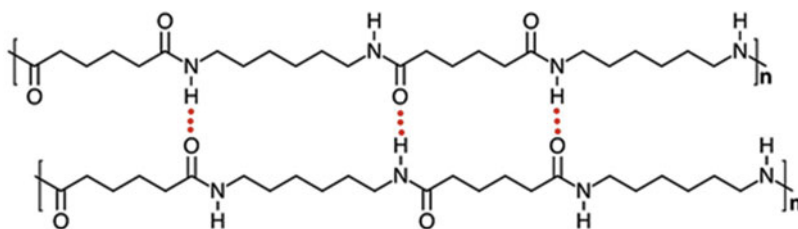
As the chains are packed more closely in these regions, so the polymer density increases. The reason why high density polyethylene (HDPE) is harder and stronger than the low density version (LDPE) now becomes clear—it is more crystalline.

Hydrogen Bonding

A hydrogen bond is one in which a hydrogen atom, covalently attached to an electronegative atom such as nitrogen or oxygen, is also weakly bonded to another electronegative atom on the same or a different molecule. The weak force between the atoms forming the hydrogen bond is thus electrostatic. The most well known hydrogen bonds are those which hold molecules of water together. Hydrogen, covalently bonded in one water molecule is also weakly bonded to oxygen in another molecule of water and by repetition an array of water molecules with weak bonding between them will exist. Without this bonding, water would be a gas at room temperature.

Both proteins and carbohydrates have many hydrogen bonds, but water will overwhelm these in an aqueous solution. A striking example from everyday life can be seen in the behavior of cotton washing as it dries. When wet there is little interchain hydrogen bonding between the cellulose molecules, but when it is completely dry the article becomes much stiffer and harsher, particularly if there is little or no movement from wind during the drying. Further examples are the behavior of paper and cardboard which are also made of cellulose—it is common experience that unless they are specially treated, they will lose much of their strength if wetted. Wetting swamps the interchain hydrogen bonds with others coming from the water, thus reducing the strength.

Hydrogen bonding can also be important in hydrophobic polymers containing the electronegative atoms oxygen or nitrogen or both. A notable example is nylon. Here you can see the hydrogen bonds shown as red dotted lines joining two chains of nylon 6,6 polymer:



It is of interest to compare this structure with that of nylon 6 which is shown on p. 59.

Reinforcement

Fillers

The physical properties of polymers can be greatly increased by incorporating certain solid fillers. Fillers are finely divided powdered solids added to polymer systems before fabrication into finished products. Examples are chalk, china clay, wood flour, carbon black and amorphous silica. Fillers may of course be added to a polymer to make it cheaper or to add color or opacity, but most importantly certain fillers impart improved physical properties, such as better tensile strength, impact resistance and abrasion resistance.

An outstanding example is the use of **carbon black** as a reinforcing filler for rubber. Carbon black is carbon in the form of small particles. Those forms with the best reinforcing properties are called “furnace” blacks, the particles of which are 15–80 nm in size, the smallest being the most effective. Take styrene/butadiene rubber (SBR) for example; a composition based on 100 parts of styrene/butadiene rubber, 40 parts of high abrasion furnace carbon black together with antioxidants and other additives, provided more than a tenfold increase in tensile strength and a huge increase in abrasion resistance compared to unfilled vulcanizates [20]. The use of carbon black for demanding purposes, such as tires, is thus almost essential.

Fibers

Fibrous materials such as straw or wool have long been used to strengthen clay, wattle, plaster etc., which otherwise were brittle. Thus, the principle of reinforcement by fibrous materials was known many years ago.

By the 20th century, with the advent of synthetic polymers, especially phenolic resins, a number of new and practical articles were introduced, reinforced with cellulosic fibers in the form of paper or cloth.

Paper impregnated with a phenolic resin was developed into the well known “Formica”, usually with a decorative melamine/formaldehyde top layer. Such layered structures are called **laminates**.

Linen cloth impregnated with a phenolic resin became widely used for demanding applications, such as the manufacture of aeroplane propeller blades. These developments took place in the 1920s and 1930s.

In the early 1930s a practical process for producing very fine glass filaments known as glass silk was introduced. Some manufacturers did not at first recognize its potential as a reinforcing agent for plastics, but when this use did become known, it was adopted by industry on a large scale, particularly just after World War II (late 1940s). By this time several new thermosetting polymers had been marketed. Those specially suitable for glass reinforcement were epoxy resins and unsaturated polyesters (see p. 61 and p. 62).

Carbon Fibers

A further breakthrough occurred during the 1960s when carbon fibers were introduced. They had been discovered by Roger Bacon at Union Carbide in the USA in 1958 [21], but it was not until several years later that economic processes for

manufacturing them were developed. Like the glass filaments, carbon fibers have a diameter of around 5 μm . In many instances they are bundled into yarns and woven into cloth. This is then impregnated with a thermosetting resin system, such as an epoxy resin with hardener, and pressed into layers. These are then heat cured in the desired shape. Articles thus reinforced have outstanding strength but they are also light in weight compared with metals of comparable strength such as aluminum alloys. Such fiber-reinforced polymers are often called composites. Those which contain carbon fiber are especially useful in aerospace applications.

The chemistry of carbon fibers is itself interesting. A common method of manufacture is to start with a polyacrylonitrile fiber and carbonize it by heating at a high temperature. The carbon then has the structure of graphite, the alignment of which along the fiber axis is responsible for the very high Young's modulus, characteristic of carbon fiber.

Plasticization

Certain compounds, when added to a polymer, confer increased flexibility. This arises from their ability to separate the polymer chains, allowing them to move more freely. In this way, rigid polymers can be made more flexible. Historically, the use of camphor to plasticize cellulose nitrate was a breakthrough which led to its widespread use under the name of Celluloid (see p. 11). In more modern times, two basically rigid polymers have enjoyed much wider use when plasticized—these are PVC (polyvinyl chloride) and PVA (polyvinyl acetate). Unplasticized PVC is rigid enough for window frames, but plasticized with dinonyl phthalate, for example, is suitable for coating textiles and other uses where flexibility is needed (see p. 55). PVA plasticized with dibutyl phthalate enables it to be used as an emulsion paint and adhesive—without plasticization its use would be very limited.

Chapter 8

Chemical Properties of Polymers

Organic chemistry is highly organized. Were it not so, one would have to remember the characteristic properties of huge numbers of chemical substances. However, one learns that the class of compounds called esters are prone to hydrolysis and are often fragrant, amines are basic and often smelly, ketones form oximes and so on. Such chemical or physical properties do depend to an extent on the composition of the rest of the molecule, but nevertheless, the chemical behavior of functional groups such as alcohols, carboxylic acids, amines, etc. is to a large extent consistent, regardless of the molecule to which they are attached. When such functional groups are attached to polymers, let us say to a polyvinyl backbone, they still display their characteristic reaction behavior, albeit often with diminished activity.

So in this chapter we are going to look at polymers from the point of view of their chemical properties rather than their physical ones, a view which is frequently ignored in elementary treatments, but is of absorbing interest.

Polymers of any molecular weight, will undergo most of the chemical transformations appropriate to their class. There may be practical problems to be addressed, such as insolubility and difficulty in purification of the products, but there are numerous interesting cases where these have been circumvented. Examples are the esterification of cellulose to cellulose acetate (p. 12), the reaction of poly(vinyl alcohol) to give poly(vinyl butyral) (pp. 55–56) and the reaction of acrylamide copolymers with formaldehyde (p. 26).

But knowing the chemistry of the repeating group is also extremely useful in assessing the properties of a polymer in order to predict how it will behave, especially important being resistance to external influences. Thus, polymers containing ester groups will not be resistant to alkalies. Those containing acetal groups will not be resistant to acids. Those containing halogen atoms will resist fire better than those without. This sort of information is vital in deciding the areas in which polymers are likely to be suitable and will always be of great importance.

Polymers as Reagents

Now at this point we shall consider some ways in which the repeating groups in polymers are useful not just for deciding their advantages or limitations outlined in the previous paragraph, but how those repeating groups can be exploited by further reaction, that is as reagents.

First of all we shall look at a list of several chemical groups common to both small molecules and polymers.

Repeating Chemical Groups of Some Common Polymers

Hydrocarbon	polystyrene (aromatic), polyethylene, polypropylene, natural and synthetic rubbers
Esters	poly(vinyl acetate), cellulose esters poly(ethylene terephthalate) poly(methyl methacrylate) poly(lactic acid)
Carbonate	polycarbonate
Amides	polyamides (nylons), polyacrylamides polypeptides (proteins)
Chlorides	poly(vinyl chloride), polychloroprene
Alcohols	poly(vinyl alcohol), cellulose
Nitriles	polyacrylonitrile and copolymers
Acetals	polyoxymethylene, poly(vinyl butyral), cellulose and derivatives
Enes	natural rubber, gutta percha polybutadiene and butadiene copolymers

That's quite an impressive array of chemical substances and of course there are other less common polymers with interesting functional groups too, for example poly(4-vinylpyridine) or poly(vinylpyrrolidone). It is noteworthy that all react much as one would expect their unit counterparts, provided one can get the polymers into

solution or react them in a finely divided or porous state with an appropriately aggressive reagent.

Ion Exchange Resins

A good example of the further reaction of polymers is found in the manufacture of ion exchange resins. Ion exchange resins are used in numerous applications, including, for example, household water softeners.

