

CHAPTER 1

Polymer Chemistry

1.1 BASIC CONCEPTS

A polymer is a large molecule built up from numerous smaller molecules. These large molecules may be linear, slightly branched, or highly interconnected. In the latter case the structure develops into a large three-dimensional network.

The small molecules used as the basic building blocks for these large molecules are known as *monomers*. For example the commercially important material poly(vinyl chloride) is made from the monomer vinyl chloride. The repeat unit in the polymer usually corresponds to the monomer from which the polymer was made. There are exceptions to this, though. Poly(vinyl alcohol) is formally considered to be made up of vinyl alcohol (CH_2CHOH) repeat units but there is, in fact, no such monomer as vinyl alcohol. The appropriate molecular unit exists in the alternative tautomeric form, ethanal CH_3CHO . To make this polymer, it is necessary first to prepare poly(vinyl ethanoate) from the monomer vinyl ethanoate, and then to hydrolyse the product to yield the polymeric alcohol.

The size of a polymer molecule may be defined either by its mass (see Chapter 6) or by the number of repeat units in the molecule. This latter indicator of size is called the *degree of polymerisation*, DP. The relative molar mass of the polymer is thus the product of the relative molar mass of the repeat unit and the DP.

There is no clear cut boundary between polymer chemistry and the rest of chemistry. As a very rough guide, molecules of relative molar mass of at least 1000 or a DP of at least 100 are considered to fall into the domain of polymer chemistry.

The vast majority of polymers in commercial use are organic in nature, that is they are based on covalent compounds of carbon. This is also true of the

silicones which, though based on silicon-oxygen backbones, also generally contain significant proportions of hydrocarbon groups. The other elements involved in polymer chemistry most commonly include hydrogen, oxygen, chlorine, fluorine, phosphorus, and sulfur, *i.e.* those elements which are able to form covalent bonds, albeit of some polarity, with carbon.

As is characteristic of covalent compounds, in addition to primary valence forces, polymer molecules are also subject to various secondary intermolecular forces. These include dipole forces between oppositely charged ends of polar bonds and dispersion forces which arise due to perturbations of the electron clouds about individual atoms within the polymer molecule. Hydrogen bonding, which arises from the particularly intense dipoles associated with hydrogen atoms attached to electronegative elements such as oxygen or nitrogen, is important in certain polymers, notably proteins. Hydrogen bonds have the effect of fixing the molecule in a particular orientation. These fixed structures are essential for the specific functions that proteins have in the biochemical processes of life.

1.2 THE HISTORY OF THE CONCEPT OF THE MACROMOLECULE

Modern books about polymer chemistry explain that the word polymer is derived from the Greek words 'poly' meaning many and 'meros' meaning part. They often then infer that it follows that this term applies to giant molecules built up of large numbers of interconnected monomer units. In fact this is misleading since historically the word polymer was coined for other reasons. The concept of polymerism was originally applied to the situation in which molecules had identical empirical formulae but very different chemical and physical properties. For example, benzene (C_6H_6 ; empirical formula CH) was considered to be a polymer of acetylene (C_2H_2 ; empirical formula also CH). Thus the word 'polymer' is to be found in textbooks of organic chemistry published up to about 1920 but not with its modern meaning.

The situation is confused, however, by the case of certain chemicals. Styrene, for example, was known from the mid-nineteenth century as a clear organic liquid of characteristic pungent odour. It was also known to convert itself under certain circumstances into a clear resinous solid that was almost odour-free, this resin then being called metastyrene. The formation of metastyrene from styrene was described as a polymerisation and metastyrene was held to be a polymer of styrene. However, these terms applied only in the sense that there was no change in empirical formula despite the very profound alteration in chemical and physical properties. There was no understanding of the cause of this change and certainly the chemists of the time had no idea of what had happened to the styrene that was remotely akin to the modern view of polymerisation.

Understanding of the fundamental nature of those materials now called polymers had to wait until the 1920s, when Herman Staudinger coined the word 'macromolecule' and thus clarified thinking. There was no ambiguity about this new term – it meant 'large molecule', again from the Greek, and these days is used almost interchangeably with the word polymer. Strictly speaking, though, the words are not synonymous. There is no reason in principle for a macromolecule to be composed of *repeating* structural units; in practice, however, they usually are. Staudinger's concept of macromolecules was not at all well received at first. His wife once recalled that he had 'encountered opposition in all his lectures'. Typical of this opposition was that of one distinguished organic chemist who declared that it was as if zoologists 'were told that somewhere in Africa an elephant was found who was 1500 feet long and 300 feet high'.

There were essentially three reasons for this opposition. Firstly, many macromolecular compounds in solution behave as colloids. Hence they were assumed to be identical with the then known inorganic colloids. This in turn implied that they were not macromolecular at all, but were actually composed of small molecules bound together by ill-defined secondary forces. Such thinking led the German chemist C. D. Harries to pursue the search for the 'rubber molecule' in the early years of the twentieth century. He used various mild degradations of natural rubber, which he believed would destroy the colloidal character of the material and yield its constituent molecules, which were assumed to be fairly small. He was, of course, unsuccessful.

The second reason for opposition to Staudinger's hypothesis was that it meant the loss of the concept of a single formula for a single compound. Macromolecules had to be written in the form $(\text{CH}_2\text{CHX})_n$, where n was a large number. Moreover, no means were available, or indeed are available, for discretely separating molecules where $n = 100$ from those where $n = 101$. Any such attempted fractionation always gives a distribution of values of n and, even if the mean value of a fraction is actually $n = 100$, there are significant numbers of molecules of $n = 99$, $n = 101$, and so on. Now the concept of one compound, one formula, with one formula being capable of both physical (*i.e.* spatial) and chemical interpretation, had been developed slowly and at some cost, with many long, hard-fought battles. Organic chemists could not easily throw it out, particularly in view of the fact that it had been so conspicuously successful with much of the rest of organic chemistry.

