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Polymers: Molecular Structure

A polymer is a very large molecule comprising hundreds or thousands of atoms, formed by successive linking of one or two, occasionally more, types of small molecules into chain or network structures. The concept of the polymer is one of the great ideas of twentieth century chemistry. It emerged in the 1920s amid prolonged controversy and its acceptance is closely associated with the name of Hermann Staudinger who received the Nobel Prize in 1953. The influence of the polymer (or *macromolecule*) concept spread rapidly into many areas of the natural sciences and technology. Within the life sciences it fostered the emergence of molecular biology through the study of natural macromolecular substances such as proteins, nucleic acids and polysaccharides. In engineering, a series of successes in commercial polymer synthesis established a new sector of the international chemical industry, devoted to producing and applying polymeric materials, notably plastics and rubbers, coatings and adhesives. This book is concerned with the materials science and engineering properties of such synthetic polymers.

1.1 The Polymer Materials Industry

Of the polymer materials in engineering use, the plastics form the largest group by production volume. It is common to subdivide plastics into *thermoplastics* and *thermosets* (or thermosetting resins). Thermoplastics comprise the four most important commodity materials – polyethylene, polypropylene, polystyrene and poly(vinyl chloride) – together with a number of more specialised engineering polymers. The term 'thermoplastic' indicates that these materials melt on heating and may be processed by a variety of moulding and extrusion techniques. Important thermosets include alkyds, amino and phenolic resins, epoxies, unsaturated polyesters and polyurethanes, substances which cannot be melted and remelted but which *set* irreversibly. The distinction is important in that production, processing and fabrication techniques for thermoplastics and thermosets differ.

Table 1.1 lists a number of plastics materials (a full discussion of polymer nomenclature appears in the appendix). The annual production of these materials in the United Kingdom and in the United States in the years 1985/1986 is shown in figure 1.1(a). The production of plastics, especially thermoplastics, demands a high level of chemical technology and is confined largely to a small number of major companies. A recent survey of the UK plastics industry showed that 90 per cent of thermoplastics production capacity is held by six companies. Table 1.2 charts the emergence of the major plastics materials.

Rubbers form another group of polymeric engineering materials. They are distinguished from plastics largely for reasons of industrial history. A rubber industry (using natural rubber latex as its raw material) was well established by

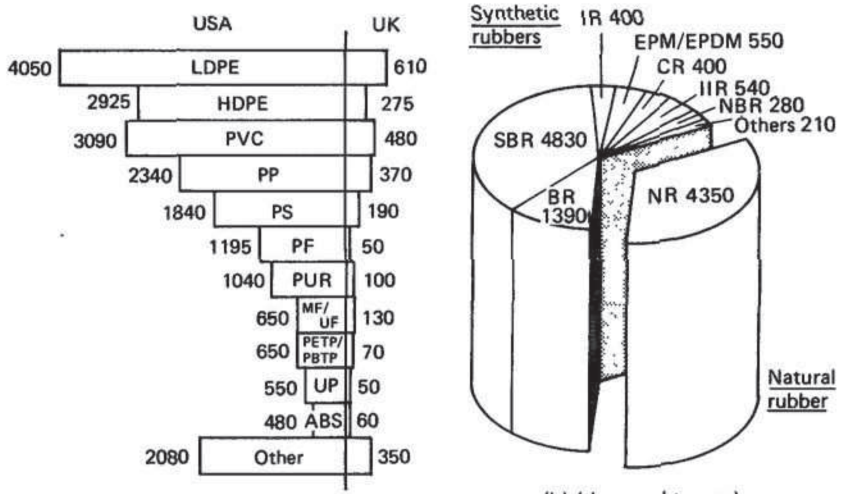
TABLE 1.1
Major polymer materials

Plastics – Thermoplastics	polyethylene	PE
	polypropylene	PP
	polystyrene	PS
	poly(vinyl chloride)	PVC
	polyacetal	POM
	acrylic	PMMA
	polyamide (nylon)	PA
	polycarbonate	PC
	polytetrafluorethylene	PTFE
Plastics – Thermosets	epoxy	EP
	melamine-formaldehyde	MF
	urea-formaldehyde	UF
	unsaturated polyester	UP
	phenolic	PF
	alkyd	
	polyurethane	PUR
Elastomers	natural rubber	NR
	styrene–butadiene rubber	SBR
	polybutadiene	BR
	butyl rubber	IIR
	polychloroprene	CR
	synthetic polyisoprene	IR
	nitrile	NBR
	silicone rubber	

TABLE 1.2
Emergence of some major plastics and rubbers

	Beginning of commercial production	
	year	country
Thermoplastics		
Cellulose nitrate CN	1870	USA
Cellulose acetate CA	1905	Germany
Polystyrene PS	1930	Germany
Poly(methyl methacrylate) PMMA	1934	UK
Poly(vinyl chloride) PVC	1933	Germany/USA
Low density polyethylene LDPE	1939	UK
Polyamide PA	1939	USA
Polytetrafluorethylene PTFE	1950	USA
Acrylonitrile–butadiene–styrene ABS	1952	USA
Poly(ethylene terephthalate) PETP	1953	USA
High density polyethylene HDPE	1955	W. Germany
Polypropylene PP	1957	Italy
Polycarbonate PC	1959	W. Germany/USA
Polyoxymethylene POM	1960	USA
Polysulphone	1965	USA
Polymethylpentene	1965	UK
Linear low density polyethylene LLDPE	1977	USA
Thermosets		
Phenol–formaldehyde PF	1909	USA
Urea–formaldehyde UF	1926	UK
Melamine–formaldehyde MF	1938	Germany
Polyurethane PUR	1943	Germany
Silicone SI	1943	USA
Polyester UP	1946	USA
Epoxy EP	1947	USA
Rubbers		
Natural rubber NR (vulcanised)	1839	UK/USA
Styrene–butadiene rubber SBR	1937	Germany
Acrylonitrile–butadiene rubber NBR	1937	Germany
Polychloroprene CR	1932	USA
Polybutadiene BR	1932	USSR
Synthetic polyisoprene IR	1959	USA
Butyl rubber IIR	1940	USA
Ethylene–propylene rubbers EPM/EPDM	1963	USA/Italy

1900, some decades before the modern plastics industry, and before it was known that rubbers are polymeric substances. Today synthetic rubbers (*elastomers*) are widely used alongside natural rubber, figure 1.1(b), and a sharp distinction between plastics and rubbers is hard to sustain. Both are simply types of polymeric materials.



(a) (thousand tonnes)

(b) (thousand tonnes)

Figure 1.1 (a) United Kingdom and United States production of plastics materials compared, 1985-86 data; US production *per capita* is twice that of the UK. (b) Projected world consumption of rubber (Eastern Europe and parts of Asia excluded) for 1989 (International Institute of Synthetic Rubber Producers)

Similarly fibres, coatings and adhesives are polymeric materials designed to serve different ends and produced in different physical forms. Each is the concern of a particular industry, with a specialised technology. However the basic materials often have much in common. For example the nylons (or polyamides), important engineering thermoplastics, are found both in textiles and in coatings; epoxies are used both in paints and in adhesives and composites.

The structure of the polymer materials industry is summarised in figure 1.2. The polymers (with the exception of a few types produced by modification of vegetable substances such as cellulose and natural rubber) are produced from petroleum or natural gas raw materials. In the United Kingdom and Europe the key petrochemicals for polymer synthesis (ethylene, propylene, styrene, vinyl chloride monomer and others) are produced largely from naphtha, one of the distillation fractions of crude oil. In the United States natural gas provides the starting point. In both cases the polymer industry competes for its chemical feedstocks with other users of petroleum resources. Once synthesised, the polymer materials are passed to major consuming industries such as textiles or paints, or to a highly diverse processing sector, producing commodities for markets such as the building, packaging, agriculture, automobile, furniture, electrical and general engineering industries.