At the heart of water softeners are polymer beads, often called resin beads, through which the water flows to be softened. These beads are hard, translucent, amber-colored particles of about 100–300 μm in diameter and are made of cross-linked polystyrene, modified to contain **sulfonic acid groups**.

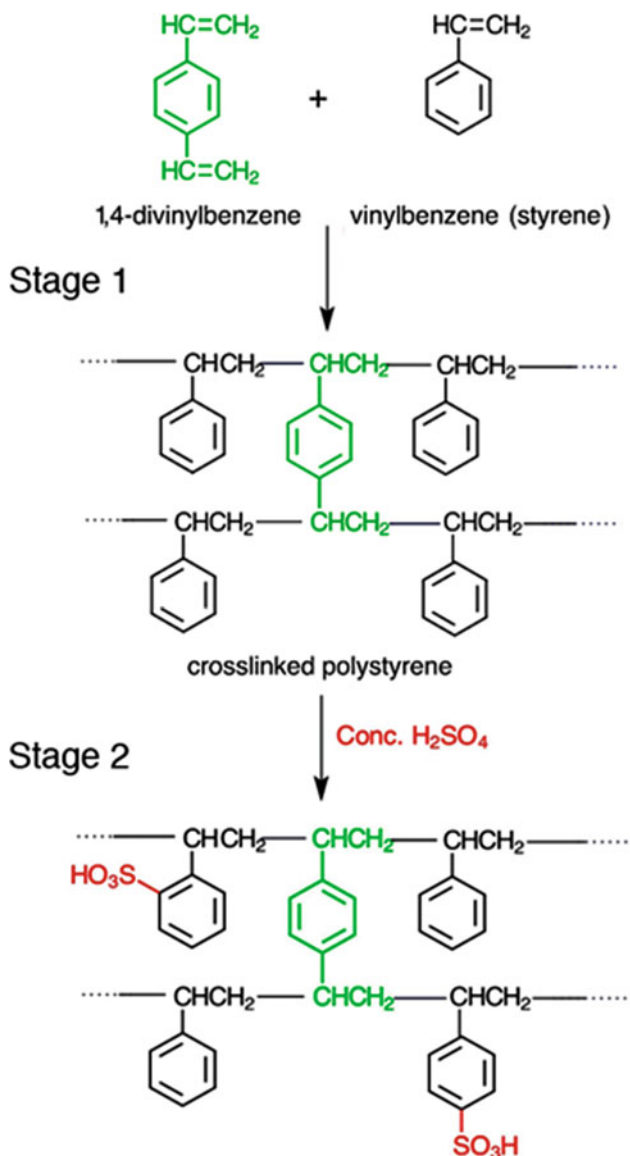
The beads are made in two stages.

First a mixture of styrene and divinylbenzene ($\sim 5\%$) is polymerized while suspended in an aqueous solution of starch or some other suspending agent which prevents coalescence. Benzoyl peroxide can be used as a source of free radicals to initiate the polymerization. The heat of polymerization is removed by cooling the mixture as required, which remains fully stirrable throughout the reaction. When the reaction is complete, the beads are removed by filtration or centrifugation and washed to remove the suspending agent and residues of initiator. A simple procedure? Well yes, but there are enough variables in formulations and conditions of reaction to yield products which are less than perfect with regard to particle size and uniformity. As with all first time procedures, extensive trials on a small scale are necessary.

The beads are stable enough to allow substitution reactions to be performed without melting and fusing together. Essentially they are like static aromatic compounds, able to undergo many of the common reactions of such compounds.

In the second stage, sulfonation using concentrated sulfuric acid, produces a strong poly-acid in the form of sulfonic acid groups attached to the solid polystyrene/divinylbenzene beads. These groups are shown in red in the scheme on the next page.

Ion exchange resins are converted into their sodium salts before use as water softeners. When hard water is flushed through the system, the sodium ions will become exchanged for calcium and magnesium ions, which are taken up by the resin. As a result the water will become “soft” i.e. soap will remain sudsy instead of forming its greasy, insoluble salts of calcium or magnesium.



In time, of course, the resin becomes saturated with calcium and magnesium ions and must be regenerated. This is easily done by treating it with concentrated sodium chloride solution, whereby the offending metal ions are exchanged back for sodium ones and flushed away to waste.

Ion exchange resins containing acidic groups like this are called **cation exchangers**, because the ionized acidic groups are negatively charged and will take up cations such as calcium ions. However, by using different reagents to treat the

crosslinked beads, several other types of chemical groups can be added. Of particular interest are amine groups, because they are positively charged, and will take up anions such as chloride, i.e. they are **anion exchangers**.

A physical mixture of anionic and cationic ion exchange resins will in fact fully deionize water, a procedure which is of great value for industry, being much cheaper than distillation. Water used for industrial boilers, such as those in power stations, has to be of high purity in order to avoid corrosion and the build up of sludge. For this purpose **demineralized water**, obtained by treatment with a mixture of anionic and cationic exchangers is widely used.

From an historical perspective, ion exchange resins based on fully synthetic polymers began in 1935, with the introduction of sulfonated crosslinked phenol/formaldehyde resins, a development pioneered at the National Chemical Laboratory in Teddington, UK, by B.A. Adams and E.L. Holmes. Then in 1944, d'Alelio in the USA produced superior ion exchangers from styrene/divinylbenzene copolymers which have been the primary materials for this purpose ever since. There are useful accounts of ion exchange history and technology by The Nuffield Foundation [22] and, in more detail, by Harland [23].

Ion exchange resins have been discussed in particular because they are an excellent illustration of how polymers can perform as reagents. Closely related to this technology is the remarkable use of crosslinked polymers as anchors for building up synthetic biopolymers.

Synthetic Biopolymers

The year 2013 marked the 50th anniversary of the publication of a seminal paper describing the synthesis of peptides. The author was an American chemist, Bruce Merrifield, who described the synthesis of a tetrapeptide using crosslinked polystyrene beads as a support [24]. The beads were similar to those used in water softening.

The dry polymer beads become swollen in organic solvents such as dichloromethane, which allows free access of chemical reagents to the reactive sites within them. There is not space here to describe the chemistry of these procedures, but essentially they depend on reacting the polymer with a chemical “anchor” which is then reacted stepwise with the desired sequence of amino acids. After each addition, excess reagents are washed away so that there is no need to isolate and purify the product at these intermediate stages. Finally, the peptide is cleaved from the polymeric substrate and then purified as necessary.

Merrifield won the Nobel Prize for Chemistry in 1984, for his pioneering work in this field [25], now called **Solid Phase Synthesis**.

Polymer supports of this kind have also been used to synthesize not only peptides, but also other biopolymers, in particular **oligonucleotides** and **carbohydrates**. It's also worth mentioning that other crosslinked polymers e.g. crosslinked polyacrylamides have been found to be suitable supports in some cases.

Using automated equipment, solid phase synthesis is now used routinely to prepare pure peptides and oligonucleotides containing up to 100 units - perhaps more, by the time you read this!

It should be added that such peptides and nucleotides can be further enlarged. For example, whole gene sequences can be made by joining up different oligonucleotides produced by solid phase synthesis. This is a field which is expanding very rapidly at the present time.

Chapter 9

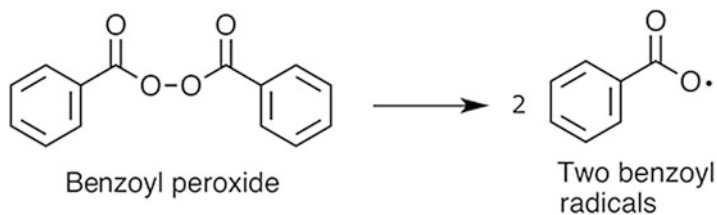
Initiation of Polymerization

Types of Polymer Initiator

Whereas processes for making condensation polymers generally rely on heating and pH control alone, addition polymers, i.e. those derived from unsaturated monomers, generally require catalysts or initiators. These terms are commonly used interchangeably, which strictly speaking is incorrect because catalysts are defined as not being consumed in reactions. The term initiator is more frequently used for those compounds which provide free radicals, fragments of which do in fact become attached to the polymer. Other initiators can be cationic, such as the strong Lewis acid boron trifluoride, organometallic, or very occasionally anionic, such as sodium metal.

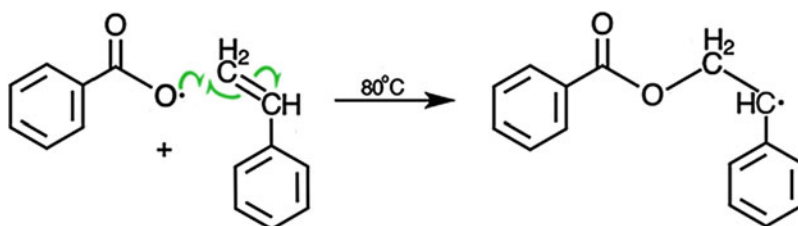
Free Radical Initiators

We saw earlier that benzoyl peroxide is used to initiate the polymerization of styrene (p. 19). Now we shall see how this works. Many peroxides and hydroperoxides dissociate on heating to give free radicals. Thus, benzoyl peroxide begins to dissociate into two benzoyl radicals when it is heated to 80 °C.



Such a radical (the dot is an unpaired electron) adds to the double bond of a monomer, say styrene, yielding a product which is itself a radical. This new radical adds to another styrene molecule and so on, building up the polymer.