The third reason for opposition lay in the nature of many of the polymeric materials then known. Not only were they apparently ill-characterised, but they were also frequently non-crystalline, existing as gums and resins. Just the sort of unpromising media, in fact, from which dextrous organic chemists had become used to extracting crystalline substances of well characterised physical

and chemical properties. To accept such resins as inherently non-crystallisable and not capable of purification in the traditional sense of the word was too much for the self-esteem of many professional organic chemists.

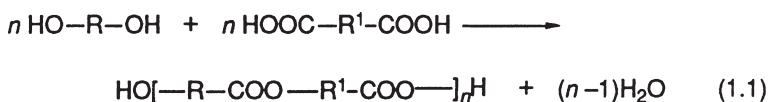
Staudinger's original paper opposing the prevalent colloidal view of certain organic materials was published in 1920 and contained mainly negative evidence. Firstly, he showed that the organic substances retained their colloidal nature in all solvents in which they dissolve; by contrast, inorganic colloids lose their colloidal character when the solvent is changed. Secondly, contrary to what would have been expected, colloidal character was able to survive chemical modification of the original substance.

By about 1930 Staudinger and others had accumulated much evidence in favour of the macromolecular hypothesis. The final part in establishing the concept was carried out by Wallace Carothers of the Du Pont company in the USA. He began his work in 1929 and stated at the outset that the aim was to prepare polymers of definite structure through the use of established organic reactions. Though his personal life was tragic, Carothers was an excellent chemist who succeeded brilliantly in his aim. By the end of his work he had not only demonstrated the relationship between structure and properties for a number of polymers, but he had invented materials of tremendous commercial importance, including neoprene rubber and the nylons.

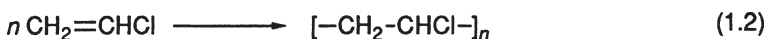
1.3 CLASSIFICATION OF POLYMERS

There are a number of methods of classifying polymers. One is to adopt the approach of using their response to thermal treatment and to divide them into thermoplastics and thermosets. Thermoplastics are polymers which melt when heated and resolidify when cooled, while thermosets are those which do not melt when heated but, at sufficiently high temperatures, decompose irreversibly. This system has the benefit that there is a useful chemical distinction between the two groups. Thermoplastics comprise essentially linear or lightly branched polymer molecules, while thermosets are substantially crosslinked materials, consisting of an extensive three-dimensional network of covalent chemical bonding.

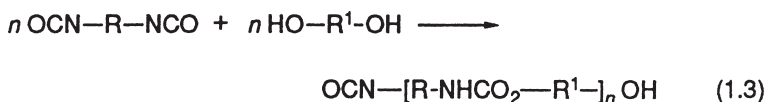
Another classification system, first suggested by Carothers in 1929, is based on the nature of the chemical reactions employed in the polymerisation. Here the two major groups are the *condensation* and the *addition* polymers. Condensation polymers are those prepared from monomers where reaction is accompanied by the loss of a small molecule, usually of water, for example polyesters which are formed by the condensation shown in Reaction 1.1.



By contrast, addition polymers are those formed by the addition reaction of an unsaturated monomer, such as takes place in the polymerisation of vinyl chloride (Reaction 1.2).



This system was slightly modified by P. J. Flory, who placed the emphasis on the mechanisms of the polymerisation reactions. He reclassified polymerisations as *step* reactions or *chain* reactions corresponding approximately to condensation or addition in Carother's scheme, but not completely. A notable exception occurs with the synthesis of polyurethanes, which are formed by reaction of isocyanates with hydroxy compounds and follow 'step' kinetics, but without the elimination of a small molecule from the respective units (Reaction 1.3).



In the first of these, the kinetics are such that there is a gradual build up of high relative molar mass material as reaction proceeds, with the highest molar mass molecules not appearing until the very end of the reaction. On the other hand, chain reactions, which occur only at a relatively few activated sites within the reacting medium, occur with rapid build up of a few high relative molar mass molecules while the rest of the monomer remains unreacted. When formed, such macromolecules stay essentially unchanged while the rest of the monomer undergoes conversion. This means that large molecules appear very early in the polymerisation reaction, which is characterised by having both high relative molar mass and monomer molecules present for most of the duration of the reaction.

Step reactions can give molecules having a variety of morphologies from the simple unbranched linear to the heavily crosslinked network. The final structure depends on the number of functional groups in the parent monomers - the greater the proportion with a functionality of greater than two, the more extensive will be the branching until, at sufficient degrees of branching, a highly crosslinked network emerges. Chain reactions, by contrast, give only linear or lightly branched polymers. Thus, in terms of the thermoplastic/thermoset classification, chain reactions give thermoplastics, while step reactions may give either thermoplastics or thermosets.

1.4 STRUCTURE AND PROPERTIES OF POLYMERS

Having established the basic principles of classification in polymer chemistry, we will now turn our attention to individual polymers and consider a little about their physical and chemical properties. Most of the examples which

follow are of commercial importance, though it is their properties that are emphasised rather than the complete chemistry of their industrial manufacture. In terms of the classification systems just referred to, it is found that the polymers of major commercial importance tend to be the thermoplastics or addition polymers rather than the thermosets, and these will be dealt with first.

1.4.1 Poly(ethylene)

This polymer has one of the simplest molecular structures ($[\text{CH}_2\text{CH}_2-]_n$) and is at present the largest tonnage plastic material, having first been produced commercially in 1939 for use in electrical insulation. There is a difficulty over the nomenclature of this polymer. The IUPAC recommended name for the monomer is ethene, rather than the older ethylene. Hence the IUPAC name for the polymer is poly (ethene). However, this name is almost never used by chemists working with the material; throughout this book, therefore, this polymer will be referred to by its more widespread name, poly(ethylene).