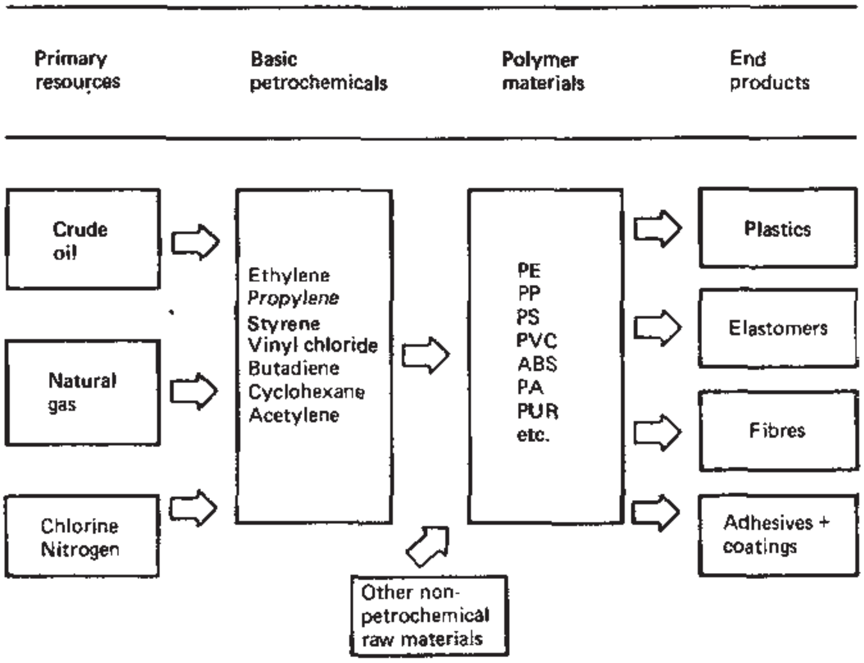


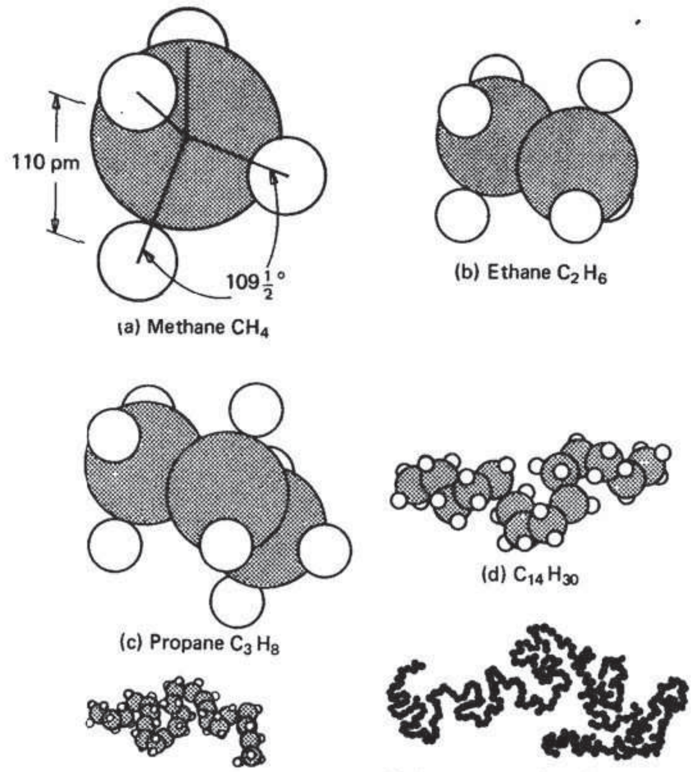
Figure 1.2 Production of polymer-based products from raw materials

Worldwide, the polymer materials industry continues to maintain the very high growth rate (perhaps 7 per cent per year overall) which has been evident for several decades. In the 1970s and 1980s, the industry has introduced many new *engineering polymers* and steadily improved the quality of its commodity products. In many applications, polymers are displacing other materials: for example, in the huge industrial and public utility piping market, where steel, cast iron, copper and fired clay are being displaced by polyethylene, polypropylene and poly(vinyl chloride) for water and gas distribution.

1.2 Hydrocarbons and Hydrocarbon Polymers

Hydrocarbons are a class of substances containing only the chemical elements carbon and hydrogen (C and H) in combination. Petroleum and natural gas are complex mixtures of hydrocarbons formed on Earth at remote times. A number of polymers (including some of the most important, PE, PP, PS and natural rubber) are also hydrocarbons: *hydrocarbon polymers.*

The difference between the individual hydrocarbon gases, liquids and solids (waxes and polymers) lies simply in *molecular structure* (figure 1.3). Fortunately since these structures involve only C and H atoms they are not difficult to depict. The simplest of all hydrocarbon molecules is that of methane, the main component of natural gas. The molecular formula is CH_4, and its molecular structure is shown in detail in figure 1.3(a). The central carbon atom of methane forms a single chemical bond with each of four hydrogen atoms, which are arranged tetrahedrally about it. Thus methane is a compact five-atom molecule. Its *relative molecular mass* (defined as the sum of the relative atomic masses of the constituent atoms) is $12.00 + 4 \times 1.008 = 16.03$. (The *molar mass* of methane is 16.03 g/mol.) Other hydrocarbon structures arise because C atoms may form chemical bonds also between themselves. Thus the molecule



(a) Methane CH_4

(b) Ethane C_2H_6

(c) Propane C_3H_8

(d) $C_{14}H_{30}$

(e) $C_{24}H_{50}$

(f) Polyethylene $(CH_2)_n$ polymer

Figure 1.3 (a) Molecular structure of methane CH_4 showing tetrahedral arrangement of C—H bonds, bond angle and bond length. (b) – (f) Molecular structures of other straight-chain hydrocarbons of ethane (C_2H_6) comprises a pair of C atoms linked by a C—C single bond; each C atom is bonded in addition to three H atoms. Ethane is thus a C_2 hydrocarbon.

Higher hydrocarbons in the series are formed by extending the chain of C atoms, and paraffinic alkane hydrocarbons of this kind are found in natural petroleum oils up to a maximum carbon chain length of about C_{38}. There is a smooth change in the physical properties of the individual hydrocarbons as the chain length increases: thus the C_1–C_4 members of the series are gases at normal ambient temperature; C_5–C_{12} are volatile liquids, including important constituents of motor fuel (gasoline); C_{13}–C_{18} are higher boiling liquids (aviation fuel, kerosene); C_{19} and higher are heavy oils and waxes. Figure 1.4 shows how the important properties of melting point and density change with chain length n for the normal hydrocarbons C_nH_{2n+2}. The difference in properties between adjacent members of the series (C_n and C_{n+1}) becomes relatively smaller as C_n increases. This simply reflects the fact that as the chains get longer the addition of one further C atom represents a relatively smaller incremental change in molecular structure, and the effect of this change on properties becomes less marked. It becomes a very difficult task to separate the various components of the higher boiling fractions of petroleum from one another.

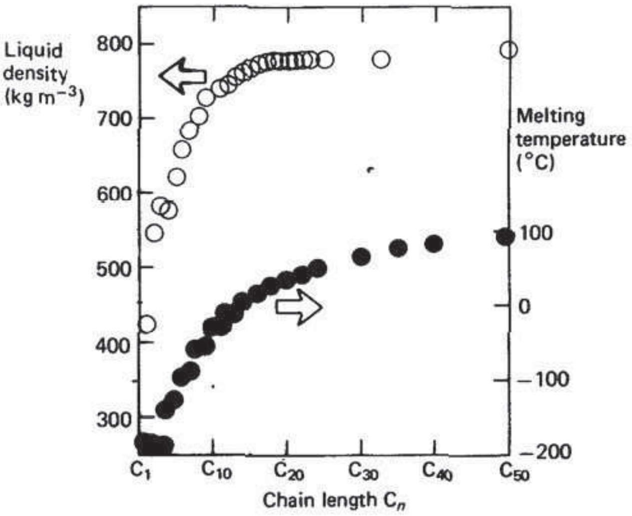


Figure 1.4 Liquid state densities and melting temperatures of normal straight-chain hydrocarbons C_nH_{2n+2} (densities at 20 °C or closest available temperature)

In 1933 a laboratory procedure was discovered which produced a synthetic hydrocarbon polymer of chain length far greater than C_{38}. The product was polyethylene (PE). PE is composed of hydrocarbon chains containing hundreds or thousands of carbon atoms. Thus we may write the molecular structure of PE as $H_3C(CH_2)_nCH_3$ or, omitting the terminal atoms, simply as $(CH_2)_n$. n is large, but we cannot assign it a unique value. The methods of synthesis of polymers normally produce a mixture of molecules of different chain lengths. As figure 1.4 suggests, such molecules differ only slightly in most physical properties and are not easily separated. We shall discuss the *distribution* of chain lengths and its consequences later.

