

# An Introduction to Polymer Physics

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# Chapter 1

## Introduction

### 1.1 Polymers and the scope of the book

Although many people probably do not realise it, everyone is familiar with polymers. They are all around us in everyday use, in rubber, in plastics, in resins and in adhesives and adhesive tapes, and their common structural feature is the presence of long covalently bonded chains of atoms. They are an extraordinarily versatile class of materials, with properties of a given type often having enormously different values for different polymers and even sometimes for the same polymer in different physical states, as later chapters will show. For example, the value of Young's modulus for a typical rubber when it is extended by only a few per cent may be as low as 10 MPa, whereas that for a fibre of a liquid-crystal polymer may be as high as 350 GPa, or 35 000 times higher. An even greater range of values is available for the electrical conductivity of polymers: the best insulating polymer may have a conductivity as low as  $10^{-18} \Omega^{-1} \text{ m}^{-1}$ , whereas a sample of polyacetylene doped with a few per cent of a suitable donor may have a conductivity of  $10^4 \Omega^{-1} \text{ m}^{-1}$ , a factor of  $10^{22}$  higher! It is the purpose of this book to describe and, when possible, to explain this wide diversity of properties.

The book is concerned primarily with *synthetic polymers*, i.e. materials produced by the chemical industry, rather than with *biopolymers*, which are polymers produced by living systems and are often used with little or no modification. Many textile fibres in common use, such as silk, wool and linen, are examples of materials that consist largely of biopolymers. Wood is a rather more complicated example, whereas natural rubber is a biopolymer of a simpler type. The synthetic polymers were at one time thought to be substitutes for the natural polymers, but they have long outgrown this phase and are now seen as important materials in their own right. They are frequently the best, or indeed only, choice for a wide variety of applications. The following sections give a brief history of their development, and indicate some of the important properties that make polymers so versatile.

A further restriction on the coverage of this book is that it deals predominantly with polymers in the *solid state*, so it is helpful to give a definition of a solid in the sense used here. A very simple definition that might be considered is that a solid is a material that has the following property: under any change of a set of stresses applied to the material it eventually takes up a new equilibrium shape that does not change further unless the stresses are changed again.

It is, however, necessary to qualify this statement in two ways. The first qualification is that the word *any* must be interpreted as *any within a certain range*. If stresses outside this range are used the material may *yield* and undergo a continuous change of shape or it may *fracture*. This restriction clearly applies to solids of almost any type. The yield and fracture of polymers are considered in chapter 8. The second qualification is that the words *does not change further* need to be interpreted as meaning that *in a time long compared with that for the new so-called equilibrium shape to be reached, the shape changes only by an amount very much smaller than that resulting from the change in the applied stresses*. This restriction is particularly important for polymers, for which the time taken to reach the equilibrium shape may be much longer than for some other types of solids, for example metals, which often appear to respond instantaneously to changes in stress.

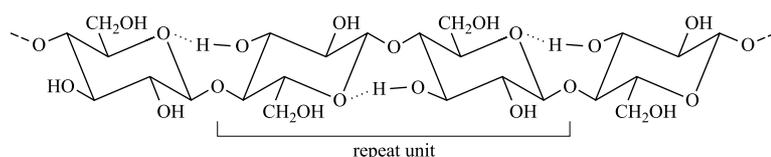
Whether a material is regarded as solid may thus be a matter of the time-scale of the experiment or practical use to which the material is put. This book will consider primarily only those polymer systems that are solids on the time-scales of their normal use or observation. In this sense a block of pitch is a solid, since at low stresses it behaves elastically or viscoelastically provided that the stress is not maintained for extremely long times after its first application. If, however, a block of pitch is left under even low stresses, such as its own weight, for a very long time, it will flow like a liquid. According to the definition, a piece of rubber and a piece of jelly are also solid; the properties of rubbers, or *elastomers* as they are often called, forms an important topic of chapter 6. Edible jellies are structures formed from biopolymers and contain large amounts of entrapped water. Similar *gels* can be formed from synthetic polymers and suitable solvents, but they are not considered in any detail in this book, which in general considers only macroscopic systems containing predominantly polymer molecules.

## 1.2 A brief history of the development of synthetic polymers

Some of the synthetic polymers were actually discovered during the nineteenth century, but it was not until the late 1930s that the manufacture and

use of such materials really began in earnest. There were several reasons for this. One was the need in the inter-war years to find replacements for natural materials such as rubber, which were in short supply. A second reason was that there was by then an understanding of the nature of these materials. In 1910, Pickles had suggested that rubber was made up of long chain molecules, contrary to the more generally accepted theory that it consisted of aggregates of small ring molecules. During the early 1920s, on the basis of his experimental research into the structure of rubber, Staudinger reformulated the theory of chain molecules and introduced the word *Makromolekül* into the scientific literature in 1922. This idea was at first ridiculed, but at an important scientific meeting in Düsseldorf in 1926, Staudinger presented results, including his determinations of molar masses, which led to the gradual acceptance of the idea over the next few years. This made possible a more rational approach to the development of polymeric materials. Other reasons for the accelerated development were the fact that a new source of raw material, oil, was becoming readily available and the fact that great advances had been made in processing machinery, in particular extruders and injection moulders (see section 1.5.3). In the next few pages a brief summary of the development of some of the more important commercial polymers and types of polymer is given.