There are four different industrial routes to the preparation of poly (ethylene), and they yield products having slightly different properties. The four routes are:

- (i) High Pressure Processes,
- (ii) Ziegler Processes,
- (iii) The Phillips Process,
- (iv) The Standard Oil (Indiana) Process.

The first group of these use pressures of 1000–3000 atm and temperatures of 80–300 °C. Free-radical initiators, such as benzoyl peroxide or oxygen, are generally used (see Chapter 2), and conditions need to be carefully controlled to prevent a runaway reaction, which would generate hydrogen, methane, and graphite rather than polymer. In general, high-pressure processes tend to yield lower density poly(ethylenes), typically in the range 0.915–0.945 g cm⁻³, which also have relatively low molar masses.

Ziegler processes are based on co-ordination reactions catalysed by metal alkyl systems. Such reactions were discovered by Karl Ziegler in Germany and developed by G. Natta at Milan in the early 1950s.

A typical Ziegler-Natta catalyst is the complex prepared from titanium tetrachloride and triethylaluminium. It is fed into the reaction vessel first, after which ethylene is added. Reaction is carried out at low pressures and low temperatures, typically no more than 70 °C, with rigorous exclusion of air and moisture, which would destroy the catalyst. The poly(ethylenes) produced by such processes are of intermediate density, giving values of about 0.945 g cm⁻³. A range of relative molar masses may be obtained for such

polymers by varying the ratio of the catalyst components or by introducing a small amount of hydrogen into the reaction vessel.

Lastly the Phillips and the Standard Oil (Indiana) Processes both yield high density poly(ethylenes), using relatively low pressures and temperatures. Details of these processes are given in Table 1.1.

The polymer is a very familiar material in the modern world. It is a waxy solid which is relatively low in cost, easily processed, and shows good chemical resistance. Low relative molar mass grades have the disadvantage that they suffer from so-called 'environmental stress cracking', that is they suddenly fail catastrophically for no apparent reason after exposure to sunlight and moisture. Despite this drawback, the various grades of poly(ethylene) have a wide range of uses. These include pipes, packaging, components for chemical plant, crates, and items for electrical insulation.

1.4.2 Poly(propylene)

This polymer, which has the structure $[-\text{CH}_2\text{CH}(\text{CH}_3)-]_n$ arose as a commercial material following the work of Natta on catalysts for the preparation of high relative molar mass polymers from alkenes. Following his work on the polymerisation of ethylene, Natta showed in 1954 that it was possible to prepare analogous polymers of propylene. Commercial exploitation followed rapidly, and poly(propylene) was first marketed in 1957.

Like poly(ethylene), there are formal problems with the nomenclature of this polymer, since its IUPAC name, poly(propene), is also rarely if ever used by polymer chemists. Since, in practice, no ambiguity is associated with the non-systematic name, this is the one that is generally used, as it will be throughout this book.

When poly(propylene) was first made, it was found to exist in two possible forms. One was similar to poly(ethylene), but had greater rigidity and hardness; the other was found to be amorphous and of little strength. The first of these is now known to be isotactic, that is with a regular stereochemistry at each alternating carbon atom. The other is now known to be atactic, that is with a random distribution of different stereochemical arrangements

Table 1.1 Details of processes for preparing poly(ethylene)

Process	Catalyst	Pressure/atm	Temperature/°C	Density of product/g cm ⁻³
Phillips	5% CrO ₃ in finely divided silica/alumina	15–35	130–160	9.6
Standard Oil (Indiana)	Supported MoO ₃ with Na, Ca metal or hydride promoters	40–80	230–270	9.6

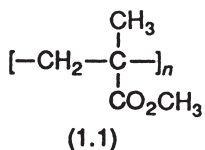
at each methyl-bearing carbon atom. This whole topic of polymer stereochemistry is dealt with in detail in Chapter 3.

Commercial poly(propylene) is usually about 90–95% isotactic and is very similar to poly(ethylene) with the following exceptions:

- (i) It has a lower density (0.90 g cm^{-3}).
- (ii) It has a higher softening point and hence can be used at higher temperatures. For example, it is used to make kettles, generally of the jug-type of design, and it is found to be well able to withstand the effects of exposure to boiling water.
- (iii) It is not susceptible to environmental stress cracking.
- (iv) It is more readily oxidised. This is a consequence of the relatively readily fragmented tertiary C—H bond within the molecule. Another interesting property of isotactic poly(propylene) is that it can be repeatedly flexed without causing weakness. Hence it is used for one-piece mouldings, such as boxes for card indexes, which can be used over many years without damage.

1.4.3 Poly(methyl methacrylate)

This polymer, whose name is often abbreviated to PMMA, is the most important of the commercial *acrylic* polymers. These polymers are formally derived from poly(acrylic acid), $[-\text{CH}_2\text{CH}(\text{CO}_2\text{H})-]_n$. In the case of PMMA, this derivation can be thought of as coming about by replacement of the tertiary hydrogen atom by a methyl group, CH_3 , and by esterification of the carboxylic acid group with methanol, CH_3OH . This gives the structure (1.1).



As with other major tonnage polymers, the IUPAC-recommended name for PMMA is almost never used, partly no doubt because it is extremely cumbersome. It is poly[1-(methoxycarbonyl)-1-methylethene].

Commercially PMMA is becoming relatively less important as time passes. For example, in the mid-1960s sales of PMMA ran at 40% of the total level of sales of poly(styrene); by 1980, they had fallen to 12%. PMMA does, though, retain certain uses, including interestingly as the material from which plastic dentures are manufactured.