PE resembles the paraffin waxes of C_{30}—C_{40} in many respects: in appearance both are waxy, translucent, white solids, easily melted, of density about 900 kg/m^3 and both are electrical insulators. Both burn easily but are otherwise chemically inert. The most striking physical differences lie in mechanical properties, for whereas paraffin wax is mechanically weak, PE is a tough and useful engineering material.

1.3 Properties of the Polymer Chain

The *relative molecular mass* of polyethylene (*see* definition given in previous section) is

$$\begin{aligned} M &= 14.02n + 2.02 \\ &\sim 14n \text{ when } n \text{ is large} \end{aligned}$$

The relationship between relative molecular mass (or molar mass) and chain length is important because it is the relative molecular mass which is usually determined experimentally. The chain length is then calculated from this. Since any sample of PE contains individual chains of different lengths (n not constant) the relative molecular mass determined on a real sample is some sort of average value. The distribution of chain lengths in two samples is illustrated in figure 1.5(a). Sample A has a narrow distribution about a rather high value. Sample B has a much broader and somewhat asymmetric distribution about a lower value. The average chain length can be defined in two main ways. The *number-average chain length* $\bar{n}_N$ is obtained by determining the total length of polymer chain in the sample, and dividing this by the total number of molecules. Referring to curve A of figure 1.5(a) we have

$$\bar{n}_N = \Sigma f_i N n_i / N = \Sigma f_i n_i$$

where f_i is the fraction of chains of length n_i in a total of N molecules. This definition gives equal weighting to every molecule, large or small, in the calculation of the average. Alternatively a different average chain length, a *length-average* $\bar{n}_L$, can be defined in which chains contribute to the average in proportion to their length, the longer chains carrying greater (statistical) weight than the shorter ones.

$$\begin{aligned} \bar{n}_L &= (\Sigma f_i N n_i \times n_i) / \Sigma f_i N n_i \\ &= \Sigma f_i n_i^2 / \Sigma f_i n_i \end{aligned}$$

Since the chain mass is directly proportional to the chain length, a *number-average relative molecular mass* $\bar{M}_N$ and a *weight-average relative molecular mass*

$\bar{M}_W$ are simply defined

$$\bar{M}_N = \bar{n}_N \times M_l$$

and

$$\bar{M}_W = \bar{n}_L \times M_l$$

where M_l is the relative molecular mass per unit length of the polymer chain. (In the SI system relative molecular mass and molar mass expressed in g/mol are numerically equal, so that $\bar{M}_N$ and $\bar{M}_W$ also define average molar masses.)

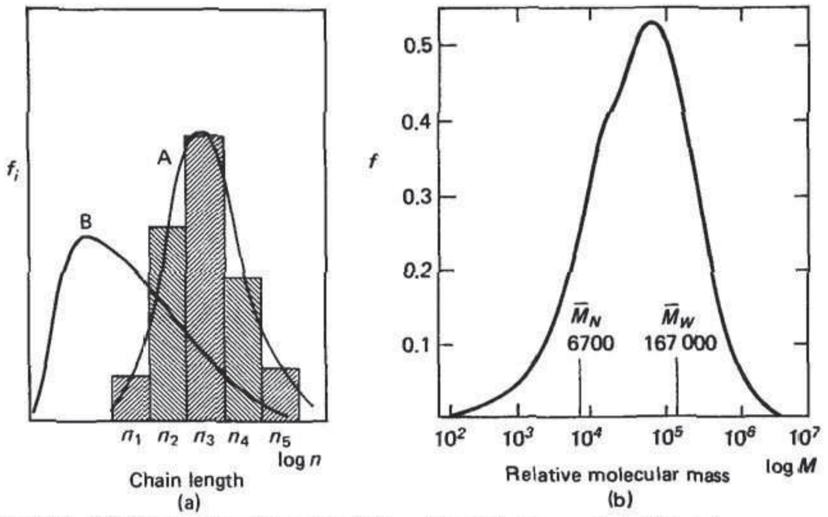


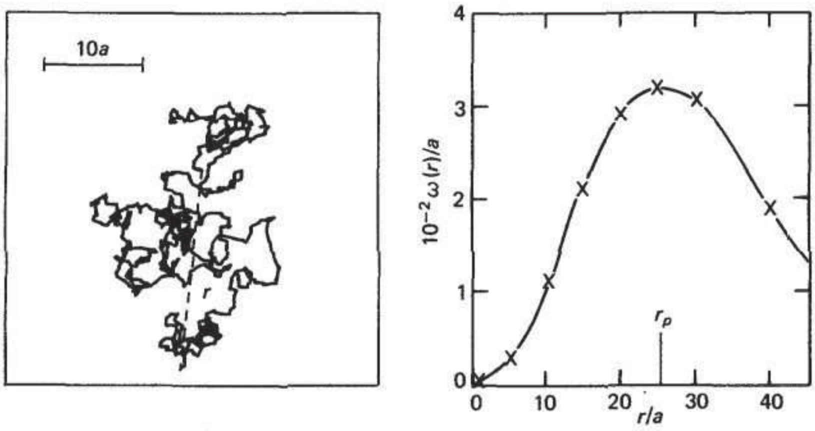
Figure 1.5 (a) Examples of narrow (A) and broad, asymmetric (B) polymer chain length distributions; curve A shown in histogram form (*see* text). (b) Experimental relative molecular mass distribution of an HDPE sample, showing $\bar{M}_N$ and $\bar{M}_W$; $f = n_i f_i / \Sigma(n_i f_i)$, obtained by size exclusion chromatography

The quantity $\bar{M}_W/\bar{M}_N$ (or $\bar{n}_L/\bar{n}_N$) equals 1 only for a polymer system in which all molecules have the same chain length and molecular mass. Such materials are called *monodisperse*. Otherwise $\bar{M}_W/\bar{M}_N > 1$ and this ratio is a measure of the broadness of molecular mass distribution – *see* figure 1.5(b). The relative molecular mass of a polymer has an important influence on flow properties in the molten state as well as on mechanical behaviour.

A polyethylene molecule containing, for example, 1000 C atoms has much the same length to thickness ratio as a piece of household string a couple of metres long. The maximum value of the end-to-end distance can easily be calculated from the C—C bond length which is accurately known to be 154 pm. Even in its fully extended conformation the molecule cannot attain a state in which all the C atoms are collinear, since the $\mathrm{C}\overset{\mathrm{C}}{\wedge}\mathrm{C}$ bond angle is fixed at 109.5 degrees. However, a regular coplanar arrangement can be adopted, and is in fact found in the crystalline regions of solid PE. In such a conformation the end-to-end distance of a fully collinear 1000 C atom chain would be 999 x 154 x sin (109.5°/2) = 0.13 x 10^6 pm = 0.13 μm.

Should we visualise the polymer chain molecule as a rigid or as a flexible entity? Since both the C—C bond angle and the bond length are fixed, chain flexibility can arise only from rotational motions about C—C bonds. Ethane is the simplest hydrocarbon which possesses a C—C bond, figure 1.3(b), and in the liquid and gaseous state the relative rotation of the CH_3 groups is known to be fairly free. The CH_3 rotors sense their orientation with respect to each other only weakly. Similarly the higher liquid and gaseous hydrocarbons may be regarded as loosely jointed chains, which are continually changing their conformations through rotational motions about C—C chain bonds, and the buffeting of thermal collisions.