This is the first step of the reaction, the green arrows representing single electron transfer:



You may be wondering where all this ends! There are several answers—two growing radicals can join to form a full bond; solvents or impurities can terminate chains; a benzoyl radical can terminate chains as well as initiate them; and there are other mechanisms operating under certain circumstances. Sometimes accelerators, such as cobalt salts, are added to promote radical-initiated polymerization at room temperature (see p. 63).

Peroxides and hydroperoxides are not the only free radical initiators used for polymerization. For example some azo compounds are also active for this purpose, notably 2,2'-azobisisobutyronitrile, usually abbreviated to AZDN or AIBN.

Cationic Initiators

Simple cationic initiators, such as the Lewis acid boron trifluoride, have been used commercially to polymerize isobutylene. Boron trifluoride will also polymerize styrene and a number of other monomers, but often the products are not of sufficiently high molecular weight to be of commercial interest.

Organometallic Initiators

Where organometallic initiators have yielded high molecular weight products when others have not, is in the production of polyalkenes. This was accomplished by Karl Ziegler [26] and Giulio Natta [27], who discovered novel catalysts based on aluminum triethyl and titanium tetrachloride (p. 65). Polypropylene made with this catalyst system has stereoregularity, that is the methyl groups are all lined up on the

same side of the polymer chain. Such a polymer is called **isotactic** (where the side groups alternate regularly on each side of the main chain, the polymers are called **syndiotactic**).

Ziegler-Natta catalysts, as they are called, are also used in producing high density polyethylene (HDPE). The process is carried out at temperatures and pressures much lower than the free radical method originally used and the properties—higher melting temperature and greater tensile strength—are also much better.

For these discoveries in the chemistry and technology of high polymers, Ziegler and Natta were jointly awarded the Nobel Prize in Chemistry for 1963 [28].

More recently, alkene polymers have been made using metallocene catalysts, these are metal complexes based on cyclopentadiene. The chemistry is extremely interesting, but perhaps beyond the scope of a “little book”! However, a good account of the mechanisms is available online [29], where it is also claimed that polyethylene thus made can have a molecular weight of several millions and rival Kevlar as a bullet-proof material.

Anionic Initiators

Anionic catalysis is a rarity in commerce but it has a place in polymer science, and as a tool it is perhaps waiting for fuller exploitation. A process known as ‘living polymerization’ was first demonstrated by Michael Szwarc [30] in 1956, using an alkali metal/naphthalene system in tetrahydrofuran. Szwarc found that after addition of monomer to the initiator system, the increase in viscosity would eventually cease, but after addition of further monomer, the viscosity would start to increase again. The product was called a ‘**living polymer**’ because it would react with further amounts of the same or another monomer. By this method, amongst others, so-called **block copolymers** can be made. These contain stretches of polymer of one kind linked to stretches of another kind. The subject of copolymers is of great importance in polymer science and is discussed in the next chapter (Chap. 10).

Inhibitors of Polymerization

Vinyl monomers and the like are prone to polymerize by the catalytic effect of light or other influences and need inhibitors to prevent them from polymerizing during storage. Hydroquinone is a common inhibitor, used at levels of around 100 parts per million. It can be removed before use by extraction with dilute sodium hydroxide solution.

Chapter 10

Copolymers

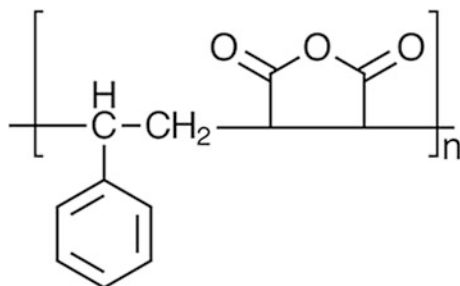
No account of polymers would be complete without at least some discussion of copolymers. As the name suggests copolymers are made up of more than one monomer. In a strict sense, all the main condensation polymers, polyesters, nylons, alkyds and thermosetting resins based on formaldehyde, are copolymers, but the term is usually restricted to addition polymers based on more than one unsaturated monomer.

We have already mentioned an example of such a copolymer on p. 26 (thermosetting acrylics). Four further examples are given on pp. 58, 59 and 64. Three of these examples include butadiene. In the first case copolymerized with styrene, in the second acrylonitrile and then on p. 64 a copolymer of all three monomers—ABS. In practice, most varieties of ABS are graft copolymers—for example when styrene and acrylonitrile are polymerized in the presence of pre-formed polybutadiene, the new polymer chains become grafted on to the polybutadiene. Other commercially valuable copolymers include ethylene/vinyl acetate copolymers useful as hot melt adhesives; acrylonitrile/(quaternary ammonium vinyl) copolymers as fibers with better dyeability and very many others.

However, one mustn't assume that just any monomers can be mixed and will give uniform copolymers; far from it. One polymer radical will not have the same reactivity towards a different monomer as towards the same monomer. This difference can be measured experimentally and is called the **reactivity ratio**. Furthermore, in most cases the polymer formed at any instant during the polymerization, will vary according to how much of each monomer remains at that instant. The reactivity ratios of the monomer pairs govern this behavior. A detailed discussion of copolymerization with tables of reactivity ratios is given by Hagiopol [31].

One example which shows unusual behavior is interesting and also lends itself to simple laboratory experiments. It is the polymerization of styrene and maleic anhydride. The polymerization can be initiated with benzoyl peroxide.

The styrene radical, call it 'A', has a strong affinity for maleic anhydride, 'B', but the resulting radical has very low affinity for further maleic anhydride—so it adds styrene. This growing radical now has a much greater affinity for maleic anhydride than for another molecule of styrene. Thus a regular alternating ABABAB... polymer is built up, the unit structure of which is shown here:



This anhydride copolymer is easily reacted with compounds containing alcohol, thiol or amine groups—i.e. common nucleophiles. Different procedures allow polymers with less maleic anhydride content to be made, several varieties of which are also available commercially, with a wide variety of uses as surfactants in coatings, inks and emulsion polymerization [32].

Related to styrene/maleic anhydride polymers are the polyesters described on pp. 62–63. These ingenious polymers make use of styrene, not only as a solvent to dissolve the maleate polyester but also to copolymerize with it forming a cross-linked product. Using a peroxide initiator with an accelerator, such as a cobalt salt, the polymerization occurs conveniently at room temperature. Reinforcement with glass fiber is usual for large scale articles, but not for the elegant high gloss wood varnishes which can be made from these polyesters.

Chapter 11

Ethical Issues

In this discussion, “ethical issues” means those aspects of polymers which impinge upon human welfare or the environment, beneficially or detrimentally—especially the latter.

Cellulose Nitrate (again)

As we have seen on p. 11, the first “plastic”, Parkesine, was based on cellulose nitrate, and was developed as a substitute for ivory, horn, tortoiseshell etc. The use of ivory for the manufacture of many everyday items, particularly billiard balls, meant the killing of multitudes of elephants. One of the first substantial uses of a successor to Parkesine, namely Celluloid [12] was in fact for the manufacture of billiard balls, a game which had become very popular, particularly in the USA. It was there that J.W. Hyatt set up his Celluloid factory in 1870 and as a result many elephants were spared.

On the other hand, cellulose nitrate (as gun cotton) was a useful explosive which, in combination with nitroglycerine, replaced black gunpowder. Better explosives for guns was clearly not adding to human welfare, although it could be argued that their use in blasting through tunnels to provide new and better railway routes, was a benefit. So there are always two sides to these questions. Nevertheless, recognition of the possible harmful consequences of scientific advances is, of course, the duty of all scientists who are in a position to influence new developments.

So what are the issues facing us today?

Environmental Damage

Probably the most important is the environmental issue. We have mentioned the huge quantity of plastics manufactured today—around 300 million tonnes annually worldwide. The trouble is, as you are probably aware, plastics are not easily broken down in the environment, so they accumulate. They are damaging to wildlife on land, in the sea and in the air—‘in the air’ meaning that seabirds can be the victims. Incineration and recycling of plastics are ways to minimize the problems, but in several countries plastic bags have been banned because of their increasing nuisance and effects on wildlife [33].

Oceans are particularly problematic because much of the rubbish there is not seen. Nevertheless vast amounts of man-made detritus finds its way into the sea, there to be broken down very slowly to microparticles which are inflicting a great deal of harm on marine life. A recent report calls for a complete re-thinking of plastics use and disposal [34].

Biodegradable Polymers

One solution to the problem of plastics disposal, which is now being urgently implemented, is the introduction of plastics which are biodegradable—that is to say they are degraded by naturally occurring agencies such as light, heat, oxidation or microorganisms (especially in compost).

Poly lactide, also known as poly(lactic acid) or PLA, is one of the most prominent of these at present (p. 66). Others include linear polyesters from butanol, adipic acid and methyl terephthalate known as PBAT, and a polyester from 1,4-butanediol and succinic acid known as PBS. Natural polymers such as casein are also being re-examined.

Poly lactide is suitable for many kinds of product: films, fibers and moldings for example, and when their useful life is ended they can be decomposed in an industrial composter.

Nowadays all bioplastic packaging materials in the European Union claiming compostability have to comply with a standard [35], namely EN 13432.

There is also another dimension to this in that although poly lactide does not depend on oil and the net CO₂ contribution can be zero, its manufacture is usually based on corn (maize) which then becomes unavailable for food. This leads to a shortage of corn and the price goes up; people may even starve as a result.

Biodegradable plastics are predicted to increase considerably in the future. Global industrial capacity was 663,000 metric tonnes in 2014 and expected to reach 1,287,000 tonnes by 2018 [36].