PMMA is a transparent, glassy material, which is known from X-ray studies to be amorphous at the molecular level. It is clearly polar, as is shown by

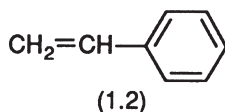
its poor insulating properties relative to poly(ethylene) and its solubility in solvents such as ethyl propanoate and trichloroethane.

The main applications for PMMA arise from the combination of its transparency and its good outdoor weathering properties. These are coupled with reasonable toughness and rigidity, so that PMMA is a useful material in a range of glazing applications. For example, it is used for display signs, street lamp fittings, and ceiling lights in factories and offices. It is also the standard material for automobile rear lamp housings.

1.4.4 Poly(styrene)

Poly(styrene) is a polymer which finds widespread use in the developed world on account of its desirable properties, combined with its relative cheapness. Among its features are excellent colour range, transparency, rigidity, and low water absorption.

The monomer, styrene, is a derivative of benzene, vinyl benzene (1.2). It is a colourless, mobile liquid that polymerises readily. The first report of the polymerisation reaction came in 1839, when E. Simon described the transformation of what was then called 'styrol'. He believed he had oxidised the material and called the product styrol oxide. Later, when it was realised that it contained no oxygen, the product became known as metastyrene.



The polymer is based on a simple head-to-tail arrangement of monomer units and is amorphous, since the specific position of the benzene ring is somewhat variable and hence inhibits crystallisation. Despite its generally desirable properties, for many applications it is considered too brittle. Because of this, a number of approaches have been made to modify the mechanical properties of poly(styrene). The most successful of these have been (i) copolymerisation and (ii) the addition of rubbery fillers.

A very large number of different copolymers of styrene have been produced and sold commercially. Among the most successful have been those polymers also containing butadiene. At the appropriate ratio of monomers, these copolymers behave as synthetic elastomers, known as styrene-butadiene rubber, SBR. Another important group of materials are the terpolymers of acrylonitrile, butadiene, and styrene, ABS. A large range of ABS materials can be made by varying not only the ratios of the three monomers but also the precise conditions of manufacture. ABS materials generally have high impact strength and can be readily moulded to give articles of good surface finish.

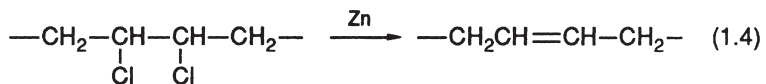
The alternative approach to producing strengthened styrene polymers is to use rubbery fillers. Such materials are known as high-impact poly(styrenes), a name which reflects their improved mechanical properties. They are typically prepared by dissolving the rubber in the styrene monomer, followed by polymerisation of the styrene in the usual way. The process gives a blend containing not only rubber and poly(styrene), but also small amounts of graft copolymer, comprising short poly(styrene) side chains attached to the molecules of the rubber. The overall effect of using this approach is to give materials with much better impact strengths than pure poly(styrene).

Lastly, the polymerisation of styrene is used for crosslinking unsaturated polyesters. Typically a polyester is produced which contains double bonds. Such a resin, known as a pre-polymer, is then mixed with styrene to give a viscous solution, and this solution is then worked into a glass fibre mat. The resulting composite material develops its final properties by polymerisation of the styrene, which essentially undergoes homopolymerisation, but also incorporates the occasional double bond from the pre-polymer molecule. This gives a large, three-dimensional network, intertwined with the glass reinforcement. The composite material has excellent properties and is widely used for boat hulls, shower units, and baths.

1.4.5 Poly(vinyl chloride), PVC

Poly(vinyl chloride) is the widely accepted trivial name for poly(1-chloroethene) and, in terms of worldwide production, is one of the three most important polymers in current use, the other two being poly(ethylene) and poly(styrene). PVC has numerous uses, including cable insulation, packaging, and toys.

PVC has been shown to have a head-to-tail structure. Typical experimental evidence for this is that when dissolved in dioxan and treated with zinc dust, it undergoes a Wurtz-type reaction to yield a product containing a small amount of chlorine and no detectable unsaturation. The alternative possible structure, the head-to-head arrangement, would yield unsaturated sites where adjacent chlorine atoms had been removed (Reaction 1.4).



Uncompounded PVC is colourless and rigid, and possesses poor stability towards heat and light. Indeed, PVC is certainly the least stable of the high tonnage commercial polymers. Exposure to either light or heat at temperatures well below the softening point brings about a number of undesirable changes. Initially discoloration is apparent, as the polymer becomes yellow

and passes progressively through deep amber to black on increasing time of exposure. At the same time the material becomes increasingly brittle.

These changes are caused by the polymer undergoing dehydrochlorination, *i.e.* loss of HCl from along the backbone. Such loss is autocatalytic, and may continue until there are only traces of chlorine left in the macromolecule. It has the effect of reducing molecular flexibility and of allowing absorption of light at the visible part of the electromagnetic spectrum. These alterations in the molecular features lead to the observed changes in the properties of the bulk polymer.

In order to fabricate articles from PVC, and then use them in locations where they will be exposed to sunlight, it is necessary to add stabilisers at the compounding stage. A large number of chemicals have been used as stabilisers for PVC, including lead soaps, barium and cadmium laurates, and organotin compounds such as tin di-iso-octylthioglycollate. These latter compounds, the organosulfurins, are relatively expensive but are used where good clarity and freedom from colour are important in the final compounded PVC.

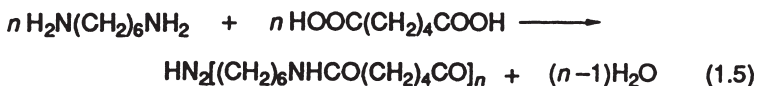
The mechanisms of degradation and the mode of action of the various PVC stabilisers have both been widely studied. Often at least one aspect of their operation is some sort of reaction with the first trace of hydrogen chloride evolved. This removes what would otherwise act as the catalyst for further dehydrochlorination, and hence significantly retards the degradation process. In addition, many stabilisers are themselves capable of reacting across any double bonds formed, thereby reversing the process that causes discoloration and embrittlement.