This is true also of linear polymer chain molecules such as polyethylene. In the melt and in solution the molecule possesses kinetic energy distributed among many different kinds of motion (including translation of the molecule as a whole, rotation of parts of the molecule, and vibration of individual bonds), which cause the conformation to change continually. In these fluid states the molecule behaves as a loosely jointed chain and adopts a largely random arrangement in space, subject only to the bond angle restriction mentioned previously. Figure 1.6(a) shows a computer calculated projection based on a



(a) (b)

Figure 1.6 (a) Random conformation of a linear polymer chain of 500 bonds, with free rotation but fixed bond angle. The random chain is computed by successive addition of N vectors $\mathbf{a}_i$ of length a, randomly oriented in space subject to the condition that $\mathbf{a}_i \cdot \mathbf{a}_{i+1} = -a^2 \cos\alpha$, where $\alpha = 110$ degrees, the C—C—C bond angle. The figure shows the projection of the chain on to the plane of the paper. The parameter r, the end-to-end distance, is the length of the broken line. (b) r has an approximately Gaussian distribution $\omega(r)$ about a most probable value $r_p = (4Na^2/3)^{1/2}$

random walk model. Although very simple, this conveys a useful idea of the state of the random polymer chain in the melt and in solution.

In the solid state, the situation is less clear-cut. In some polymer solids the molecules adopt ordered crystalline arrangements; alternatively the solid polymer may be amorphous and lack long-range internal order. In either case, vibrational motion persists down to the lowest temperatures. Rotational motions also occur but are impeded by strong interactions between neighbouring molecules. Certain modes of molecular motion now require cooperation between molecular neighbours. The temperature is an important factor, for it determines how much kinetic energy the molecules possess. As the temperature falls various types of molecular motion are progressively frozen out. These effects underlie the mechanical behaviour of polymer materials and are discussed more fully in chapter 3.

1.4 Branched Chains

So far we have considered only linear polymer chains. We look now at the occurrence of branching during chain building. No such possibility arises in the case of the C_2 or C_3 hydrocarbons, but two C_4 alkane hydrocarbons can be envisaged

(I)

(II)

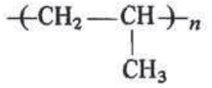
(I) is *n*-butane, $CH_3CH_2CH_2CH_3$ (the hydrogen atoms are omitted here to emphasise the chain backbone structure); (II) is isobutane, $CH(CH_3)_3$. (I) and (II) have different molecular structures, but they have the same number of C and H atoms in all, C_4H_{10}, and hence the same molar mass. They are butane *isomers*, distinct substances which differ in physical properties, such as melting points and boiling points: (I) −0.5 °C, (II) −12 °C. The physical differences arise simply from the different molecular *shapes*, illustrating the importance of chain branching.

Whereas there are only two C_4 alkane isomers, three C_5 isomers exist

Clearly as the number of C atoms in the chain increases, the number of branching options (and of isomers) rises rapidly. In fact the chains of polyethylene and other major thermoplastics are not highly branched. However a limited degree of chain branching is frequently found, and has important consequences. In PE produced by the high pressure process (*see* section 1.12) the molecules have (typically) short side branches about 4C long every 100C or so along the chain, and occasionally form long branches in addition. These branch points arise by molecular accidents during synthesis. The branch material is only a small proportion of the total material, but impedes crystalline packing of molecules. Moreover, points of weakness in the chain occur where branch and main chain join, and make the polymer vulnerable to degradation by ultraviolet light.

1.5 Stereoregularity

Polypropylene is another major commodity polymer closely related to polyethylene. It has the molecular structure



$$-\!\!\left(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}\right)\!\!-_n$$

and thus is formally derived from PE by the substitution of one of the H atoms on alternate C atoms of the chain by a CH_3 group. Polypropylene thus contains only C and H atoms and is a hydrocarbon polymer. Figure 1.7 shows the configuration of atoms in a short length of PE chain, and it is apparent that the PP structure can be derived from it in several ways. Structure (I) has all pendant CH_3 groups attached on the same 'side' of the chain; more precisely, all units have a spatially identical arrangement of atoms. Such a structure is called *isotactic.* Structure (II) on the other hand shows a random arrangement of pendant CH_3 groups in an *atactic* molecule. Structures (I) and (II) are distinct configurations, which cannot be interconverted by simple rotation about bonds. The *tacticity* or stereoregularity of polymer molecules is of profound importance for the properties of materials. It affects the way in which adjacent molecules can fit together in the dense packing of the solid and hence controls the strength of forces between molecules from which the mechanical properties of the material spring. The commercial form of PP is isotactic; atactic PP has no useful properties as a solid engineering material (*see also* section 6.1).

Tacticity arises in all chain polymers in which atoms of the backbone carry two dissimilar atoms or groups. Thus commercial PS is atactic; PMMA is largely *syndiotactic*, that is, the configuration at the C atom carrying the side groups shows a regular alternation along the chain.

1.6 Other Hydrocarbon Polymers

There are several other important polymers which like PE and PP are based on

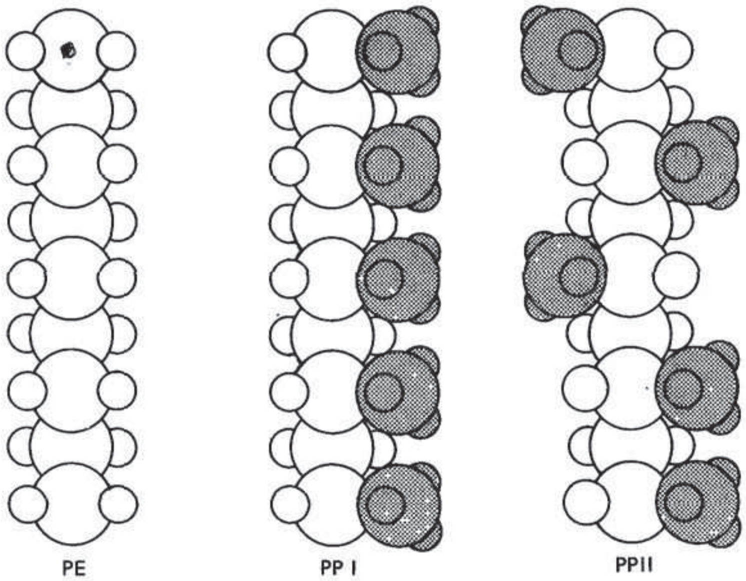


Figure 1.7 Relationship between the molecular structures of polyethylene (PE) and the isotactic (I) and atactic (II) forms of polypropylene (PP)

C—C linear chains and contain only C and H atoms. Table 1.3 shows that the structures can easily be understood by reference to PE.

1.7 Other Carbon Chain Polymers

Atoms of other elements may be incorporated into polymer structures (table 1.4). Substitution of H by chlorine Cl or fluorine F leads to several major polymers, PVC, PTFE, PVDC, PCTFE. The cyano group CN may similarly be incorporated, as in PAN. More complicated substituents composed of groupings of H, C and O atoms also occur, as in PMMA, PVAC, PVAL and others.

1.8 Heterochain Polymers

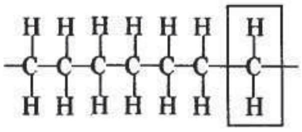
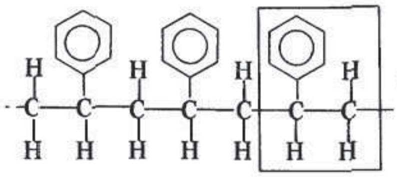
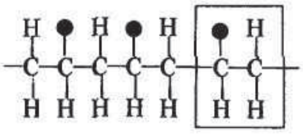
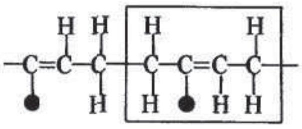
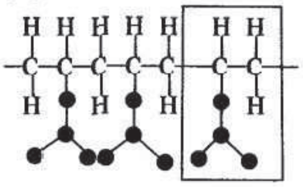
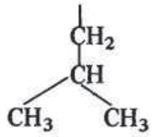
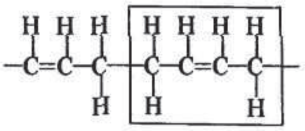
All the polymer chain structures listed in tables 1.3 and 1.4 are based on C chain backbones. The replacement of C atoms in the backbone itself by atoms of other elements produces *heterochain* polymers. A structurally simple heterochain polymer is polyoxymethylene (POM)

$$-CH_2-O-CH_2-O-CH_2-O-$$

which may be thought of as a PE chain in which O atoms replace alternate CH_2 groups. POM and closely related materials are important engineering plastics

TABLE 1.3

Some major hydrocarbon polymers

PE		
PS		 $-C_6H_5$
PP		 $-CH_3$
NR		 $-CH_3$
Polymethylpentene		 
BR		

(commonly known as acetals). Other heterochain polymers are listed in table 1.5 and include the PA group, the PUR group and PETP. Incorporating heteroatoms in the chain generates great structural diversity.