Air Pollution

Serious air pollution in the form of smog can arise from the large amounts of organic solvents which are put into the atmosphere when paints and varnishes dry—for example when coating the inside of tin cans. A considerable research effort is continually being made to diminish this problem, one way being to use water as a medium for the polymer instead of organic solvents. That requires altering the chemical composition of the polymer in such a way that it is soluble or dispersible in water, but insensitive to water when dry. Quite a challenge!

Another way to avoid organic solvents is to use the polymer in the form of a fine powder, applied for example electrostatically. On heating, the powder particles sinter to form the coating, often with simultaneous crosslinking. Epoxy resins are widely used in powder coatings for their toughness and durability.

Toxicity

Many of the raw materials used in the manufacture of polymers are undoubtedly toxic. The term is relative, ranging from substances like phenol which at low concentrations is usefully antiseptic, but at high concentrations extremely toxic, to acrylamide (a nerve poison) or vinyl chloride (carcinogenic) where toleration levels are as near to zero as possible. But the chemical industry is used to handling dangerous substances and in modern times has an extremely good record in this respect.

The main concern with polymer toxicity is in regard to the additives and monomer residues which may be in them and which might migrate during use to affect human or animal health. Examples are: PVC stabilizers containing lead; phthalate plasticizers; various unpleasant and possibly harmful amines used in rubber as antioxidants and so on. Take note, however, that polymers which come into contact with foodstuffs are subject to particularly stringent regulation. In the USA, this regulation is the responsibility of the Food and Drug Administration, but most countries have similar authorities of their own.

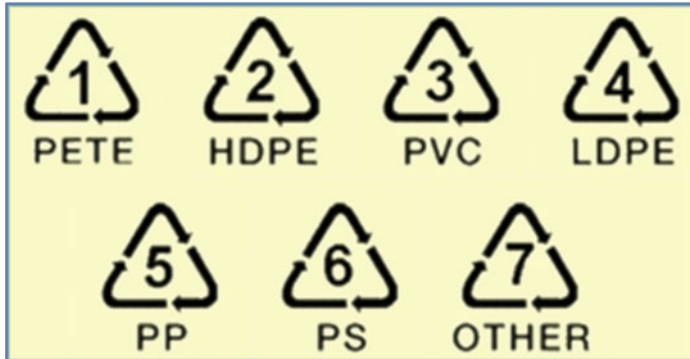
Recycling

Many of the environmental difficulties would be much easier to solve if plastics were fully recyclable by reconversion to monomer. We note on p. 58 that poly (methyl methacrylate) can be depolymerized on heating, with a good yield of monomer. Maybe this approach will be developed in the future, but at the moment it is uneconomical.

In recent years much progress has been made with collection and recycling of plastics, but current systems are far from perfect. Yes, some thermoplastics are

remelted and used again, but not all thermoplastic polymers lend themselves to this treatment—either they decompose on heating to melt temperatures or they do not blend with other polymers. There is also the problem of sorting waste, which has to be contended with.

To assist with this, there has been a simple marking system in use since 1988, identifying different types of plastics. Here are the currently used markings or “icons” for different polymers:



PETE = poly(ethylene terephthalate) usually abbreviated as PET

HDPE = high density polyethylene

PVC = poly(vinyl chloride)

LDPE = low density polyethylene

PP = polypropylene

PS = polystyrene

Rather than being used neat, recycled plastics are frequently blended with new; for example milk bottles containing 30% of recycled HDPE have been reported [37].

Chapter 12

The Chronology of Polymers

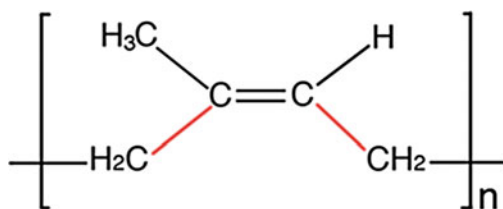
The story of macromolecules now continues with a brief look at each of the major polymers in the order they were first made available on a large scale. The name of the polymer is followed by the country where it was first made and the date (in **bold**) is given at the right.

In most cases, dates given are approximately when significant industrial production was started and frequently will not coincide with the date of discovery or production of materials in development.

We start with rubber:

Natural Rubber

South America **centuries ago**

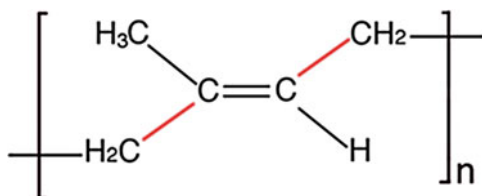


cis-1,4-polyisoprene

Rubber is a naturally occurring polymer from the rubber tree *Hevea brasiliensis*. To obtain the rubber, a wound is made in the trunk of the tree, whereupon a milky white latex slowly drips into a collecting vessel placed underneath. The latex is then coagulated, separated, dried and smoked to give sheets of raw rubber. However, articles made from this get too hard in winter and become too soft in summer unless vulcanized with sulfur [38] (see also pp. 6–7). With added sulfur (3–4%) and heating, rubber is lightly crosslinked and becomes a strong, durable elastic material.

Gutta percha

South Asia centuries ago

*trans*-1,4-polyisoprene

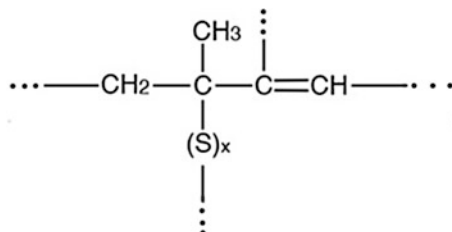
Gutta percha is a naturally occurring polymer obtained from the latex of *Palaquium* trees. It has useful properties without being chemically treated. Perhaps it shouldn't be included in a book about man-made polymers, except that it can be further improved by vulcanization with sulfur. In addition, gutta percha is a stereoisomer of natural rubber (*trans*, not *cis*) and a comparison of their properties is particularly interesting. Thus, gutta percha is not elastic, it is hard at room temperature, but softens when heated and is then easily molded. On the other hand, raw rubber is elastic at room temperature and sticky and practically useless when hot.

Gutta percha was used in the 19th century as an electrical insulator as well as for many other purposes such as bottle stoppers and golf balls. The insulation of submarine cables [39] was a notable use; initially from Dover to Calais in 1851 and then transatlantic in 1866. As you might expect, vulcanization gave gutta percha greater strength, and, according to a publication dated 1857 [40], made it specially useful for demanding uses such as machinery and conveyor belts. Nowadays, however, comparatively little gutta percha is used, having been replaced by modern synthetic polymers such as polyethylene.

Highly vulcanized rubber (Ebonite, Vulcanite)

UK and USA 1843

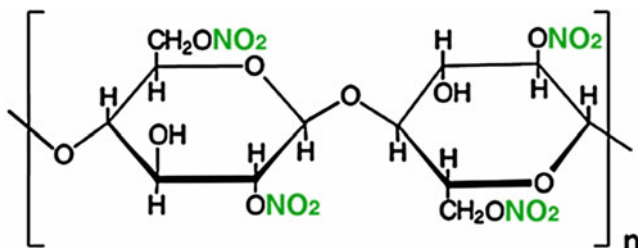
When relatively large amounts of sulfur (30–40%) are reacted with rubber the product is hard, tough and infusible, quite unlike normally vulcanized rubber. It is truly thermoset (see p. 8). The crosslinking reaction itself is complex, but probably quite similar whether large or small amounts of sulfur are used. Experiments with model compounds indicate that crosslinks of the following type can be formed:



This structure shows one or more sulfur atoms ($x = 1, 2, \dots$ etc.) present in the crosslinking bond. Other structures are also produced, according to the effect of other ingredients in the rubber mix, especially accelerators [38]. Note that, as in an earlier figure, the dotted lines extending from bonds indicate that the polymer network continues indefinitely at these points.

Cellulose nitrate, also known as nitrocellulose

UK 1892

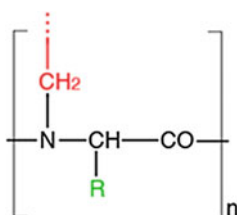


The polymeric component of Parkesine, the first man-made plastic. Cellulose nitrate ultimately became useful mainly as a very tough and durable lacquer or paint and as the explosive gun cotton. It was also used as an interlayer in safety glass, known as Triplex. For many other uses it was too inflammable (see pp. 11–12).

Casein/formaldehyde

France/Germany 1900

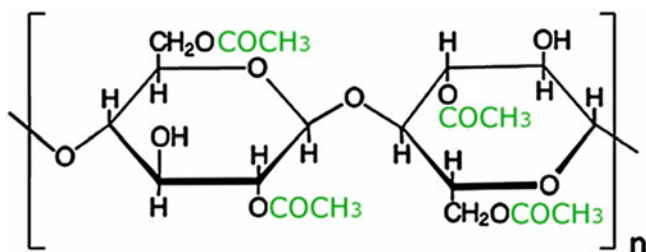
Casein is a protein found in milk. Proteins are polypeptides of the general structure shown here, except that before reaction with formaldehyde the nitrogen atom has H attached. R can be various groups or H. Formaldehyde reacts at the peptide nitrogen, crosslinking to give a methylene (CH_2) bond between the chains. This is shown in red. Some side groups in the protein, such as NH_2 from the amino acid lysine, will also crosslink the chains by reaction with formaldehyde.