1.4.6 The Nylons

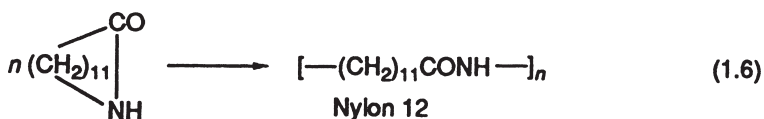
The name Nylon was given by the Du Pont company of America to their first synthetic condensation polymer formed by the reaction of difunctional acids with difunctional amines. It had been made as part of the fundamental programme of W. H. Carothers to investigate the whole topic of polymerisation. The term has gradually been extended to other related polymers. These materials are strictly polyamides, but this term includes that otherwise distinct class of natural macromolecules, the proteins. The term nylon is retained for its usefulness in distinguishing synthetic polyamides from the broader class of such polymers.

As mentioned a moment ago, nylons are condensation or step polymers and, because of this, they are different from all of the other commercially important polymers described so far. The nylons are distinguished from each other by a numbering system based on the number of carbon atoms in the starting materials. Thus, nylon 6,6, which was first prepared in 1935 and is still the major

commercial nylon, is prepared by reaction of hexamethylenediamine (six carbon atoms) with adipic acid (six carbon atoms) (Reaction 1.5).



Similarly nylon 6,10 is prepared from hexamethylenediamine and sebacic acid (ten carbon atoms). Certain nylons are designated not by two numbers, but by a single number; these are the nylons prepared from a single starting material. Such a starting material can be either a long-chain amino acid, such as ω -aminodecanoic acid (eleven carbon atoms) which undergoes self-condensation to yield nylon 11, or a closed ring amide-type compound, known as a lactam, which will undergo a ring-opening reaction to yield a polymer. This is the method by which nylon 6 is prepared from caprolactam (six carbon atoms) and nylon 12 is prepared from dodecyl-lactam (twelve carbon atoms). The latter reaction may be represented by the equation shown in Reaction 1.6.



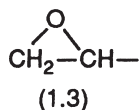
The various nylons tend to have similar physical properties. These include high impact strength, toughness, flexibility, and abrasion resistance. Also, because of the linear structure, they form excellent fibres. This was the basis of the early commercial success of nylon 6,6. Commercial production of fibres of nylon 6,6 began in 1938, and two years later nylon stockings became generally available in the USA. As is well known, they were a huge success, and became highly fashionable during the years of World War II.

Nylons tend to show very good resistance to organic solvents, and also to fuels and oils. They are, however, readily attacked by concentrated mineral acids at room temperature and by alkalis at elevated temperatures.

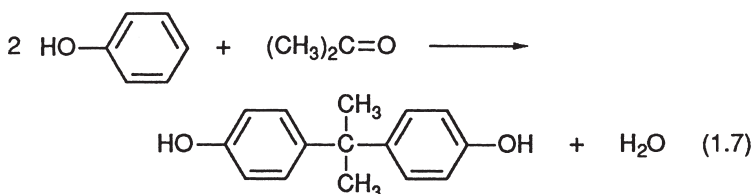
Nylons 6,6 and 6 are the ones usually employed as textile fibres. Where individual monofilaments are used, such as in brushes, sports equipment, or surgical sutures, nylons 6,10 and 11 tend to be used, because of their greater flexibility and water resistance. All nylons can be injection moulded and the resulting articles have found widespread use in engineering applications, such as bearings and gears.

1.4.7 Epoxy Resins

These polymers are based on the three-membered heterocyclic system either as the epoxy or oxirane ring (1.3).



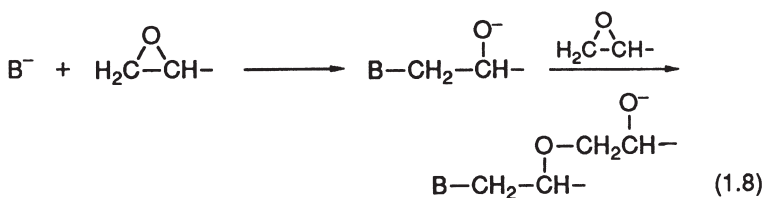
For commercial application, diepoxides such as those derived from bisphenol A are employed, and they are cured via ring-opening crosslinking reactions, into which the epoxy group enters readily. Bisphenol A is so-called because it is formed from two moles of phenol and acetone (Reaction 1.7).



A variety of reagents can bring about these ring openings, including amines and anhydrides used in stoichiometric amounts, or Lewis acids such as SnCl_4 and Lewis bases such as tertiary amines, used in catalytic amounts.

The crosslinking reactions are illustrated in Reaction 1.8, and they demonstrate that, in principle, only a trace of curing agent is necessary to bring about cure of epoxy resins. Selection of curing agent depends on various considerations, such as cost, ease of handling, pot life, cure rates, and the mechanical, electrical, or thermal properties required in the final resin.

Epoxy resins are relatively expensive, but despite this, they are firmly established in a number of important applications. These include adhesives, protective coatings, laminates, and a variety of uses in building and construction.



1.4.8 Phenol-Formaldehyde Polymers

These are thermoset polymers made from phenol or, less commonly, phenolic-type compounds such as the cresols, xylenols, and resorcinol, together with formaldehyde. They had been known for some time – G.T. (later Sir Gilbert) Morgan discovered them in the early 1890s when attempting (unsuccessfully) to make artificial dyestuffs by reaction of phenol with formaldehyde. But this knowledge had not been exploited before 1907, the year in which Leo

Baekeland in America obtained his first patent for materials prepared from these two compounds. In 1910 he founded the General Bakelite Company to exploit this development, in the process making phenol-formaldehydes, the first synthetic polymers to achieve commercial importance.