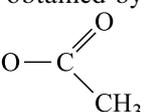
The first synthetic polymer, cellulose nitrate, or *celluloid* as it is usually called, was derived from natural cellulosic materials, such as cotton. The chemical formula of cellulose is shown in fig. 1.1. The formula for cellulose nitrate is obtained by replacing some of the —OH groups by —ONO<sub>2</sub> groups. Cellulose nitrate was discovered in 1846 by Christian Frederick Schönbein and first produced in a usable form by Alexander Parkes in 1862. It was not until 1869, however, that John Wesley Hyatt took out his patent on celluloid and shortly afterwards, in 1872, the Celluloid Manufacturing Company was set up. It is interesting to note, in view of the current debates on the use of ivory, that in the 1860s destruction of the elephant herds in Africa was forcing up the price of ivory and it was Hyatt's interest in finding a substitute that could be used for billiard balls that led to his patenting of celluloid. In the end the material unfortunately turned out to be too brittle for this application.



**Fig. 1.1** The structure of cellulose. (Reproduced by permission of Academic Press.)

The second important plastic to be developed was *Bakelite*, for which the first patents were taken out by Leo Baekeland in 1907. This material is obtained from the reaction of phenol, a product of the distillation of tar, and formaldehyde, which is used in embalming fluid. Resins formed in this way under various chemical conditions had been known for at least 30 years. Baekeland's important contribution was to produce homogeneous, mouldable materials by careful control of the reaction, in particular by adding small amounts of alkali and spreading the reaction over a fairly long time. It is interesting how frequently important discoveries are made by two people at the same time; a striking example is the fact that the day after Baekeland had filed his patents, Sir James Swinburne, an electrical engineer and distant relative of the poet Swinburne, attempted to file a patent on a resin that he had developed for the insulation of electrical cables, which was essentially Bakelite. The properties of such lacquers were indicated in the punning, pseudo-French name that Swinburne gave to one of his companies – The Damard Lacquer Company. Baekeland is commemorated by the Baekeland Award of the American Chemical Society and Swinburne by the Swinburne Award of the Institute of Materials (London).

A second polymer based on modified cellulose, *cellulose acetate*, was also one of the earliest commercial polymers. This material is obtained by

replacing some of the —OH groups shown in fig. 1.1 by —O—

groups. Although the discovery of cellulose acetate was first reported in 1865 and the first patents on it were taken out in 1894, it was only 30 years later that its use as a plastics material was established. Its development was stimulated by the 1914–18 war, during which it was used as a fire-proof dope for treating aircraft wings, and after the war an artificial silk was perfected using it. By 1927 good-quality sheet could be made and until the end of World War II it was still by far the most important injection-moulding material, so the need to process cellulose acetate was a great contributor to the development of injection moulders. Cellulose acetate is still used, for example, in the manufacture of filter tips for cigarettes and in packaging materials.

Before leaving the early development of the cellulosic polymers it is worth mentioning that the first artificial silk, called *rayon*, was made from reconstituted cellulose. The first patents were taken out in 1877/8 and the *viscose process* was patented by Cross, Bevan and Beadle in 1892. It involves the conversion of the cellulose from wood-pulp into a soluble derivative of cellulose and its subsequent reconstitution. The material is thus not a synthetic polymer but a processed natural polymer.

The first of what may be called the modern synthetic polymers were developed during the inter-war years. The first commercial manufacture of polystyrene took place in Germany in 1930, the first commercial sheet of poly(methyl methacrylate), 'Perspex', was produced by ICI in 1936 and the first commercial polyethylene plant began production shortly before the beginning of World War II. Poly(vinyl chloride), or PVC, was discovered by Regnault in 1835, but it was not until 1939 that the plasticised material was being produced in large quantities in Germany and the USA. The production of rigid, unplasticised PVC also took place in Germany from that time. The chemical structures of these materials are described in section 1.3.3.

Apart from the rather expensive and inferior methyl rubber produced in Germany during World War I, the first industrial production of synthetic rubbers took place in 1932, with polybutadiene being produced in the USSR, from alcohol derived from the fermentation of potatoes, and neoprene (polychloroprene) being produced in the USA from acetylene derived from coal. In 1934 the first American car tyre produced from a synthetic rubber was made from neoprene. In 1937 butyl rubber, based on polyisobutylene, was discovered in the USA. This material has a lower resilience than that of natural rubber but far surpasses it in chemical resistance and in having a low permeability to gases. The chemical structures of these materials are shown in fig. 6.10.

In 1928 Carothers began to study condensation polymerisation (see section 1.3.3), which leads to two important groups of polymers, the polyesters and the polyamides, or nylons. By 1932 he had succeeded in producing aliphatic polyesters with high enough molar masses to be drawn into fibres and by 1925 he had produced a number of polyamides. By 1938 nylon-6,6 was in production by Du Pont and the first nylon stockings were sold in 1939. Nylon moulding powders were also available by 1939; this was an important material for the production of engineering components because of the high resistance of nylon to chemicals and abrasion and the low friction shown by such components, in combination with high strength and lightness.

The years 1939–41 brought important studies of polyesters by Whinfield and Dickson and led to the development of poly(ethylene terephthalate) as an example of the deliberate design of a polymer for a specific purpose, the production of fibres, with real understanding of what was required. Large-scale production of this extremely important polymer began in 1955. Its use is now widespread, both as a textile fibre and for packaging in the form of films and bottles. Polymers of another class, the polyurethanes, are produced by a type of polymerisation related to condensation polymerisation and by 1941 they were being produced commercially in Germany, leading to the production of polyurethane foams.