A number of *inorganic* polymers exists in which the backbone contains no carbon atoms at all. Pre-eminent amongst these are the polysiloxanes, linear Si—O polymers which have important properties of inertness and heat resistance.

TABLE 1.4

Some important carbon chain polymers

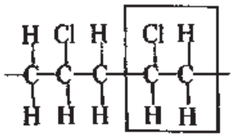
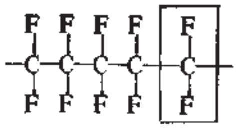
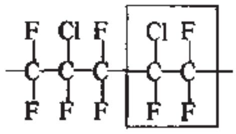
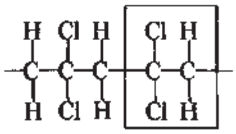
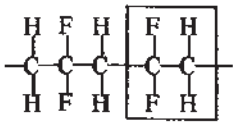
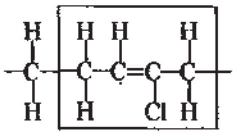
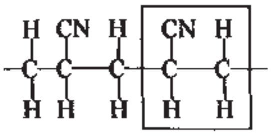
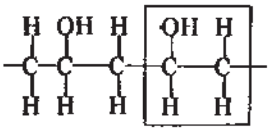
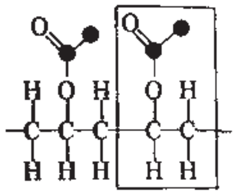
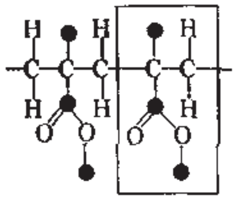
	PVC
	PTFE
	PCTFE
	PVDC
	PVDF
	CR
	PAN
	PVAL

TABLE 1.4 continued

	PVAC
	PMMA

1.9 Copolymers

Further types of polymer structure arise when two or more kinds of *mer* are mixed in a single polymer chain. For example, ethylene and propylene may be *copolymerised* to give a copolymer, which has properties somewhat different from the parent *homopolymers* PE and PP. To be able to describe the copolymer chain structure fully it is necessary to know how the two types of mer are arranged within the chain. Three possible distinct copolymer classes can be envisaged at once, and all three types are found among engineering polymer materials: the *alternating* copolymer, the *random* copolymer and the *block* copolymer.

The structures of these basic copolymer classes are shown schematically in table 1.6, together with the graft copolymer and the terpolymer.

1.10 Network Polymers

So far we have discussed polymers which have essentially linear molecular chains. Some branching may occur but it is limited, and the individual chain molecules are distinct and separable (by heat or solvent action) so that the materials we have listed are generally thermoplastics. As well as linear chain polymers there are materials with structures consisting of two- or three-dimensional networks of chemical bonds. Several materials with regular network structures lie on the

TABLE 1.5

Some important heterochain polymers

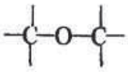
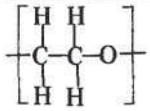
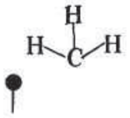
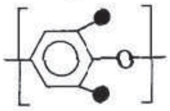
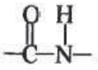
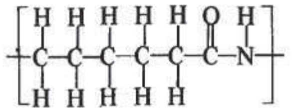
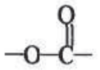
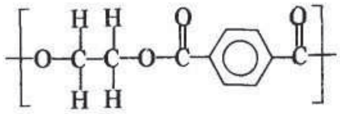
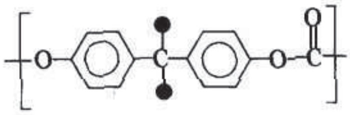
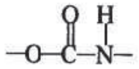
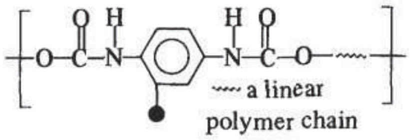
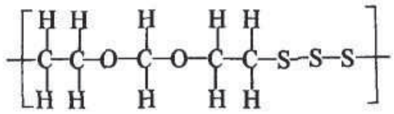
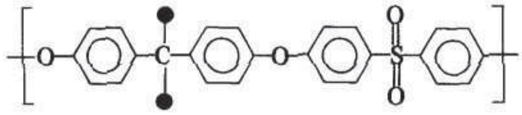
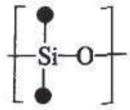
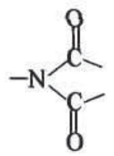
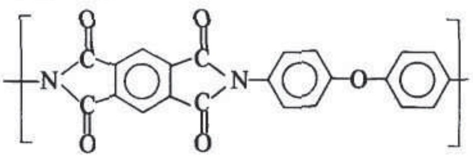
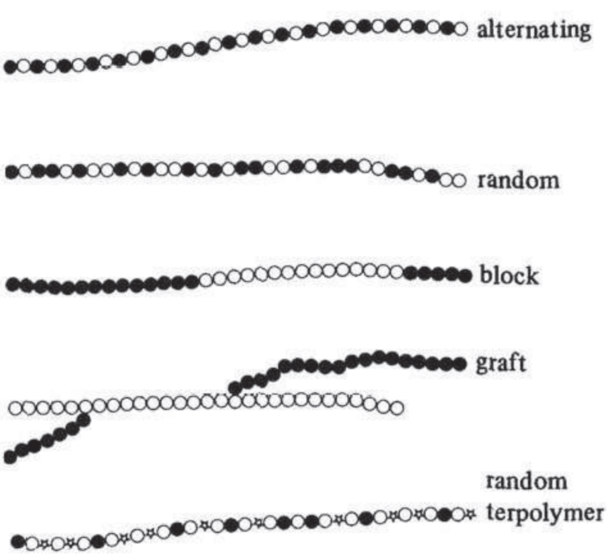
Type	*Characteristic chain group*	*Example*	
Polyether		PEO	 
		PPO	
Polyamide		PA6	
Polyester		PETP	
		PC	
Polyurethane			 ~~~ a linear polymer chain
Polysulphide	—C—S—S—		
Polysulphone			
Silicone (siloxane)	—Si—O—		
Polyimide			

TABLE 1.6
Classification of copolymers



borderline between polymers and ceramics (figure 1.8). For example, regular two-dimensional networks occur in graphite and boron nitride; diamond has a regular three-dimensional lattice. Many silicate minerals are based on polymeric *Si—O layer and lattice structures.*

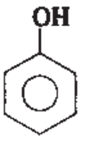
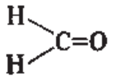
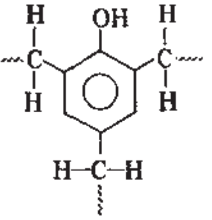
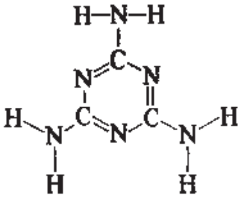
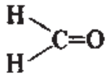
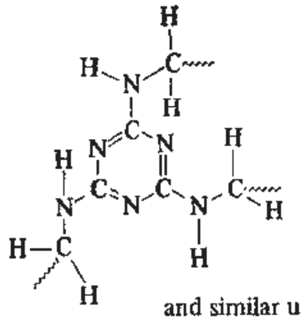
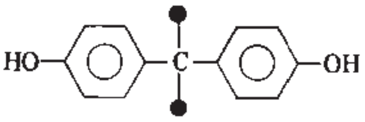
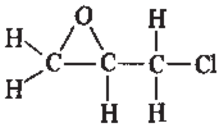
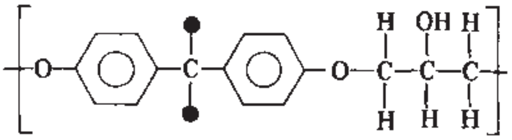
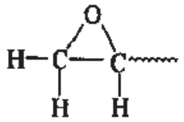
Most common network polymers are not regular in structure. Such materials are generally thermosets or elastomers, since the entire network is interconnected through primary chemical bonds and distinct, separable molecules do not exist. There are two principal types of network materials

(1) Those formed by the linking of linear chains by small molecules.