Baekeland had to make important discoveries before he could bridge the gap between the initial concept and final products. In particular, he found that the base-catalysed condensation of phenol and formaldehyde can be carried out in two parts. If the process is carefully controlled, an intermediate product can be isolated, either as a liquid or a solid, depending on the extent of reaction. At this stage, the material consists of essentially linear molecules and is both fusible and soluble in appropriate solvents. When heated under pressure to 150 °C, this intermediate is converted to the hard, infusible solid known as 'bakelite'. This second stage is the one at which the three-dimensional cross-linked network develops.

Phenol-formaldehydes may no longer hold the centre-stage where synthetic polymers are concerned, but they are still of some commercial importance. They are produced for electrical mouldings, appliance handles, household fittings, and also as adhesives and specialised surface coatings.

Cured phenol-formaldehydes are resistant to attack by most chemicals. Organic solvents and water have no effect on them, though they will swell in boiling phenols. Simple resins are readily attacked by sodium hydroxide solutions, but resins based on phenol derivatives, such as cresol, tend to be less affected by such solutions. Simple phenol-formaldehyde polymers are resistant to most acids, though formic and nitric acids will tend to attack them. Again, cresol-based polymers have resistance to such attack.

1.4.9 Amino Resins

Amino resins are those polymers prepared by reaction of either urea or melamine with formaldehyde. In both cases the product that results from the reaction has a well crosslinked network structure, and hence is a thermoset polymer. The structures of the two parent amino compounds are shown in Figure 1.1.

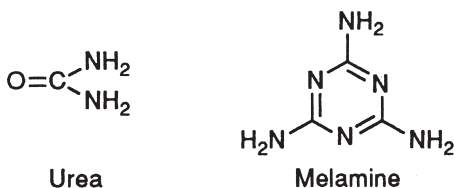


Figure 1.1 Structures of urea and melamine

The initial step of the polymerisation process is reaction of the amine groups with formaldehyde to generate methylol units, as illustrated in Reaction 1.9. Further heating of the polymer then leads to a variety of reactions. For example, the methylol groups can undergo self-condensation (Reaction 1.10).



Alternatively the methylol groups can react with further amino groups, also evolving a molecule of water in what is another condensation reaction (Reaction 1.11).



Unlike phenol–formaldehyde polymers, the amino resins are not themselves deeply coloured, but are of a naturally light appearance. They can be easily pigmented to give a variety of shades, which leads to application in uses where good appearance is highly valued, for example in decorative tableware, laminated resins for furniture, and modern white electrical plugs and sockets.

When crosslinked, amino resins are very resistant to most organic solvents, though they tend to be attacked by both acids and alkalis. Urea–formaldehyde polymers are more susceptible to attack than those prepared from melamine and formaldehyde.

1.4.10 Poly(tetrafluoroethylene), PTFE

This polymer is the completely fluorine-substituted analogue of poly(ethylene) *i.e.* $[\text{CF}_2\text{CF}_2-]_n$. The amount of this polymer produced commercially is very small compared with the output of many other synthetic polymers, but it has a number of important specialised uses and so is worth considering briefly.

PTFE is a white solid with a waxy appearance. It is very tough and flexible, with a good electrical insulation properties. The surface energy and coefficient of friction are both very low, the latter being the lowest of any solid. The combination of low surface energy and low coefficient of friction cause PTFE to have excellent non-stick characteristics, a feature which underlies many of the everyday uses of this polymer.

In addition to its unique mechanical properties, PTFE has excellent chemical resistance to a very wide range of reagents, with the exception of molten alkali metals and fluorine. There is no known solvent for PTFE.

PTFE is a linear polymer of the addition type, formed by polymerisation of the unsaturated monomer tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$. Despite the fact

that this structure ought to impart thermoplastic character to the polymer, PTFE does not show conventional melting behaviour. It does not apparently liquify on heating, nor does it give a melt that will flow. Instead it forms a high-viscosity translucent material which fractures rather than flows when an appropriate force is applied.

Because PTFE cannot be dissolved or melted, there are problems with fabricating articles out of the polymer. These are overcome by using a technique similar to powder metallurgy, in which granular particles are fused under high pressures and temperatures.

The main domestic use for PTFE is on non-stick utensils such as frying pans. Industrially, the polymer is used for gaskets, pump parts, and laboratory equipment.

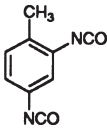
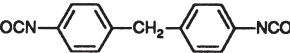
1.4.11 Polyurethanes

'Urethane' is the name given to the functional group formed from the reaction of an isocyanate group with a hydroxy-group (Reaction 1.12).



Polyurethanes are thermoset polymers formed from di-isocyanates and polyfunctional compounds containing numerous hydroxy-groups. Typically the starting materials are themselves polymeric, but comprise relatively few monomer units in the molecule. Low relative molar mass species of this kind are known generally as *oligomers*. Typical oligomers for the preparation of polyurethanes are polyesters and polyethers. These are usually prepared to include a small proportion of monomeric trifunctional hydroxy compounds, such as trimethylolpropane, in the backbone, so that they contain pendant hydroxyls which act as the sites of crosslinking. A number of different di-isocyanates are used commercially; typical examples are shown in Table 1.2.