A quite different class of polymer was developed during the early 1940s, relying on a branch of chemistry originated by Friedel and Crafts in 1863, when they prepared the first organosilicon compounds. All the polymers described so far (and in fact the overwhelming majority of polymeric materials in use) are based on chain molecules in which the atoms of the main chain are predominantly carbon atoms. The new polymers were the silicone polymers, which are based on chain molecules containing silicon instead of carbon atoms in the main chain. Silicone rubbers were developed in 1945, but they and other silicones are restricted to special uses because they are expensive to produce. They can withstand much higher temperatures than the organic, or carbon-based, rubbers.

The 1950s were important years for developments in the production of polyolefins, polymers derived from olefins (more properly called alkenes), which are molecules containing one double bond and having the chemical formula  $C_nH_{2n}$ . In 1953 Ziegler developed the low-pressure process for the production of polyethylene using catalysts. This material has a higher density than the type produced earlier and also a greater stiffness and heat resistance. The chemical differences among the various types of polyethylene are described in section 1.3.3. The year 1954 saw the first successful polymerisation of propylene to yield a useful solid polymer with a high molar mass. This was achieved by Natta, using Ziegler-type catalysts and was followed shortly afterwards by the achievement of stereospecific polymerisation (see section 4.1) and by 1962 polypropylene was being manufactured in large volume.

Another important class of polymers developed in these years was the polycarbonates. The first polycarbonate, a cross-linked material, was discovered in 1898, but the first linear thermoplastic polycarbonate was not made until 1953 and brought into commercial production in 1960. The polycarbonates are tough, engineering materials that will withstand a wide range of temperatures.

The first verification of the theoretical predictions of Onsager and of Flory that rod-like molecular chains might exhibit liquid-crystalline properties (see section 1.3.2 and chapter 12) was obtained in the 1960s and fibres from para-aramid polymers were commercialised under the name of Kevlar in 1970. These materials are very stiff and have excellent thermal stability; many other materials of this class of rigid main-chain liquid-crystal polymers have been developed. They cannot, however, be processed by the more conventional processing techniques and this led to the development in the 1980s of another group of liquid-crystal polymers, the thermoplastic co-polyesters.

The development and bringing into production of a new polymer is an extremely expensive process, so any method of reducing these costs or the cost of the product itself is important. For these reasons a great interest developed during the 1970s and 1980s in the blending of polymers of different types to give either cheaper products or products with properties that were a combination of those of the constituent polymers. It was also realised that new properties could arise in the blends that were not present in any of the constituents. The number of polymer blends available commercially is now enormous and developments continue. Even as early as 1987 it was estimated that 60%–70% of polyolefins and 23% of other polymers were sold as blends. Blends are considered in chapter 12.

Another important way in which existing types of polymer can be used to form new types of material and the expense of development of new polymers can be avoided is by influencing their properties by various physical treatments, such as annealing and stretching. As described in later sections, some polymers are non-crystalline and some can partially crystallise under suitable conditions. Heat treatment of both kinds of polymer can affect their mechanical properties quite considerably. An important example of the usefulness of the combination of stretching and heat treatment is to be found in the production of textile fibres from polyester. Stretching improves the tensile strength of the fibre, but unless the fibre is partially crystallised by suitable heat treatment, called 'heat setting', it will shrink under moderate heating as the molecules randomise their orientations. From the 1970s to the present time continuous improvements have been made in the properties of thermoplastic polymers such as polyethylene by suitably orienting and crystallising the molecules, so that even these materials can rival the more expensive liquid-crystal polymers in their stiffnesses.

It must not, however, be thought that the development of new polymers has come to an end. This is by no means the case. Polymer chemists continue to develop both new polymers and new polymerisation processes for older polymers. This leads not only to the introduction of polymers for special uses, which are often expensive, but also to the production of polymers specially constructed to test theoretical understanding of how specific features of structure affect physical properties. Totally novel types of polymer are also synthesised with a view to investigating whether they might have useful properties. These developments are considered further in section 1.3.4, and the following section describes the chemical nature of polymers in more detail than has so far been considered.

## 1.3 The chemical nature of polymers

### 1.3.1 Introduction

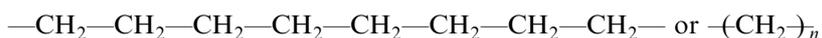
In this book the term *polymer* is used to mean a particular class of macromolecules consisting, at least to a first approximation, of a set of regularly repeated chemical units of the same type, or possibly of a very limited number of different types (usually only two), joined end to end, or sometimes in more complicated ways, to form a *chain molecule*. If there is only one type of chemical unit the corresponding polymer is a *homopolymer*; if there is more than one type it is a *copolymer*. This section deals briefly with some of the main types of chemical structural repeat units present in the more widely used synthetic polymers and with the polymerisation methods used to produce them. Further details of the structures of individual polymers will be given in later sections of the book.

It should be noted that the term *monomer* or *monomer unit* is often used to mean either the *chemical repeat unit* or the small molecule which polymerises to give the polymer. These are not always the same in atomic composition, as will be clear from what follows, and the chemical bonding must of course be different even when they are.