(2) Those formed by the direct reaction of small molecules (including short prepolymer chains) which give rise to chain-branching.

The first type includes many elastomers. For example, raw natural rubber is a hydrocarbon polymer, polyisoprene, which contains reactive C=C bonds. In vulcanising rubber, molecules of sulphur form crosslinks between C=C bonds on adjacent molecules. In a similar way, unsaturated polyesters UP can be crosslinked by molecules such as styrene to produce network polymers. The second type is represented by important thermosets such as PF, MF and EP (table 1.7). The structure of the polymerised material is highly complicated but figure 1.9(a) shows the type of network which is formed.

TABLE 1.7
Synthetic network polymers (thermosets)

Type	*Starting materials*	*Network polymer*
PF	 phenol  formaldehyde	 and similar units randomly connected by a variety of links
MF	 melamine  formaldehyde	 and similar units randomly connected by a variety of links
EP	 bisphenol A  epichlorhydrin	 crosslinked through terminal epoxy groups 

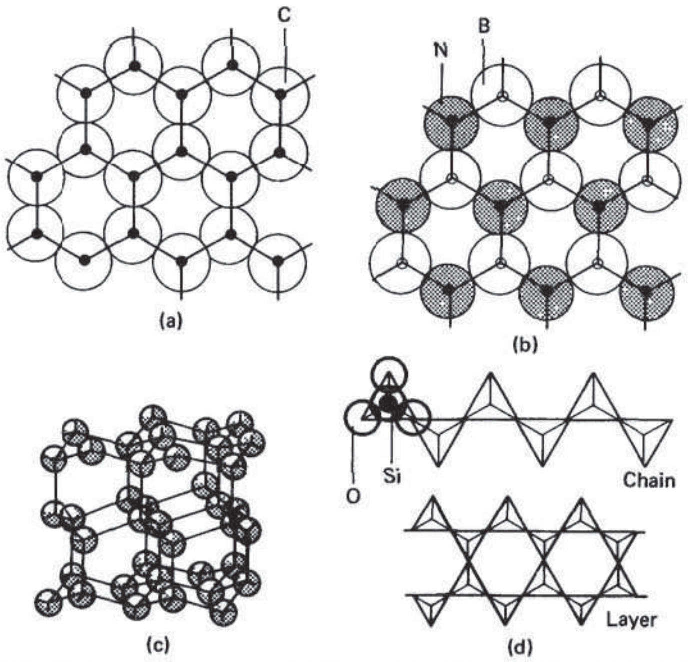


Figure 1.8 Polymeric structures in (a) graphite (sheets of interlinked hexagons, each formed of six carbon atoms); (b) boron nitride (graphite-like structure with boron and nitrogen atoms replacing carbon); (c) diamond (another form of carbon with a three-dimensional network of C—C bonds arranged tetrahedrally); and (d) chain and layer silicates based on the SiO_4 tetrahedron (including minerals such as asbestos and talc)

Crosslinking of polypeptide chains by covalent bonds occurs in many important protein biopolymers, notably in collagen (a main component of bone, tendon, cartilage and skin, and hence leather) and in keratin (feather, hair and horn). Few random branched polymers of the second type occur in biology, but one major example is lignin, the structural material which accompanies cellulose in woody plants – figure 1.9(b).

1.11 Primary Bonds and van der Waals' Forces

The polymer molecular structures we have described are more or less complicated arrangements of atoms held together by primary chemical bonds. Relatively few elements appear in the structures of the common polymers.

The principal chain building bonds are C—C, C—O and C—N; and C—H, C—F, C—Cl, C=O, O—H and N—H occur frequently, attached directly or indirectly to

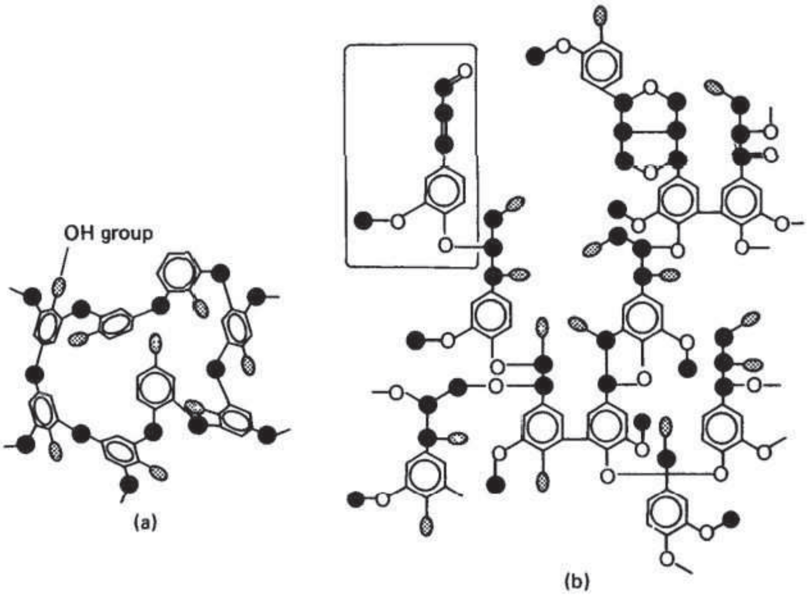


Figure 1.9 (a) Random network structure of a PF thermoset. (b) Proposed illustrative structure for lignin (Adler): random network polymer based on phenylpropane unit, top left

the chain backbone. All these chemical bonds are formed by rearranging valency electrons from the outer regions of the participating atoms into new spatial distributions which embrace both atoms. If the two atoms forming the bond are dissimilar (as in all those listed except C—C) the sharing of the valency electrons is unequal. The electron distribution is not symmetrical and the bond has a definite electrostatic polarity, which arises because one atom is able to draw electron charge more strongly to itself than the other. A measure of the electron-attracting power of an atom in a chemical bond is the *electronegativity* of the element, and the electronegativity difference of the two atoms of the bond is a good guide to bond polarity. The electronegativities of the main elements appearing in polymer materials are

C	2.5
H	2.1
N	3.0
O	3.5
F	4.0
Cl	3.5

The electronegativity differences for the bonds we have listed are

C—C	0	C—F	1.5
C—H	−0.4	C—Cl	1.0
C—O	1.0	O—H	1.4
C—N	0.5	N—H	0.9

Electronegativity differences of more than about 0.8 indicate a strongly developed bond polarity. Thus C—C and C—H are effectively nonpolar; but in C—O, C—F and C—Cl the carbon atoms are at the positive ends of polar bonds. In O—H and N—H, the hydrogen atoms are likewise situated at the positive ends of polar bonds.

All these primary chemical bonds, whether polar or not, are strong and stable, and the polymer molecules built from them can generally be broken down or modified only by the action of vigorous thermal or chemical forces. But in the solid or molten state, the individual polymer molecules lie close together, and the properties of the bulk material depend as much on the forces acting between the molecules as on the chemical bonds within them. What are the forces that operate between atoms which are in contact but not joined by primary chemical bonds? Collectively these secondary interactions are known as van der Waals' forces. Unlike primary chemical bonding, their operation does not involve sharing or transfer of electrons between atoms. The weakest of the interactions is a feeble force of attraction known as a dispersion force which exists between all atoms as the result of rapid fluctuations of the atomic electron distributions. The dispersion force between each pair of adjacent $-CH_2-$ mers on two polyethylene chains lying side by side is about 200 times weaker than the force acting within each C—H bond.