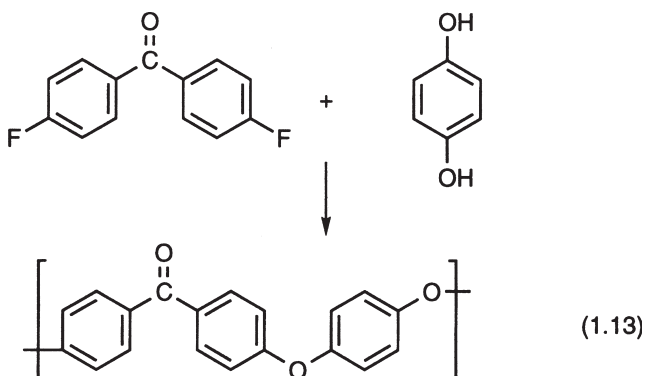
Table 1.2 *Commercially important di-isocyanates*

Name	Abbreviation	Structure
Toluene di-isocyanate	TDI	
Hexamethylene di-isocyanate	HMDI	$\text{OCN(CH}_2)_6\text{NCO}$
Diphenylmethane 4,4'-di-isocyanate	MDI	

The major use of polyurethanes is as rigid or flexible foams. The rigid polyurethanes have a variety of uses, including insulating material for filling cavity walls of houses. Flexible polyurethanes have been widely used in soft furnishing. They suffer from the considerable disadvantage that they burn easily with a very smokey and toxic flame, which has led to severe problems in accidental domestic fires. The use of these materials for this purpose is now declining.

1.4.12 Poly(ether ether ketone)

Poly(ether ether ketone), known as PEEK, is a crystalline high-temperature thermoplastic. It is produced by a step (condensation) process (see Chapter 2) in which 4,4-difluorobenzophenone is reacted with the anion of hydroquinone. This reaction is carried out in a high boiling point polar solvent, such as *N*-cyclohexyl-2-pyrrolidone (1.13).

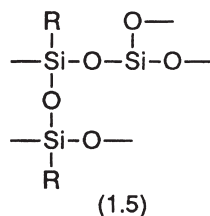
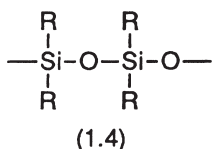


An indication of the thermal stability of PEEK is given by the fact that it can be used at temperatures of up to 250 °C without loss of physical properties. Its melting temperature is 334 °C. The degree of crystallinity can be reduced by copolymerisation with monomers containing diphenyl units, thus reducing the degree of regularity in the linear array of linked phenyl rings.

Industrial applications of PEEK take advantage of the outstanding thermal properties, and include use in high-performance automotive and aerospace components, and in printed circuit boards.

1.4.13 Silicones

Silicones are polymers with alternating silicon and oxygen atoms in the backbone in which the silicon atoms are also joined to organic groups. Typical structures found are (1.4) and (1.5).



The possibility of all kinds of morphology from linear, low relative molar mass molecules to three-dimensional networks means that silicones are found in a range of physical forms, from fluids through to insoluble solids.

The name silicone was originally coined because of the resemblance of the empirical formulae of silicones, *e.g.* R_2SiO , with ketones, R_2CO . However, because of the different nature of the silicon and carbon atoms, in particular that silicon is too large to form stable double bonds, this resemblance is merely superficial.

Silicones are relatively expensive, but they do have excellent thermal stability and water repellency. Hence they tend to find application where these properties are particularly necessary.

1.4.14 Naturally Occurring Polymers

There are a number of naturally occurring polymers which find technical application, including cellulose and its derivatives, starch, and rubber. In addition, a number of important biological materials, most notably the proteins, are made up of macromolecules. These will be considered briefly in the sections which follow.

1.4.15 Cellulose

This is a very widely available polymer, since it is the main component of the cell walls of all plants. It is a carbohydrate of molecular formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, where n runs to thousands. The cellulose ‘monomer’ is D-glucose, and the cellulose molecules are built up from this substance, effectively by condensation and removal of the elements of water.

D-Glucose itself is highly soluble in water, but cellulose is not. This is essentially a kinetic phenomenon; the hydroxy-groups in cellulose would, in principle, readily form hydrogen bonds with water molecules, and hence the cellulose macromolecule would be carried off into aqueous solution. But these hydroxy-groups interact with neighbouring cellulose molecules, making it impossible for water molecules to penetrate, or solvate, the individual molecules. Cellulose will, however, dissolve in the somewhat strange medium aqueous ammoniacal cupric hydroxide, $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$.

Cellulose is a linear polymer. Despite this, it is not thermoplastic, essentially because of its extensive intermolecular hydrogen bonding which never allows the molecules to move sufficiently for the polymer to melt.

Cellulose may be solubilised by treatment with sodium hydroxide and carbon disulfide. It can be regenerated by acidification of the solution. This is the basis of the production of regenerated cellulose fibre, so-called 'viscose rayon', which is a major textile fibre. The technique is also used for the production of continuous cellulose-derived film, so-called 'cellophane' (from 'cellulose' and 'diaphane', the latter being French for transparent).

Cellulose is also commercially modified by acetylation to produce a material suitable for X-ray and cine film. Commercially cellulose ethers are also prepared, such as methylcellulose. This material is water-soluble and gives a highly viscous solution at very low concentrations. Hence it is widely used as a thickener in latex paints and adhesives, in cosmetics and for coating pharmaceutical tablets.

1.4.16 Starch

Starch is a widely distributed material which occurs in roots, seeds, and fruits of plants. For commercial use, corn is the principal source, though wheat and potatoes are also used. Starch is extracted by grinding with water, filtering, centrifuging, and drying, a process which yields starch in a granular form.

Starch consists of two components, amylose and amylopectin. The ratio of these varies with the source of the starch, with amylopectin usually predominating and representing some 70–85% of the total mass of the starch.