The simplest polymers are chain-like molecules of the type



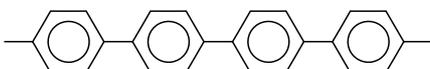
where A is a small group of covalently bonded atoms and the groups are covalently linked. The simplest useful polymer is polyethylene



wherein a typical length of chain, corresponding to  $n \sim 20\,000$  (where  $\sim$  means 'of the order of'), would be about  $3\ \mu\text{m}$ . A piece of string typically has a diameter of about  $2\ \text{mm}$ , whereas the diameter of the polyethylene chain is about  $1\ \text{nm}$ , so that a piece of string with the same ratio of length to diameter as the polymer chain would be about  $1.5\ \text{m}$  long. It is the combination of length and flexibility of the chains that gives polyethylene its important properties.

The phrase 'typical length of chain' was used above because, unlike those of other chemical compounds, the molecules of polymers are not all identical. There is a *distribution of relative molecular masses* ( $M_r$ ) (often called *molecular weights*) and the corresponding molar masses,  $M$ . This topic is considered further in section 3.2. The value of  $M_r$  for the chain considered in the previous paragraph would be  $280\,000$ , corresponding to  $M = 280\,000\ \text{g mol}^{-1}$ . Commercial polymers often have average values of  $M$  between about  $100\,000$  and  $1\,000\,000\ \text{g mol}^{-1}$ , although lower values are not infrequent.

The flexibility of polyethylene chains is due to the fact that the covalent bonds linking the units together, the so-called *backbone bonds*, are non-collinear single bonds, each of which makes an angle of about  $112^\circ$  with the next, and that very little energy is required to rotate one part of the molecule with respect to another around one or more of these bonds. The chains of other polymers may be much less flexible, because the backbone bonds need not be single and may be collinear. A simple example is poly-paraphenylene<sup>†</sup>,



for which all the backbone bonds are collinear and also have a partial double-bond character, which makes rotation more difficult. Such chains are therefore rather stiff. It is these differences in stiffness, among other factors, that give different types of polymer their different physical properties.

The chemical structures of the repeat units of some common polymers are shown in fig. 1.2, where for simplicity of drawing the backbone bonds are shown as if they were collinear. The real shapes of polymer molecules are considered in section 3.3. Many polymers do not consist of simple linear chains of the type so far considered; more complicated structures are introduced in the following section.

### 1.3.2 The classification of polymers

There are many possible classifications of polymers. One is according to the general types of polymerisation processes used to produce them, as considered in the following section. Two other useful classifications are the following.

- (i) Classifications based on structure: *linear*, *branched* or *network* polymers. Figure 1.3 shows these types of polymer schematically. It should be noted that the real structures are three-dimensional, which is particularly important for networks. In recent years interest in more complicated structures than those shown in fig. 1.3 has increased (see section 1.3.4).
- (ii) Classifications based on properties: *(thermo)plastics*, *rubbers (elastomers)* or *thermosets*.

<sup>†</sup> It is conventional in chemical formulae such as the one shown here not to indicate explicitly the six carbon atoms of the conjugated benzene ring and any hydrogen atoms attached to ring carbon atoms that are not bonded to other atoms in the molecule. In the molecule under consideration there are four such hydrogen atoms for each ring. Carbon and hydrogen atoms are also often omitted from other formulae where their presence is understood.



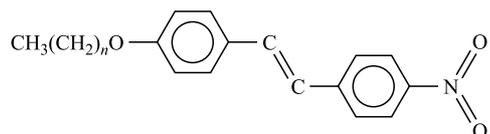
These two sets of classifications are, of course, closely related, since structure and properties are intimately linked. A brief description of the types of polymer according to classification (ii) will now be given.

*Thermoplastics* form the bulk of polymers in use. They consist of linear or branched molecules and they soften or melt when heated, so that they can be moulded and remoulded by heating. In the molten state they consist of a tangled mass of molecules, about which more is said in later chapters. On cooling they may form a *glass* (a sort of ‘frozen liquid’) below a temperature called the *glass transition temperature*,  $T_g$ , or they may crystallise. The glass transition is considered in detail in chapter 7. If they crystallise they do so only partially, the rest remaining in a liquid-like state which is usually called *amorphous*, but should preferably be called *non-crystalline*. In some instances, they form a *liquid-crystal phase* in some temperature region (see below and chapter 12).

*Rubbers*, or *elastomers*, are network polymers that are lightly cross-linked and they are reversibly stretchable to high extensions. When unstretched they have fairly tightly *randomly coiled molecules* that are stretched out when the polymer is stretched. This causes the chains to be less random, so that the material has a lower entropy, and the retractive force observed is due to this lowering of the entropy. The cross-links prevent the molecules from flowing past each other when the material is stretched. On cooling, rubbers become glassy or crystallise (partially). On heating, they cannot melt in the conventional sense, i.e. they cannot flow, because of the cross-links.

*Thermosets* are network polymers that are heavily cross-linked to give a dense three-dimensional network. They are normally rigid. They cannot melt on heating and they decompose if the temperature is high enough. The name arises because it was necessary to heat the first polymers of this type in order for the cross-linking, or *curing*, to take place. The term is now used to describe this type of material even when heat is not required for the cross-linking to take place. Examples of thermosets are the epoxy resins, such as Araldites, and the phenol- or urea-formaldehyde resins.