Somewhat stronger than the dispersion force is the van der Waals' force acting between suitably oriented polar bonds. A particularly strong and important type of polar force is the *hydrogen bond*, found in several synthetic polymer materials and widely in biopolymers. The hydrogen bond is formed between a markedly electronegative atom and a hydrogen atom already bonded to another electronegative atom – figure 1.10(a). Thus O—H . . . O hydrogen bonds occur in PVAL and cellulose. N—H . . . O hydrogen bonds are formed between PA molecules – figure 1.10(b), and in proteins, including the fibrous proteins such as wool keratin and silk fibroin. (N—H. . .O hydrogen bonds also link the two antiparallel macromolecular chains forming the double helix of DNA, so that the properties of the hydrogen bond lie at the roots of molecular biology). The strength of a hydrogen bond depends on the identity of the electronegative atoms involved and on their exact relation to other atoms, but it is often as great as one-tenth of the strength of a typical primary chemical bond. Hydrogen bonds are frequently sufficiently strong to survive the forces arising from molecular thermal motion at normal temperatures. We return to the role of intermolecular forces in polymer materials in chapter 2.

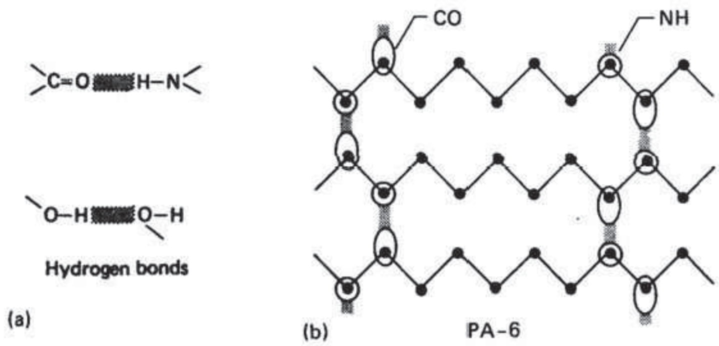


Figure 1.10 The hydrogen bond. (a) O–H. . .O and N–H. . .O hydrogen bonds. (b) H-bond formation between extended PA- 6 chains; similar hydrogen bonds occur in other polyamides

1.12 Polymer Synthesis: Chain Reaction Polymerisation

We conclude this chapter with a brief survey of the chemical reactions in which polymer chains are formed from substances of low molar mass. The treatment is brief because polymer synthesis is a somewhat specialised topic for the polymer chemist and the chemical engineer. A fuller discussion would call for a greater knowledge of the principles of chemical reactivity on the part of the reader than has been assumed. Many excellent texts on polymerisation chemistry are available, and several are listed at the end of the chapter.

In the first laboratory synthesis of polyethylene the hydrocarbon gas ethylene (ethene) was heated to 170 °C at a pressure of 1300 bar. The white solid formed in the reaction vessel was rapidly and correctly identified as a polymer of ethylene. The ethylene had reacted according to the equation

$$n/2\ \mathrm{C_2H_4} \longrightarrow \left(\mathrm{CH_2}\right)_n$$

This is an example of one of the two major classes of polymerisation reaction, the *addition polymerisation*, which may be written more generally

$$n\mathrm{M} \longrightarrow \mathrm{M}_n$$

In addition reactions the polymer is the sole product of the reaction. Addition polymerisation almost invariably occurs by a *chain reaction* mechanism, frequently involving free radicals. Such reactions, which are of great industrial importance, proceed according to the following scheme

$$\begin{array}{ll}
\mathrm{I} \longrightarrow 2\mathrm{R}\cdot & \text{initiation} \\
\mathrm{R}\cdot + \mathrm{M} \longrightarrow \mathrm{RM}\cdot & \text{propagation} \\
\mathrm{RM}\cdot + \mathrm{M} \longrightarrow \mathrm{RMM}\cdot & \text{etc.} \\
\mathrm{RM}\sim\sim\mathrm{M}\cdot + \mathrm{RM}\sim\sim\mathrm{M}\cdot \rightarrow & \mathrm{RM}\sim\sim\mathrm{MM}\sim\sim\mathrm{MR} \\
 & \text{termination}
\end{array}$$

An initiator molecule breaks down to give free radicals R•, highly reactive chemical species which attack monomer molecules to yield products RM•, etc., which are themselves free radicals. The reactivity of the initiating free radical is therefore preserved, and further attack on a monomer molecule occurs to add a further unit to the chain. This process continues (*propagation*), the growing chain with a free radical at one end scavenging the reaction medium for monomers. The process comes to a halt only if the supply of monomer is exhausted or if free radicals combine together to *terminate* the chain reaction. The latter process is usually statistically improbable so long as the supply of monomer is maintained, for the radicals are present in only minute quantities.

The mechanism of a free radical chain reaction may be illustrated by the example of the polymerisation of vinyl chloride. A variety of initiators may be used, for example lauroyl peroxide

$$\text{Initiator I} \longrightarrow 2\text{R}\cdot$$

$$\text{R}{-}(\text{CH}_2{-}\text{CHCl})_n{-}\text{CH}_2{-}\dot{\text{C}}\text{HCl} + \text{CH}_2{=}\text{CHCl}$$

$$\longrightarrow \text{R}{-}(\text{CH}_2{-}\text{CHCl})_{n+1}{-}\text{CH}_2{-}\dot{\text{C}}\text{HCl} \qquad \text{etc.}$$

Propagation

$$\text{R}{-}(\text{CH}_2{-}\text{CHCl})_n{-}\text{CH}_2{-}\dot{\text{C}}\text{HCl}$$

$$+\ \text{R}{-}(\text{CH}_2{-}\text{CHCl})_m{-}\text{CH}_2{-}\dot{\text{C}}\text{HCl}$$

$$\downarrow$$

$$\text{R}{-}(\text{CH}_2{-}\text{CHCl})_n{-}\text{CH}_2{-}\text{CHCl}{-}\text{CHCl}{-}\text{CH}_2{-}(\text{CHCl}{-}\text{CH}_2)_m{-}\text{R}$$

Combination termination

$$\downarrow$$

$$\text{R}{-}(\text{CH}_2{-}\text{CHCl})_n{-}\text{CH}{=}\text{CHCl} + \text{R}{-}(\text{CH}_2{-}\text{CHCl})_m{-}\text{CH}_2{-}\text{CH}_2\text{Cl}$$

Disproportionation termination

Each initiator is responsible for the formation of one polymer chain. The rate of growth of a chain is roughly constant as it is largely determined by chemical factors which change little as propagation proceeds. Towards the end of the reaction the rate of polymerisation may be affected by depletion of monomer and by an increase in viscosity caused by the accumulation of the long polymer chains themselves.

Once initiated, polymer chains usually grow very rapidly until a chain termination occurs and growth abruptly ceases. The average final length of the chain depends on the relative probabilities of propagation and termination. As the bulk reaction proceeds, the number of polymer chains increases steadily, but the average length of the chains is roughly constant. These features of chain growth polymerisation reactions may be contrasted with the characteristics of the step reactions described below.

The high reactivity of the free radical species (both the initiators themselves and the active centre on the growing chain) means that there is often a tendency for side reactions to occur. These side reactions may influence the degree of polymerisation which occurs in a practical synthesis, as well as the molar mass distribution of the product.

Free radicals are not the only reactive chemical substances which can act as initiators in chain polymerisations. The active centre in the propagating polymer may be an ion rather than a free radical. Generally the character of the polymerisation is similar to that described above. One class of such reactions is especially important because the tacticity or stereoregularity of the polymer product is controlled. Stereospecific polymerisations can be achieved by using a wide variety of reactive initiators and catalysts, particularly the *Ziegler–Natta catalysts.*

In order to produce a stereoregular polymer such as isotactic polypropylene the orientation of the monomer molecule has to be firmly controlled at the point at which it is added to the growing chain. Ziegler–Natta catalysts achieve this by pinning the active end of the chain to the solid catalyst surface throughout the polymerisation. This restricts the direction of approach of the incoming monomer and orients it in relation to the chain.

Ziegler–Natta catalysts (of which very many variants exist, see figure 1.11) have made it possible to synthesise several stereoregular polymers of commercial importance, particularly PP and the rubbers polyisoprene (IR) and polybutadiene (BR). Ziegler catalysts are also used in low pressure processes to produce the linear form of PE known as high density polyethylene (HDPE). Karl Ziegler and Giulio Natta shared the 1963 Nobel Prize for chemistry for their work on stereoregular polymerisation. Other important low pressure catalytic routes to HDPE have subsequently been introduced by Phillips Petroleum and Standard Oil of Indiana.