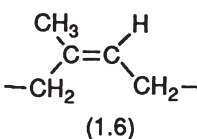
Amylopectin is the polymeric component of starch and consists mainly of glucose units joined at the 1,4-positions. Relative molar mass tends to be very high, *e.g.* between 7 and 70 million. A variety of modified starches are used commercially which are produced by derivatisation to give materials such as ethanoates (acetates), phosphates, and hydroxyalkyl ethers. Modified and unmodified starches are used in approximately equal tonnages, mainly in paper-making, paper coatings, paper adhesives, textile sizes, and food thickeners.

1.4.17 Natural Rubber

Rubber is obtained from the juice of various tropical trees, mainly the tree *Hevea brasiliensis*. The juice is a latex consisting of a dispersion of polymer phase at a concentration of about 35% by mass, together with traces of proteins, sterols, fats, and salts. The rubber is obtained either by coagulation of the latex with acid, either ethanoic or methanoic, or by evaporation in air or over a flame. The material that results from this process is a crumbly, cheese-like substance, sometimes called raw rubber or caoutchouc. In order to

develop the mechanical properties that are considered characteristic of rubber, *i.e.* so-called rubberlike elasticity, this raw rubber needs further processing, and in particular lightly crosslinking. This is achieved in the process known as vulcanisation, as will be discussed later.

The polymer in natural rubber consists almost entirely of *cis*-poly(isoprene) (1.6). The molecules are linear, with relative molar mass typically lying between 300 000 and 500 000. The macromolecular nature of rubber was established mainly by Staudinger in 1922, when he hydrogenated the material and obtained a product that retained its colloidal character, rather than yielding fragments of low relative molar mass.



Vulcanisation is the term used for the process in which the rubber molecules are lightly crosslinked in order to reduce plasticity and develop elasticity. It was originally applied to the use of sulfur for this purpose, but is now used for any similar process of cross-linking. Sulfur, though, remains the substance most widely used for this purpose.

Sulfur reacts very slowly with rubber, and so is compounded with rubber in the presence of accelerators and activators. Typical accelerators are thiazoles and a typical activator is a mixture of zinc oxide and a fatty acid. The chemistry of the vulcanisation reactions is complicated, but generates a three-dimensional network in which rubber molecules are connected by short chains of sulfur atoms, with an average of about five atoms in each chain.

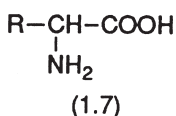
A much more heavily crosslinked material can be obtained by increasing the amount of sulfur in the mixture, so that it represents about a third of the mass of the product. Heating such a mixture of raw rubber and sulfur at 150 °C until reaction is complete gives a hard, thermoset material that is not at all elastic. This material is called ebonite and is used to make car battery cases.

1.4.18 Proteins

The proteins are a group of macromolecular substances of great importance in biochemistry. Their very name provides testimony to this – it was coined by Mulder in 1838 from the Greek word ‘*proteios*’, meaning ‘of first importance’. They appear in all cells, both animal and plant, and are involved in all cell functions.

Proteins are linear polyamides formed from α -amino acids. An α -amino acid is one in which carboxylic acid and the amino group reside on the same carbon atom (1.7).

In nature, there are 20 amino acids available for incorporation into the protein chain. They are arranged in a specific and characteristic sequence along the molecule. This sequence is generally referred to as the 'primary structure' of the protein. Also part of the primary structure is the relative molar mass of the macromolecule.



As a result of the particular amino acid sequence, the protein molecule adopts a characteristic arrangement, such as symmetrical coils or orderly foldings. This is known as the 'secondary structure'. Such individual coils or folded structures bring about a longer range stable arrangement called the 'tertiary structure'. Lastly, several protein molecules may join together to form a complex, this final grouping being known as the 'quaternary structure'.

Proteins themselves consist of large molecules with several hundred amino acids in the primary structure. Smaller units, known as polypeptides, may be formed during physiological processes. There is no clear distinction between a protein and a polypeptide; about 200 amino acid units in the primary structure is usually taken to be the minimum for a substance to be considered a protein.

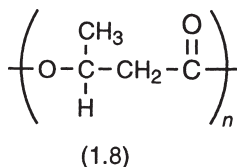
The diversity in primary, secondary, tertiary, and quaternary structures of proteins means that few generalisations can be made concerning their chemical properties. Some fulfil structural roles, such as the collagens (found in bone) and keratin (found in claws and beaks), and are insoluble in all solvents. Others, such as albumins or globulins of plasma, are very soluble in water. Still others, which form part of membranes of cells, are partly hydrophilic ('water-loving', hence water-soluble) and partly lipophilic ('lipid-loving', hence fat-soluble).

Because proteins are not composed of identical repeating units, but of different amino acids, they do not fall within the formal definition of polymers given at the start of this chapter. They are nevertheless macromolecular and techniques developed for the study of true polymers have been applied to them with success. However, for the most part they are outside the scope of this book and accordingly will receive very little attention in the chapters that follow.

1.4.19 Poly(3-hydroxybutyrate)

Poly(3-hydroxybutyrate) (1.8) is a bacterial polyester that behaves as an acceptable thermoplastic, yet can be produced from renewable agricultural feedstocks and is biodegradable. It is typically produced not in the pure state,

but formed alongside minor amounts of poly(3-hydroxyvalerate). The ratio of these two polymers in a given sample is determined by the ratio of glucose and propionic acid in the medium in which the bacteria live and carry out their metabolic processes.



The carbon atom which carries the methyl group is chiral, but biosynthesis is stereoselective, and gives rise to a natural polymer with the *R* configuration. The polymer is a partially crystalline thermoplastic which melts at about 80 °C.

Poly(3-hydroxybutyrate) has attracted interest as an environmentally degradable thermoplastic that can be used in packaging, agriculture and medicine. It undergoes enzymic degradation quite readily, becoming less crystalline and rapidly decreasing in molar mass. The rate of degradation depends on a number of factors, such as moisture level, nutrient supply, temperature, and pH. Further details are given in Chapter 8.