*Liquid-crystal polymers (LCPs)* are a subset of thermoplastics. Consider first non-polymeric liquid crystals. The simplest types are rod-like molecules with aspect ratios greater than about 6, typically something like



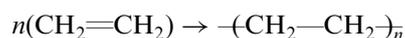
In some temperature range the molecules tend to line up parallel to each other, but not in crystal register. This leads to the formation of anisotropic regions, which gives them optical properties that are useful for displays etc. Polymeric liquid-crystal materials have groups similar to these incorporated in the chains. There are two principal types.

- (a) *Main-chain LCPs* such as e.g. Kevlar. These are stiff materials that will withstand high temperatures and are usually used in a form in which they have high molecular orientation, i.e. the chains are aligned closely parallel to each other. A schematic diagram of a main-chain LCP is shown in fig 1.4(a).
- (b) *Side-chain LCPs* may be used as non-linear optical materials. Their advantage is that it is possible to incorporate into the polymer, as chemically linked side-chains, some groups that have useful optical properties but which would not dissolve in the polymer. A schematic diagram of a side-chain LCP is shown in fig. 1.4(b).

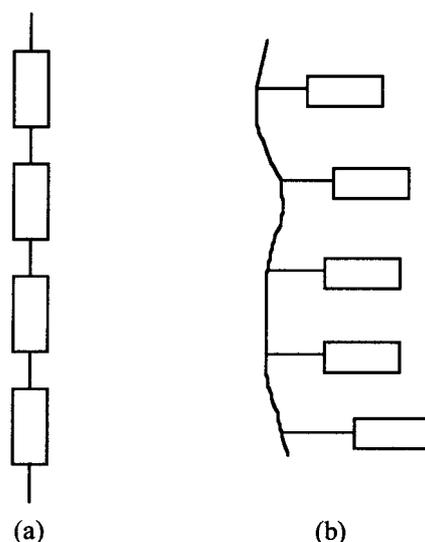
Liquid-crystal polymers are considered in detail in chapter 12.

### 1.3.3 'Classical' polymerisation processes

In *polymerisation*, monomer units react to give polymer molecules. In the simplest examples the chemical repeat unit contains the same group of atoms as the monomer (but differently bonded), e.g. ethylene  $\rightarrow$  polyethylene



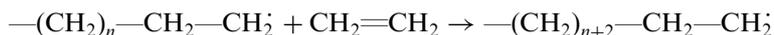
**Fig. 1.4** Schematic representations of the principal types of liquid-crystal polymers (LCPs): (a) main-chain LCP and (b) side-chain LCP. The rectangles represent long stiff groups. The other lines represent sections of chain that vary in length and rigidity for different LCPs.



More generally the repeat unit is not the same as the monomer or monomers but, as already indicated, it is nevertheless sometimes called the ‘monomer’. Some of the simpler, ‘classical’ processes by which many of the bulk commercial polymers are made are described below. These fall into two main types, *addition polymerisation* and *step-growth polymerisation*.

The sequential addition of monomer units to a growing chain is a process that is easy to visualise and is the mechanism for the production of an important class of polymers. For the most common forms of this process to occur, the monomer must contain a double (or triple) bond. The process of addition polymerisation occurs in three stages. In the *initiation* step an *activated species*, such as a free radical from an initiator added to the system, attacks and opens the double bond of a molecule of the monomer, producing a new activated species. (A free radical is a chemical group containing an unpaired electron, usually denoted in its chemical formula by a dot.) In the *propagation* step this activated species adds on a monomer unit which becomes the new site of activation and adds on another monomer unit in turn. Although this process may continue until thousands of monomer units have been added sequentially, it always terminates when the chain is still of finite length. This *termination* normally occurs by one of a variety of specific chain-terminating reactions, which lead to a corresponding variety of end groups. Propagation is normally very much more probable than termination, so that macromolecules containing thousands or tens of thousands of repeat units are formed.

The simplest type of addition reaction is the formation of polyethylene from ethylene monomer:



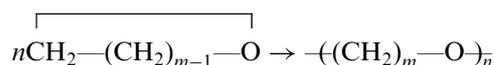
There are basically three kinds of polyethylene produced commercially. The first to be produced, low-density polyethylene, is made by a high-pressure, high-temperature uncatalysed reaction involving free radicals and has about 20–30 branches per thousand carbon atoms. A variety of branches can occur, including ethyl,  $-\text{CH}_2\text{CH}_3$ , butyl,  $-(\text{CH}_2)_3\text{CH}_3$ , pentyl,  $-(\text{CH}_2)_4\text{CH}_3$ , hexyl,  $-(\text{CH}_2)_5\text{CH}_3$  and longer units. High-density polymers are made by the homopolymerisation of ethylene or the copolymerisation of ethylene with a small amount of higher  $\alpha$ -olefin. Two processes, the Phillips process and the Ziegler–Natta process, which differ according to the catalyst used, are of particular importance. The emergence of a new generation of catalysts led to the appearance of linear low-density polyethylenes. These have a higher level of co-monomer incorporation and have a higher level of branching, up to that of low-density material, but the branches in any given polymer are of one type only, which may be ethyl, butyl, isobutyl or hexyl.