Casein plastics [14] were sold under the names of Galalith and Erinoid and they were hugely successful in the manufacture of small items such as buttons and costume jewellery.

Cellulose acetate

Switzerland 1905

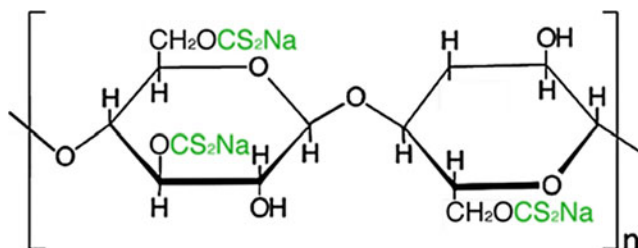


An interesting early use for cellulose acetate was for coating the canvas skin of aircraft with a solution of the polymer. The Dreyfus brothers in Switzerland were persuaded to set up a plant in Britain during the first World War making cellulose acetate for this purpose. After the war there was a sudden surfeit of cellulose acetate and so its use in moldings and as films and fibers had to be increasingly developed. A mixed ester, cellulose acetate/butyrate became widely used for the handles of chisels, screwdrivers etc., the longer chain of the butyl groups conferring more flexibility and toughness.

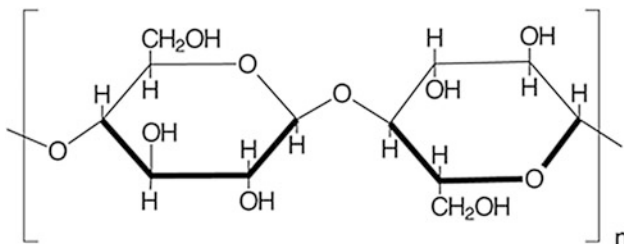
Viscose rayon (regenerated cellulose)

UK 1905

The cellulose xanthate process was discovered in England in 1891 and the commercial manufacture of viscose rayon was begun there in 1905 by the firm Courtauld's. In this process cellulose is first solubilized by treating it with sodium hydroxide solution followed by carbon disulfide which converts it to the xanthate salt, shown here:



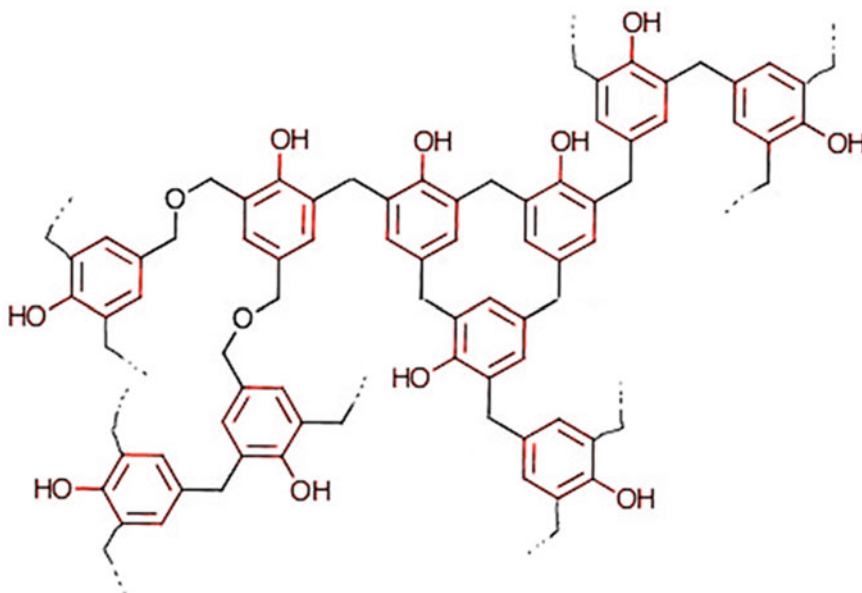
On extrusion of the xanthate solution through spinnerets into an acidic solution, cellulose is regenerated as a fine fiber, often known simply as viscose:

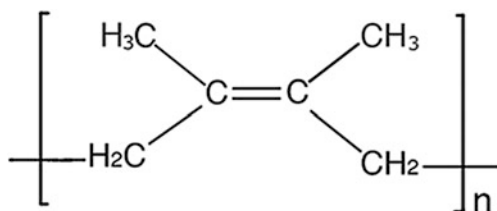


Phenol/formaldehyde (Bakelite)

USA 1909

The chemistry of PF resins is discussed on pp. 22–25. PF moldings are used in many fields, but especially for electrical components, for which they are well suited. They are usually brown or black in color, unless pigmented. Below is a notional representation of the structure of the crosslinked material:



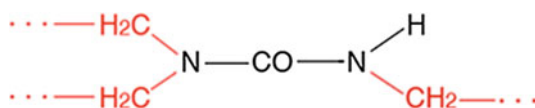
Poly(2,3-dimethyl-1,3-butadiene) also called methyl rubber Germany 1910

This was the first synthetic rubber to be manufactured on a large scale. Quality was very poor compared to natural rubber, but in wartime (1914–1918) anything was better than nothing. Production totalled about 2350 tons but ceased at the end of the war [41, 42]. The *cis* configuration is shown, but in practice it is probable that a mixture of *cis* and *trans* isomers was made.

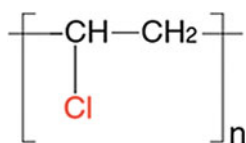
As an afterword on methyl rubber, it is surprising that development reached such an advanced stage in 1910–1918 even though the science of macromolecules was still in its infancy and most scientists believed that large molecules could not exist.

Cellophane (regenerated cellulose) Switzerland/France 1912

Cellophane is made from the same viscose dope, as the fiber (see Viscose rayon, pp. 52–53).

Urea/formaldehyde USA 1923

In principle all four hydrogen atoms in urea can be reacted with formaldehyde. In practice about three are reacted, as shown in red, forming methylene (CH₂) bridges between the urea molecules. UF resins are colorless. Early resins included thiourea.

Poly(vinyl chloride) known as PVC USA 1926

PVC is familiar to all of us. It is made by the polymerization of vinyl chloride.

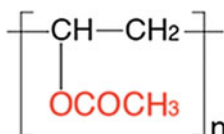
It is fascinating to realize that the monomer was discovered as long ago as 1835 by Liebig (of condenser fame). Then in 1838 his student Henri Victor Regnault exposed vinyl chloride to sunlight and obtained a white solid. This was actually the first discovery of PVC, but of course nothing was known about its structure at the time and it was not exploited as a useful material. That had to wait until 1926 when the American firm B.F. Goodrich started manufacturing it as a coating for fabrics. Since then its uses have multiplied and include pipes, moldings, insulating coatings and floor tiles. It is arguably the most versatile of all plastics.

However, one of the drawbacks of PVC is that it needs quite a lot of additives to make it suitable for all these purposes. In particular, it needs stabilizers because it has a tendency to dehydrochlorinate. Lead compounds were widely used [43], but are being phased out because of concerns about their toxic effects in the environment. Compounds of calcium and zinc, organotin compounds and epoxidized soya bean oil are still commonly used stabilizers.

PVC is a rigid polymer at ambient temperatures, which makes it suitable for window frames, gutters and pipes, but it responds very well to plasticization. Thus, PVC articles which are flexible will contain plasticizers, sometimes as much as 50%. However, plasticizers themselves can give rise to problems such as leaching out or being toxic in some respect, so they must be chosen carefully to ensure that they are suitable for the proposed use.

Poly(vinyl acetate)

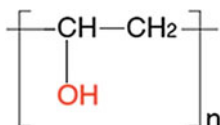
Canada/Germany 1928



Most poly(vinyl acetate) is made by polymerizing an emulsion of the monomer in water. Afterwards, a plasticizer, such as dibutyl phthalate, is added. The product can be used directly as an adhesive, because on drying, the minute particles of the dispersed polymer merge to give a film, which bonds the surfaces to be adhered. Alternately, the plasticized product can be mixed intensively with finely dispersed titanium dioxide to give a paint. When this is painted on to a surface, the water evaporates and the titanium dioxide particles become bonded into the film which itself adheres to the surface being painted.

Poly(vinyl alcohol)

Germany 1928

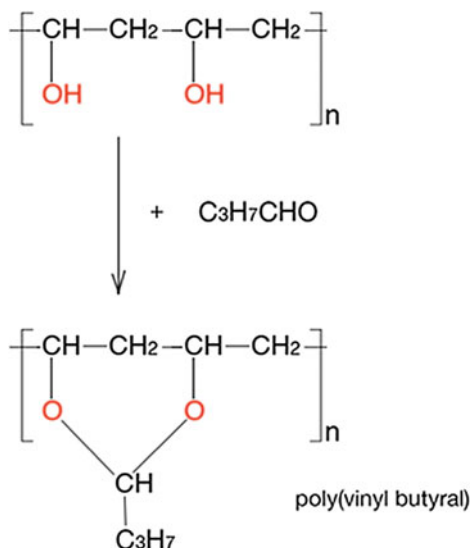


Vinyl alcohol is too unstable to exist (except possibly in space!) so the polymer is made by hydrolysis of poly(vinyl acetate). Poly(vinyl alcohol) is used as a thickener, for example in emulsion polymerization, but in some parts of the world, notably Japan and North Korea, it is used as a fiber.