Polyethylene is a special example of a generic class that includes many of the industrially important macromolecules, the *vinyl* and *vinylidene* polymers. The chemical repeat unit of a vinylidene polymer is  $-(\text{CH}_2-\text{CXY})-$ , where X and Y represent single atoms or chemical groups. For a vinyl polymer Y is H and for polyethylene both X and Y are H. If X is  $-\text{CH}_3$ , Cl,  $-\text{CN}$ ,  $-\text{C}_6\text{H}_5$  or  $-\text{O}(\text{C}=\text{O})\text{CH}_3$ , where  $-\text{C}_6\text{H}_5$  represents the mono-substituted benzene ring, or phenyl group, and Y is H, the well-known materials polypropylene, poly(vinyl chloride) (PVC), polyacrylonitrile, polystyrene and poly(vinyl acetate), respectively, are obtained.

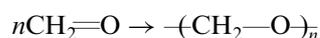
When Y is not H, X and Y may be the same type of atom or group, as with poly(vinylidene chloride) (X and Y are Cl), or they may differ, as in poly(methyl methacrylate) (X is  $-\text{CH}_3$ , Y is  $-\text{COOCH}_3$ ) and poly( $\alpha$ -methyl styrene) (X is  $-\text{CH}_3$ , Y is  $-\text{C}_6\text{H}_5$ ). When the substituents are small, polymerisation of a tetra-substituted monomer is possible, to produce a polymer such as polytetrafluoroethylene (PTFE), with the repeat unit  $-(\text{CF}_2-\text{CF}_2)-$ , but if large substituents are present on both carbon atoms of the double bond there is usually steric hindrance to polymerisation, i.e. the substituents would overlap each other if polymerisation took place.

*Polydienes* are a second important group within the class of addition polymers. The monomers have two double bonds and one of these is retained in the polymeric structure, to give one double bond per chemical repeat unit of the chain. This bond may be in the backbone of the chain or in a side group. If it is always in a side group the polymer is of the vinyl or vinylidene type. The two most important examples of polydienes are polybutadiene, containing 1,4-linked units of type  $-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)-$  or 1,2-linked vinyl units of type  $-(\text{CH}_2-\text{CH}(\text{CH}=\text{CH}_2))-$ , and polyisoprene, containing corresponding units of type  $-(\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2)-$  or  $-(\text{CH}_2-\text{C}(\text{CH}_3)(\text{CH}=\text{CH}_2))-$ . Polymers containing both 1,2 and 1,4 types of unit are not uncommon, but special conditions may lead to polymers consisting largely of one type. Acetylene,  $\text{CH}\equiv\text{CH}$ , polymerises by an analogous reaction in which the triple bond is converted into a double bond to give the chemical repeat unit  $-(\text{CH}=\text{CH})-$ .

Ring-opening polymerisations, such as those in which cyclic ethers polymerise to give polyethers, may also be considered to be addition polymerisations:

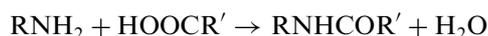


The simplest type of polyether, polyoxymethylene, is obtained by the similar polymerisation of formaldehyde in the presence of water:

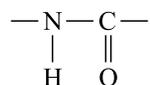


*Step-growth* polymers are obtained by the repeated process of joining together smaller molecules, which are usually of two different kinds at the beginning of the polymerisation process. For the production of linear (unbranched) chains it is necessary and sufficient that there should be two reactive groups on each of the initial 'building brick' molecules and that the molecule formed by the joining together of two of these molecules should also retain two appropriate reactive groups. There is usually no specific initiation step, so that any appropriate pair of molecules present anywhere in the reaction volume can join together. Many short chains are thus produced initially and the length of the chains increases both by the addition of monomer to either end of any chain and by the joining together of chains.

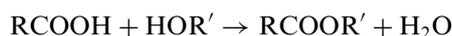
*Condensation* polymers are an important class of step-growth polymers formed by the common condensation reactions of organic chemistry. These involve the elimination of a small molecule, often water, when two molecules join, as in *amidation*:



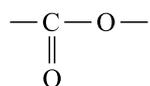
which produces the *amide linkage*



and *esterification*



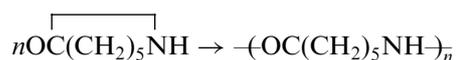
which produces the *ester linkage*



In these reactions R and R' may be any of a wide variety of chemical groups.

The amidation reaction is the basis for the production of the *polyamides* or *nylons*. For example, nylon-6,6, which has the structural repeat unit  $-(\text{HN}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO}-)_n$ , is made by the condensation of hexamethylene diamine,  $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ , and adipic acid,  $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ , whereas nylon-6,10 results from the comparable reaction between hexamethylene diamine and sebacic acid,  $\text{HOOC}(\text{CH}_2)_8\text{COOH}$ . In the labelling of these nylons the first number is the number of carbon atoms in the amine residue and the second the number of carbon atoms in the acid residue. Two nylons of somewhat simpler structure, nylon-6 and nylon-11,

are obtained, respectively, from the ring-opening polymerisation of the cyclic compound  $\epsilon$ -caprolactam:

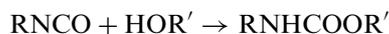


and from the self-condensation of  $\omega$ -amino-undecanoic acid:

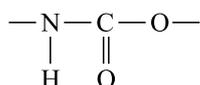


The most important *polyester* is poly(ethylene terephthalate),  $-(\text{CH}_2)_2\text{OOC}-\text{C}_6\text{H}_4-\text{COO}-$ , which is made by the condensation of ethylene glycol,  $\text{HO}(\text{CH}_2)_2\text{OH}$ , and terephthalic acid,  $\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$ , or dimethyl terephthalate,  $\text{CH}_3\text{OOC}-\text{C}_6\text{H}_4-\text{COOCH}_3$ , where  $-\text{C}_6\text{H}_4-$  represents the *para*-disubstituted benzene ring, or *p*-phenylene group. There is also a large group of unsaturated polyesters that are structurally very complex because they are made by multicomponent condensation reactions, e.g. a mixture of ethylene glycol and propylene glycol,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$ , with maleic and phthalic anhydrides (see fig. 1.5).