Poly(vinyl butyral)

Canada/USA 1938

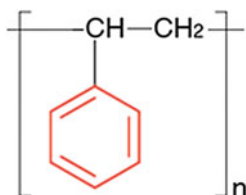
Included here because of its relationship to poly(vinyl alcohol) which can be reacted with aldehydes to form cyclic polyacetals, e.g. poly(vinyl butyral). When plasticized, this stable, transparent polymer is widely used today as an interlayer for safety glass, e.g. for car windscreens [44]. This is the transformation from poly(vinyl alcohol) to poly(vinyl butyral):



In practice a number of hydroxyl groups remain unreacted, so in a certain sense the product is a copolymer of poly(vinyl alcohol) and poly(vinyl butyral) [45].

Polystyrene

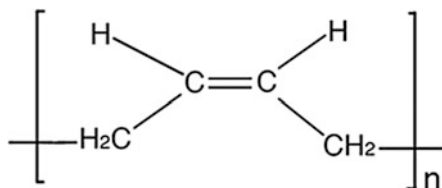
Germany 1931



Like PVC, polystyrene was first discovered in the 1830s, but again its nature was not understood at the time. It is a hard, clear, colorless and relatively inexpensive polymer, used extensively today in numerous applications. Foamed polystyrene is widely used for packaging. The polymerization reaction of styrene is shown on p. 39 and the mechanism on p. 40.

Polybutadiene rubber, also known as BR

Russia/Germany 1932



The Russian scientist Sergei Lebedev [46] first produced a laboratory sample of this synthetic rubber from butadiene in 1910. He later became an authority on synthetic rubbers. Improvements eventually led to large scale Russian manufacture of BR from 1932 onwards. In Germany, production of similar rubbers started at around the same time. Sodium was used as the polymerization catalyst, and the German product was known then as BUNA (from BUTadiene and NAtrium [sodium]). An improved product of *cis* configuration (as shown here) is widely used today in tire treads and sidewalls.

Polychloroprene rubber, also known as Neoprene

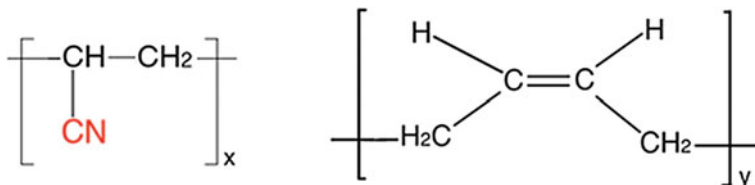
USA 1933

Polychloroprene was first manufactured by DuPont. It is a good general purpose synthetic rubber with excellent flame resistance and good oil resistance [47]. It has found extensive use as a binding layer for textiles, especially in wet suits [48], for which purpose the neoprene is foamed to give it good buoyancy and insulation properties.

improved SBR is widely used in many applications, competing with natural rubber with which it is sometimes blended.

Acrylonitrile/butadiene rubber or nitrile rubber

Germany 1937



Nitrile rubber is a copolymer of butadiene and acrylonitrile, noted for its excellent oil resistance, which is much superior to that of natural rubber. It was first manufactured in Germany under the name BUNA N, (N for Nitrile).

Polyurethanes

Germany 1937

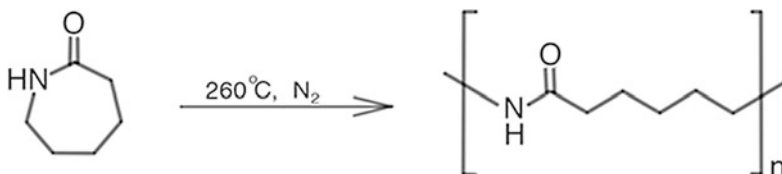
Polyurethanes were discovered in Germany as part of a program to challenge Nylon. Shown here is the urethane linkage (in red in the product) and its formation from an isocyanate RNCO and an alcohol $\text{R}'\text{OH}$.



If compounds with two isocyanate groups and an alcohol with more than two hydroxyl groups are reacted, a network of crosslinking urethane bonds will be formed. These processes are generally carried out in two stages. For example, an excess of tolylene di-isocyanate (TDI), a very toxic raw material, reacts with polyesters or polyethers having available hydroxyl groups, to make an isocyanate-terminated prepolymer. Being of low volatility, this is a much less hazardous material which can then be safely crosslinked with further polyols by the end user. Such polyurethanes [49] are widely used to produce foams for upholstery. Linear polyurethanes can also be made and are valuable for many purposes, particularly as elastic fibers. For these, hexamethylene di-isocyanate is commonly employed.

Polyamides, known as nylons

USA 1939

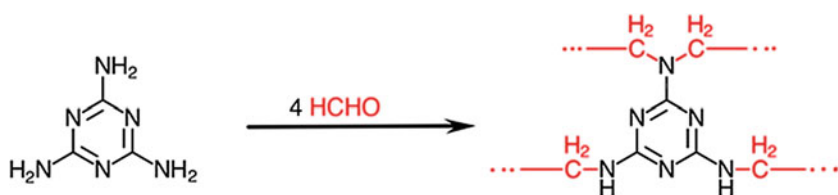


Nylon was discovered in 1935 by the notable polymer chemist W.H. Carothers, working for DuPont in the United States [50]. Manufacture started in 1939. Part of the reason for its excellent physical properties lies in the fact that there are hydrogen bonds crosslinking the chains (cf. p. 30). There are two common types of nylon, those made by ring-opening polymerization of ϵ -caprolactam, as shown above, which is known as **nylon 6** (6 denotes the number of carbon atoms in the starting material). The other common nylon is made by the reaction of adipic acid and hexamethylenediamine and is known as **nylon 6,6** (structure on p. 30). A range of other nylons is available for special purposes, usually based on components containing alkyl groups of various chain lengths. Examples are nylon 11 and nylon 12 used in high performance applications such as automotive fuel lines and toothbrush bristles. Nylon 11 is made from 11-aminoundecanoic acid, which is obtained in several stages from castor oil [51].

However, when **aromatic** diamines are reacted with terephthaloyl dichloride the extremely tough ‘Aramid’ polyamides [52] are obtained. They are used in making flameproof clothing and bullet proof vests, the best known examples of which are ‘Kevlar’ and ‘Nomex’.

Melamine/formaldehyde

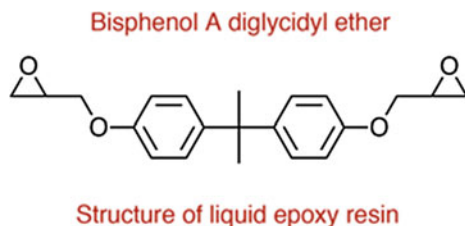
USA 1939



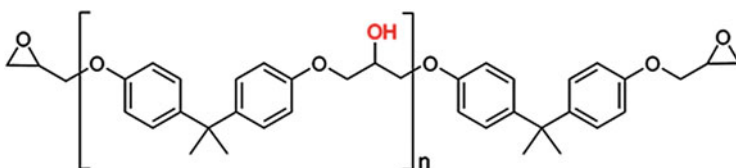
Melamine, which is manufactured from urea, has six possible sites for reaction with formaldehyde. As with urea, not all of these are utilized in practice. The final cross-linked product is shown here with the melamine nucleus in black and four methylene groups from formaldehyde in red. In practice, the crosslinked product is obtained in two stages, the first being reaction with formaldehyde to give a prepolymer, which is then followed by the application of heat and pressure in a mold or press. In this way very strong, durable molded articles or laminates are made. Melamine resins are also used in coatings such as baking enamels for domestic appliances (see Alkyd/amino resins on p. 62). In contrast to phenolics, melamine resins are inherently colorless, which allows them to be used when pale colors or whites are required.

Epoxy resins

Germany 1939



Epoxy resins are best known in two-part adhesives such as 'Araldite'. The resin part is comprised largely of Bisphenol A diglycidyl ether, which is a viscous liquid, not easily crystallizable. The structure is shown above. The other part of the adhesive is a polyamine which reacts with the epoxy groups, forming a system which crosslinks at room temperature. No gases or other volatile by-products are formed. That type of epoxy resin is made from Bisphenol A and a large excess of epichlorohydrin (1-chloro-2,3-epoxypropane). However, if the excess of epichlorohydrin is reduced, products of the following type result:

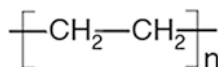


The value of n depends upon the amount of excess epichlorohydrin used. Those resins where n averages more than 2 or 3 are solids. One use of these higher molecular weight resins, with added fillers and phthalic anhydride as crosslinker, is for casting into molds. Such systems crosslink when heated to give excellent high voltage insulators.

Note, however, that in some applications the chemistry of epoxy resins varies considerably from the simple examples shown here, especially in the crosslinkers used.

Polyethylene

UK 1939



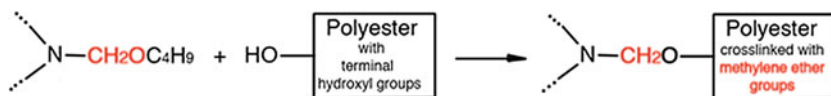
Polyethylene was first manufactured by ICI in Britain by polymerizing ethylene at high pressures and temperatures [53]. Later, special catalysts enabled lower temperatures and pressures to be used and gave denser products which had

improved properties. Somewhat confusingly, polyethylene made at high pressure is called LDPE (low density polyethylene); the low pressure process, involving special catalysts, gives HDPE (high density polyethylene)—see also pp. 40–41.