An important example of a reaction employed in step-growth polymerisation that does not involve the elimination of a small molecule is the reaction of an isocyanate and an alcohol

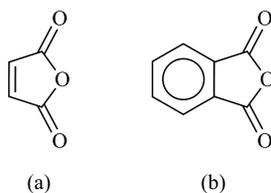


which produces the *urethane linkage*



One of the most complex types of step-growth reaction is that between a di-glycol,  $\text{HOROH}$ , and a di-isocyanate,  $\text{O}=\text{C}=\text{NR}'\text{N}=\text{C}=\text{O}$ , to produce a *polyurethane*, which contains the structural unit  $-\text{O}-\text{R}-\text{O}-(\text{C}=\text{O})-(\text{NH})-\text{R}'-(\text{NH})-(\text{C}=\text{O})-$ . Several subsidiary reactions can also take place and, although all of the possible reaction products are unlikely to be present simultaneously, polyurethanes usually have complex structures. Thermoplastic polyurethanes are copolymers that usually incorporate sequences of polyester or polyether segments.

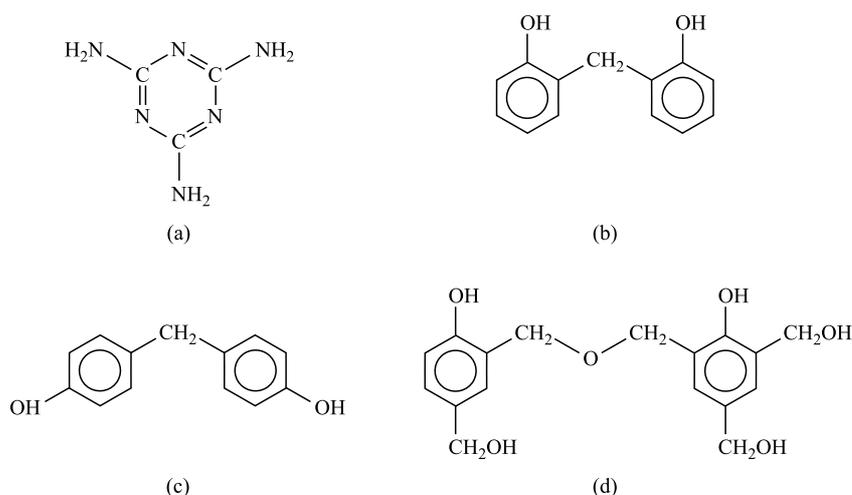
**Fig. 1.5** The chemical formulae of (a) maleic anhydride and (b) phthalic anhydride. (Reproduced from *The Vibrational Spectroscopy of Polymers* by D. I. Bower and W. F. Maddams. © Cambridge University Press 1989.)



Formaldehyde,  $\text{H}_2\text{C}=\text{O}$ , provides a very reactive building block for step-growth reactions. For example in polycondensation reactions with phenol,  $\text{C}_6\text{H}_5\text{OH}$ , or its homologues with more than one  $-\text{OH}$  group, it yields the *phenolic resins*, whereas with urea,  $\text{O}=\text{C}(\text{NH}_2)_2$ , or melamine (see fig. 1.6(a)) it yields the *amino resins*. The products of such condensation reactions depend on the conditions employed but they are usually highly cross-linked. Acid conditions lead to the formation of methylene-bridged polymers of the type shown in figs. 1.6(b) and (c), whereas alkaline conditions give structures containing the methylol group,  $-\text{CH}_2\text{OH}$ , which may condense further to give structures containing ether bridges, of the form  $\text{R}-\text{O}-\text{R}'$  (fig. 1.6(d)).

### 1.3.4 Newer polymers and polymerisation processes

The polymerisation processes described in the previous section are the classical processes used for producing the bulk commercial polymers. Newer processes have been and are being developed with a variety of aims in mind. These involve the production of novel polymer topologies (see box); precise control over chain length and over monomer sequences in copolymers; control of isomerism (see section 4.1); production of polymers with special reactive end groups, the so-called *telechelic polymers*; production of specially designed thermally stable polymers and liquid-crystal polymers with a variety of different structures and properties. Other developments include the production of polymers with very precisely defined molar masses, and of networks with precisely defined chain lengths

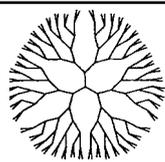


**Fig. 1.6** The chemical formulae of (a) melamine; and (b), (c) and (d) various bridging structures in phenolic resins. (Reproduced from *The Vibrational Spectroscopy of Polymers* by D. I. Bower and W. F. Maddams. © Cambridge University Press 1989.)

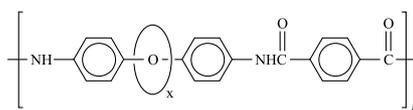
Examples of new topologies, Figs 1(a) and (b) and Fig. 2. (1(a) Adapted by permission of the American Chemical Society; 1(b) reproduced by permission of the Polymer Division of the American Chemical Society.)