Alkyd/amino resins

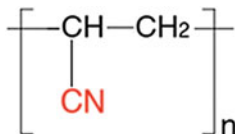
USA 1940s

Polyesters of fairly low molecular weight are used as components of thermosetting coatings together with amino resins, which in practice means mostly urea/formaldehyde and melamine/formaldehyde resins. Appropriate polyesters are made by the reaction of polyols such as glycerol, and acids such as phthalic anhydride and saturated fatty acids, for example those derived from coconut oil. The resulting branched chain polyester, sometimes called an alkyd, is formulated to provide a surplus of hydroxyl groups which are the points for crosslinking. The amino resins are purpose made in order to be compatible with the polyesters. This is achieved by etherifying the initially formed hydroxymethyl groups with an alcohol such as butanol. The crosslinking reaction is then one of transesterification. The pigmented resin solution coated on metal is used for domestic appliances etc. and is known as a baking enamel. Typically the coated articles are baked for 30 min at 120 °C to effect crosslinking. Just one of the crosslinks is shown here:



Polyacrylonitrile

USA 1940



Polyacrylonitrile fiber is the main component of “acrylic” clothing materials. To improve its properties, especially to improve its dyeability, other monomers are included in the mixture to be polymerized.

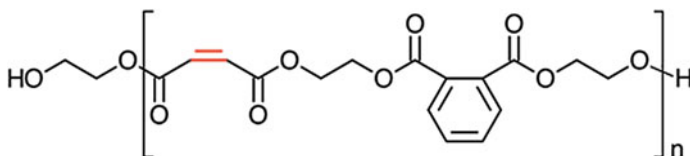
Unsaturated polyesters

USA 1941

These are linear polyesters of relatively low molecular weight, made from phthalic anhydride and ethylene glycol with a proportion of maleic anhydride, and then dissolved in styrene monomer. Maleate unsaturation has a great propensity to copolymerize with styrene. The intermediate polyester dissolved in styrene monomer is sold as such. On adding a free radical initiator and an accelerator (often a cobalt salt), the mixture begins to set, the maleate groups in the polyester chains being crosslinked by the styrene. Some isomerization of maleate to fumarate groups

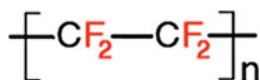
occurs during the esterification process, but fumarates too copolymerize actively with styrene. Glass fiber is frequently used as reinforcement. The reaction starts at room temperature, but is exothermic and requires careful control. Nevertheless, very large structures such as oil storage tanks and boat hulls can be fabricated from unsaturated polyesters reinforced with glass fibers.

These polyester resins are manufactured with low acid values which enhances their resistance to alkalis. This low acidity is achieved by using a slight excess of the glycol and reacting for a high degree of conversion. This is the structure of the polyester, with glycol chain termination. The maleate double bond is shown in red:



Polytetrafluoroethylene, known as Teflon

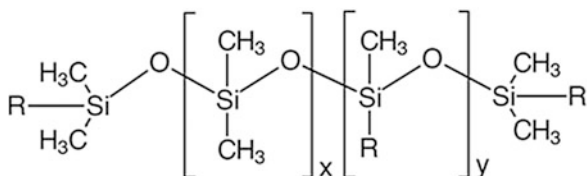
USA 1943



Teflon was discovered accidentally in 1938 by Roy Plunkett at DuPont, when a cylinder of tetrafluoroethylene was found to have lost pressure but not weight. On opening it, a white solid was found, which proved to be polytetrafluoroethylene [54]. This hydrogen-free polymer exhibits exceptionally low friction, high melting point, good electrical properties, chemical inertness and low wetting by water or fats. It is well known as a non-stick coating for cooking pans, but has many other uses.

Polysiloxanes known as silicone rubbers

USA/Germany 1947

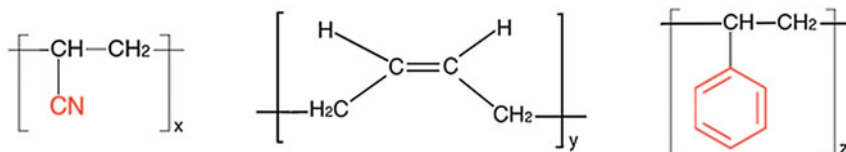


R = OH, -CH=CH₂, -CH₃ or other alkyl or aryl group

The chemistry of polysiloxanes [55] is quite different from that of the substances discussed so far, notably in that the backbone chain is composed of alternating silicon and oxygen atoms only. Therefore it isn't surprising to find that the

properties are quite different too. The most important properties are flexibility, high temperature resistance and resistance to oils and solvents, a combination seldom available with carbon chain polymers, Teflon being an exception (p. 63).

Poly(acrylonitrile/butadiene/styrene) known as ABS Germany 1948

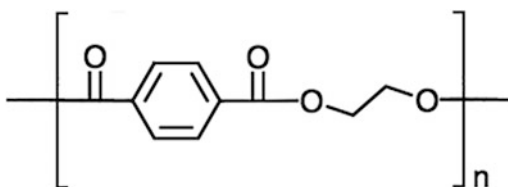


ABS is a copolymer made from acrylonitrile, butadiene and styrene

Hard polymers, particularly polystyrene, can be toughened by incorporating minor proportions of rubbers. A three component system, made from acrylonitrile, butadiene rubber and styrene, called ABS was found to have very desirable properties, not as a rubber but as an exceptionally strong, dimensionally stable polymer. It is one of a group of polymers collectively called engineering plastics, because of these properties (cf. Delrin on p. 65). It was most famous for making Lego pieces, replacing cellulose acetate, which had been used previously.

A typical ABS polymer [56] can be made from 20% polybutadiene (in latex form) mixed with 62% styrene and 18% acrylonitrile and copolymerized in an emulsion system. There are many variations in both the composition and the method of polymerization, depending on the exact properties required.

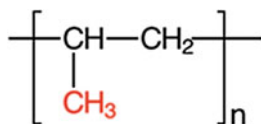
Poly(ethylene terephthalate) known as Terylene or PET UK 1950



The fiber poly(ethylene terephthalate) was discovered in 1941 by J.R. Whinfield and J.T. Dickson, working for the Calico Printers' Association in Lancashire, UK. When they recognized the huge potential of this discovery the firm decided to license the whole project to ICI and DuPont. ICI called the fiber Terylene. By 1950 ICI were producing commercial quantities. Nowadays poly(ethylene terephthalate) fibers are simply called polyester, and are widely used in blends with wool or cotton. In the 1970s to 1980s poly(ethylene terephthalate) was introduced for making beverage bottles, replacing glass and PVC. Today the polymer in such bottles is called PET poly(ethylene terephthalate) or sometimes PETE.

Polypropylene

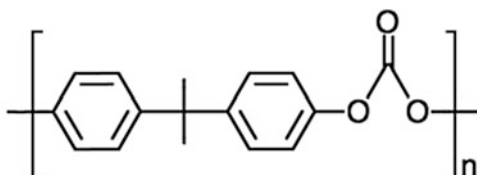
Italy 1957



For many years polypropylene was known as a material of low molecular weight, not much good for anything. However, as mentioned on p. 40, in 1953 two scientists, Karl Ziegler in Germany and Giulio Natta in Italy, developed catalysts based on titanium tetrachloride and aluminum triethyl which would polymerize alkenes to give high molecular weight products. The polypropylene made with these catalysts had structural regularity, crystallinity and excellent physical properties. Polypropylene is particularly valued over polyethylene (especially the low density type) on account of its relatively high heat distortion temperature. It was first manufactured by the Italian firm Montecatini in 1957.

Polycarbonates

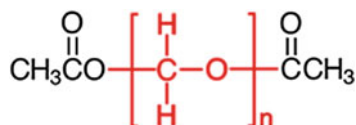
Germany/USA 1958



Polycarbonates are remarkable for their very high impact resistance. They are made from compounds containing two phenol groups reacted with phosgene (COCl_2). The most frequently used phenol is called Bisphenol A, which is also a raw material for epoxy resins. It is called Bisphenol A because it is made from phenol and acetone. Polycarbonates are used for roofing, camera bodies and even lenses as well as for many other applications where transparency, durability and toughness are at a premium.

Polyoxymethylene, known as Delrin

USA 1960

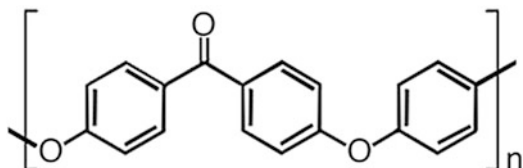


As you can see from this structure, apart from the end groups, Delrin has the same empirical formula as formaldehyde (CH_2O). It is a **polyacetal**. That is an unusual polymer in that the backbone comprises alternating carbon and oxygen atoms. Low molecular weight polymers of formaldehyde have been known for a long time, for example as paraformaldehyde. However, the formaldehyde needed to

make a polymer of **high molecular weight** (100,000 or more) has to be obtained pure, which in practice is not too straightforward. A final step in the production of the polymer is to esterify the end hemiformal groups with acetic anhydride, which stabilizes the product by effectively preventing depolymerization. The acetate end groups are shown in black in the above structural formula. The products are extremely tough and suitable for demanding applications, often replacing metals. They belong to the group of engineering plastics.

Polyetheretherketone, known as PEEK

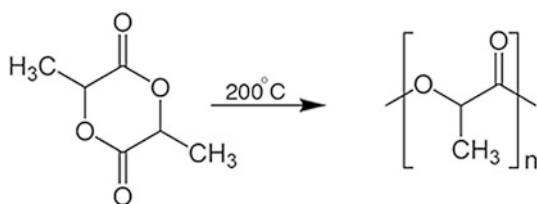
UK 1978



Research efforts to produce polymers stable at high temperatures, have been active since the 1950s, largely motivated by the need for better lightweight materials in military and space applications. It was realized that aromatic groups were likely to be important structural components of such polymers and eventually a range of specialty aromatic polymers became available by the late 1970s. Important among these was the product given the interesting name polyetheretherketone, or PEEK [57], and launched by ICI in 1978. It is one of the family of polyaryletherketones (PAEK) and melts at about 340 °C. It is a semi-crystalline thermoplastic material withstanding continuous service temperatures from sub-zero to 260 °C. It is also highly robust, being especially resistant to impact and aggressive substances [58, 59].

Poly lactide also known as poly(lactic acid) or PLA

USA 1997



PLA was first produced on a bulk commercial scale by Cargill Dow in 1997 [60]. It is derived from sugars or starch, especially corn starch, from which lactic acid is obtained by fermentation. The lactic acid must then be converted to the cyclic di-lactide which is purified by vacuum distillation to provide the starting material for the ring-opening polymerization reaction shown above. The resulting polymer is biodegradable. Plastic bags made from it will break down in an industrial composting environment (see p. 46). It is also possible, by heating the polymer, to recover a proportion of the parent dimer.

Chapter 13

Summary and Conclusions

Nature has been polymerizing since life began on earth, the polymers of greatest note being the nucleic acids DNA and RNA (polyesters) and proteins (polyamides).

Ultimately mankind started making useful plastics by modifying natural polymers such as cellulose and rubber in the 19th century and then, after clarifying the chemistry, went on to synthesize an abundance of new ones in the 20th century.

We saw how fully synthetic plastics flourished during the early part of that century, culminating in the 1950s; polymer science developed alongside.

We looked at some of the factors which affect the physical properties of polymers, particularly their strength and toughness and we have also considered how their chemical properties have been exploited. The important field of copolymers has been briefly touched upon.

In addition we have drawn attention to several “ethical” issues which belong to any discussion of polymers. Matters of toxicity and environmental damage are taken very seriously by the chemical industry and the idea of biodegradable polymers is now a reality which will undoubtedly grow in the future.

Yet much still remains to be done and polymers of quite new types will appear and be useful for applications not yet dreamed of, and old polymers will be combined and modified to meet many of tomorrow’s needs as well.

Our story has now come to an end. It is to be hoped that the information, although briefly put, will be useful as a reference and perhaps a starting point for further study.

Much more could be said, but for the present—enjoy your chemistry and don’t forget the people who invented and developed synthetic polymers!

A Few Suggestions for Further Reading

Clayden J, Greeves N, Warren S (2012) *Organic chemistry*, 2nd edn. Oxford University Press, Oxford (Additional Chapter 52 Polymerization, pp. 1451–1479 (2001) available online as a free downloadable PDF: <http://global.oup.com/uk/orc/chemistry/clayden2e/01resources/chapters/>. Accessed 23 Dec 2016)

Cowie JMG, Arrighi V (2007) *Polymers: chemistry & physics of modern materials*, 3rd edn. CRC Press ((quote) ‘to provide a broadly based text on polymer science at an elementary level.’ It is, nevertheless, considerably more advanced than the book you are reading!)

Flory PJ (1953) *Principles of polymer chemistry*. Cornell University Press, Ithaca, New York (This book is a classic. All will enjoy the historical introduction, but the main themes of the book are for advanced students)

Howard FA (1947) *BUNA Rubber—the birth of an industry*. D. Van Nostrand, New York (A fascinating first hand account of the development of synthetic rubber)

Kaufman M (1963) *The first century of plastics—celluloid and its sequel*. Plastics Institute, London (Authoritative account of plastics from 1863 to 1963)

Kaufmann CB (2012) *Grand Duke, Wizard and Bohemian—a biographical profile of Leo Hendrik Baekeland (1863–1944)*. Meta4 Press Llc, Santa Barbara, California (Much family detail. Only available at present as an ebook)

McMillan FM (1979) *The chain straighteners, fruitful innovation: the discovery of linear and stereoregular synthetic polymers*. Macmillan, London (Mostly about stereoregular poly(ethylene) and polypropylene)

Moncrieff RW (1974) *Man-made fibres*. Wiley, New York (A comprehensive, account of artificial fibers of all kinds known at that time. Includes their structure, properties and processing)

Yarsley VE (1967) *Hermann Staudinger—his life and work*. *Chemistry & Industry* 18:250–271 (A Memorial Lecture delivered by Dr. Yarsley to the Plastics & Polymer Group of the Society of Chemical Industry in September 1966, a year after Staudinger’s death. Recommended)

Glossary

Addition polymer A polymer made by opening a double bond

Alkyd Name given to a diverse family of branched polyesters of comparatively low molecular weight used in paints and varnishes

Araldite Trade name for epoxy resins made by Ciba-Geigy/Huntsman

Bakelite Trade name for cured phenolic resins

Biopolymer A polymer occurring in nature or one made from naturally occurring raw materials such as sugar. Such polymers may or may not be biodegradable

Bioplastic A biopolymer for use in typical plastics applications

Bisphenol A The reaction product of acetone and two mols of phenol

Block copolymer A copolymer comprising blocks of monomers. With monomers A and B, an example would be the sequence
AAAAAAAAAAAAAAAAAABBBBBBBBBBBB

Bonding point A point on a molecule where it can be bonded to another

Bridge The chemical group joining two bonding points

Colloid A submicron solid dispersed in a fluid

Composite A system comprising a resin with embedded reinforcing fibers

Condensation polymer One made by a process in which water is split out

Copolymer A polymer made from more than one kind of monomer

Crosslinking Forming chemical bonds between chains of a polymer

Cure To carry out a procedure which crosslinks a polymer

Delrin Trade name for high molecular weight polyformaldehyde made by DuPont

Ebonite Trade name for highly crosslinked rubber

Elasticity The ability of a substance to return to its original dimensions after stretching

Elastomer An elastic polymer

Emulsion polymerization In which the monomer is finely dispersed in water

Extrusion A process whereby a polymer melt or solution is forced through an orifice

Free radical A molecule or atom with an unpaired electron

Functional group A chemical group which can react with another

Gel A product which takes the physical form of a jelly. This often means it is a partially crosslinked system

Glass transition temperature The temperature at which a polymer is between the rigid and rubbery states

Hydrogen bond A weak bond between an electronegative atom and a hydrogen atom covalently attached to another electronegative atom, usually oxygen or nitrogen

Inhibitor A substance added to a monomer to prevent premature polymerization

Initiator A substance added to a polymer system to start the polymerization. Often incorrectly referred to as a catalyst

Isotactic Having a regular conformation in which all the larger attached groups are on the same side of the polymer chain

Kevlar Trade name for an aromatic polyamide made by DuPont

Kodak A well known US photographic and chemical company

Laminate A cured paper or fiber reinforced resin system in the form of flat pressed sheets

Linear polymer A polymer without branching or crosslinks

Living polymer A polymer with an active anionic end group capable of extending when further monomer is added

Macromolecule A very large molecule

Micelle A colloidal particle so arranged that ionic groups, and possibly others, are on the outside

Mol Short form of 'molecule', usually meaning the molecular weight in grams

Monomer An unsaturated compound of low molecular weight which can be polymerized

Neoprene Trade name for polychloroprene rubber made by DuPont

- Nylon** Trade name for polyamide made by DuPont
- Oligonucleotide** A short sequence of a nucleic acid (RNA or DNA)
- Peptide** A compound containing at least two amino acids bonded by amide links. Proteins are polypeptides
- Perspex** Trade name for poly(methyl methacrylate) made by ICI
- Plasticizer** A substance added to a polymer to make it more flexible - often a phthalate ester
- Polymer** A large molecule made up of repeating groups
- Polypeptide** See Peptide
- Polyol** A molecule with more than one alcohol hydroxy group
- Prepolymer** A polymer which has not yet been fully cured or crosslinked
- Reactivity ratio** During a copolymerization it is the ratio of the reactivity of a monomer radical towards a further molecule of that same monomer, compared with its reactivity towards a molecule of a different monomer
- Resin** A very loosely applied term generally meaning a polymer of low molecular weight. Unfortunately the word "resin" has also been applied to such high molecular weight materials as polyethylene and water softening polymers
- Solid phase synthesis** A process for the synthesis of polypeptides, nucleic acids etc., during which the molecule is covalently attached to a solid polymer such as crosslinked polystyrene
- Syndiotactic** Having a regular conformation in which all the larger attached groups are arranged on alternating sides of the polymer chain
- Teflon** Trade name of poly(tetrafluoroethylene) made by ICI
- Tensile strength** The amount of tensile stress before breakage
- Terylene** Trade name for poly(ethylene terephthalate) made by ICI
- Thermoplastic** Able to be melted by heat and resolidify on cooling
- Thermosetting** Not able to be melted without decomposition
- Triplex** Trade name for safety glass with an interlayer of cellulose nitrate
- Ultramicroscope** Such a microscope enables one to see colloidal particles smaller than the wavelength of light. It depends on their illumination by light scattering

Vulcanization The process of treating rubber with crosslinking agents, principally sulfur

Vulcanite Common name for a hard rubber made by vulcanizing with 30–40% of sulfur

Young's modulus Also known as 'modulus of elasticity', it is a measure of rigidity

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