### Examples of new topologies

Figure 1(a) shows the topology of a *dendritic polymer*.



(a)



(b)

Fig. 1

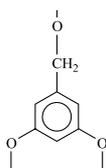


Fig. 2

Each junction point is formed by a chemical group that can join to several other groups, in the case illustrated to three. An example of such a group is shown in fig. 2. Although fig. 1(a) is two-dimensional, whereas the true polymer structure is three-dimensional, it does convey the correct impression that the density of units increases on going outwards from the centre, which puts a limit on the degree of polymerisation for such structures. It also shows that the structure can contain cavities, which could be useful for incorporating small unbonded molecules into the structure. Figure 1(b) shows a *polymeric rotaxane*, in which  $x$  represents a ring molecule that is not attached to the chain backbone by any chemical bonds, but which is prevented from leaving the chain by means of large end groups or by chain folds.

between entanglements or made from stiff rather than flexible chains. Some of the developments are already in commercial use, whereas others are still in the experimental stages.

A development of particular importance for the controlled production of block copolymers is the perfection of various so-called *living polymerisation* techniques. In the classical addition polymerisations there was always a termination stage, leading to the production of chains with non-reactive groups at both ends of the polymer chain. Polymerisation could therefore stop before all monomer had been exhausted, although ideally the termination step was of much lower probability than the propagation step. In living polymerisations there is no termination step and the reaction proceeds in the ideal case until all monomer has been exhausted. The chains still have reactive ends and a second type of monomer can then be added to the reaction to produce a block of a different type of polymer.

## 1.4 Properties and applications

Some of the properties of polymers have already been mentioned in preceding sections and, of course, form the subject matter of the rest of the

Table 1.1. *World production of various materials in 1984 and 1993 (millions of metric tons)<sup>a</sup>*

Material	1984	1993
Polyethylene	19.5	24.7
Poly(vinyl chloride)	12.1	14.8
Polypropylene	7.4	12.5
Polystyrene	6.8	7.5
Synthetic rubbers	9.0	7.4
Phenolic and cresylic plastics	1.4	2.6
Amino plastics	2.3	2.6
Alkyd resins	1.7	1.5
Regenerated cellulose	0.5	0.2
Non-cellulosic fibres	4.6	5.7
Cellulosic fibres	0.9	0.7
Crude steel	717.8	717.9
Unwrought aluminium	18.2	18.3
Unrefined copper	8.7	8.6

<sup>a</sup>Data from *Industrial Commodities Statistics Yearbook*, UN, New York, 1995.

book. Some of the uses have also been mentioned. This section contains some rather general comments on the reasons why the properties of polymers make them so important for a wide variety of applications. Tables 1.1 and 1.2 give first some statistical information about the production and use of polymers.

Table 1.1 illustrates the growth in production of polymers compared with the static state of production of some important metals. When it is remembered that aluminium has a density roughly twice, and copper and steel have densities of order six times, those of even the denser polymeric materials, table 1.1 also illustrates that the volume production of some of the commoner polymers roughly equals or exceeds that of aluminium and copper, and that the total volume production of all the polymers listed is about 60% of the volume production of steel.

The versatility of polymers, already commented on, must be taken to apply not only to these materials as a class, but also to many of its individual members. Poly(ethylene terephthalate) (PET), for instance, is used not only as a textile fibre but also as a packaging material in the form of both film and bottles. Poly(vinyl chloride) (PVC) is used not only as a rigid material for making mouldings but also, in plasticised form, for making flexible tubing and artificial leather.

Table 1.2. *Estimated end uses of plastics by weight*<sup>a</sup>

Packaging	37% <sup>b</sup>
Building and construction	23%
Electrical and electronic	10%
Transport	9%
Furniture	5%
Toys	3%
Housewares	3%
Agriculture	2%
Medical	2%
Sport	2%
Clothing	1%
Others	3%

<sup>a</sup>Reproduced by permission of the Institute of Materials from *Plastics: The Layman's Guide* by James Maxwell, IOM Communications Ltd, 1999.

<sup>b</sup>Since this table was compiled, use for packaging has increased and now probably represents about 50%.

As well as the classification of uses in table 1.2, polymers can also be classified broadly as being used as plastics, rubbers, fibres, coatings, adhesives, foams or speciality polymers. In many of their uses, as in plastics and fibres, it is often the combination of properties such as high strength-to-weight or stiffness-to-weight ratio and high resistance to chemical attack that gives them their importance. In other uses it is flexibility combined with toughness. In yet others it is resistance to chemical attack combined with high electrical resistance. One of the most important properties for many applications is the ability to be cast or moulded into complex shapes, thus reducing machining and assembly costs. Non-medical speciality uses include conducting polymers for rechargeable batteries; polymer sensors for many applications; high-density information storage, including CD and holographic devices; smart windows that can react to levels of light; and liquid-crystal displays, among many others. Medical uses include tooth fillings, components for hip-joint replacement and contact and implant lenses. It is not quite a matter of 'you name it and polymers will solve it', but their uses continue to expand into an ever-increasing variety of fields.

Although rubbers, or elastomers, form only a few per cent of polymers in use, they are vital for many applications, in particular for tyres and tyre products, which now consume about 50% of all rubber produced. The production of both synthetic and natural rubbers has expanded steadily