1.13 Step Reaction Polymerisation

The second major class of polymerisation reaction, the condensation reaction occurring by a step reaction mechanism, may be illustrated by the formation of the polyamide from an amino acid

$$n\mathrm{NH_2(CH_2)_{10}CO_2H} \longrightarrow \mathrm{+\!NH(CH_2)_{10}CO\!+}_n + (n-1)\mathrm{H_2O}$$

Condensation polymerisations have the following general form

$$n\mathrm{MN} + n\mathrm{PQ} \longrightarrow (\mathrm{MP})_n + n\mathrm{NQ}$$

MN and PQ may be the same, as in the example given, or may be different. Thus polyamides are often formed by the condensation of a diacid and a diamine,

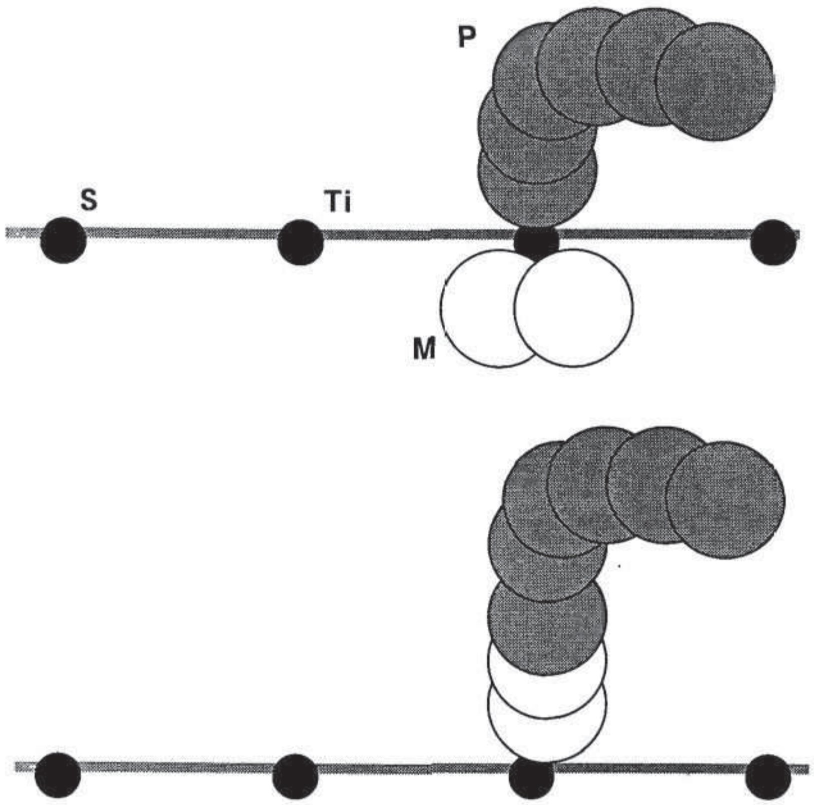


Figure 1.11 A typical high-activity Ziegler-Natta catalyst is made by reaction of titanium tetrachloride, magnesium chloride and triethylaluminium, forming a solid catalyst surface S. A free monomer molecule M bonds briefly to a titanium ion Ti exposed at the catalyst surface and to which the end of the growing polymer chain P is already attached. A spontaneous and rapid rearrangement of chemical bonds then occurs to insert the monomer into the chain. The polymerisation continues until a termination reaction eventually intervenes. It is the geometry of the active site on the catalyst surface which provides the remarkable steric control as the polymer chain grows. The configuration of the catalytic site, acting as a template, ensures that each successive reacting monomer is identically oriented in relation to the end of the polymer chain

for example

$$n\mathrm{H_2N(CH_2)_6NH_2} + n\mathrm{HO_2C(CH_2)_4CO_2H} \longrightarrow$$
$$\mathrm{H{+}NH(CH_2)_6NHCO(CH_2)_4CO{+}}_n\mathrm{OH} + (2n-1)\mathrm{H_2O}$$

This necessarily generates an alternating copolymer, although the product is not usually so regarded. The polymer itself is not the sole product of a condensation polymerisation, a major point of difference between addition and condensation reactions. In the examples above, one molecule of water (H_2O) is formed for every pair of reactant molecules which combine. The term 'condensation' is used generally in organic chemistry to refer to reactions in which molecules combine together through the elimination of a small molecule such as water.

There are several contrasts between step and chain polymerisation reactions. Step reaction monomers do not require activation by an initiator but are intrinsically reactive. Since initiation is not required, all monomers present at the start of the reaction have an equal chance of reacting. In the early stages of the reaction, monomers combine to form short chains. Since the rate of these step reactions is typically much slower than the rate of the propagation stage in chain reactions, long chains do not develop at all in the early stages. As the amount of free monomer in the system diminishes, the step reaction occurs increasingly between functional groups on the ends of chains. As the reaction progresses, there is an increase in the average chain length from initially low values to ultimately large values. To obtain very long chains it is necessary that the step reactions should proceed almost to completion. It is in the last stages of the reaction when links are being forged between already well-developed chains that the average chain length rises most rapidly.

The mechanisms and kinetics of polymerisation reactions were intensively investigated in the period from about 1928 until the 1950s, culminating in 1953 in the publication of Paul Flory's book, *The Principles of Polymer Chemistry*, one of the classic works of polymer science. Flory received the Nobel prize in 1974, the fourth and most recent Nobel award in the field of synthetic polymers. The standard theory of polymerisation provides a quantitative description of both step and chain reactions. In particular, it successfully predicts the way in which the rates of polymerisation reactions depend on the concentrations of reacting monomers and how the distributions of chain lengths alter during the course of these reactions. This understanding of course is essential to the design of all industrial polymer syntheses.

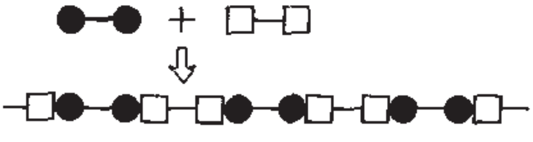
1.14 *Thermoset Polymerisation*

If one of the reacting substances in a step polymerisation possesses more than two functional groups, then the reaction will lead naturally to branched structures (table 1.8). As these intercombine, random three-dimensional networks are developed. Ultimately the network extends throughout the mass of polymerised material, which therefore in effect constitutes a single giant molecule. Such structures are by their very nature incapable of melting or of truly dissolving. Polymer materials of this type are called *thermosets*, since once produced they cannot be returned to a fluid condition by heating. Important

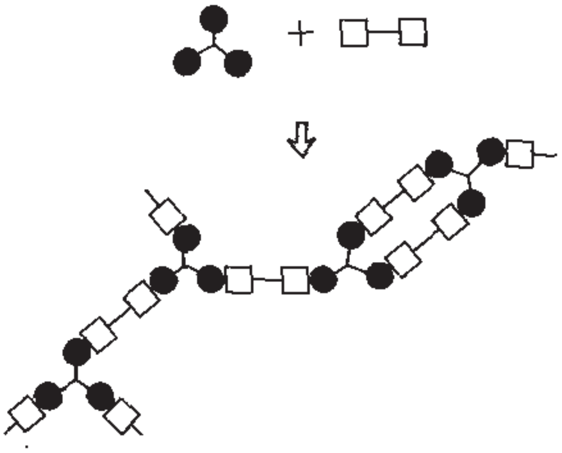
TABLE 1.8

Formation of linear and branched chains

Linear chain formation:



Branched chain (network polymer) formation:



examples are the phenolic and amino resins. Similar thermoset network structures may be formed by crosslinking linear chains in a second post-polymerisation or 'curing' reaction, which may be free radical initiated. Tables 1.9 and 1.10 show how thermosets derived from unsaturated polyesters and epoxides are produced by two-stage reactions – curing following resin (prepolymer) formation. The irreversibility of set (and, frequently, stiffness and good resistance to heat) underlies the great technical value of thermosets, notably as adhesives and as the bonding component of fibre-reinforced and mineral-filled composite materials. A number of important surface-coating polymers (notably polyurethanes and alkyds) are thermosets.

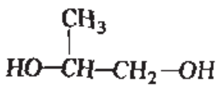
1.15 Polymerisation Conditions

We have mentioned earlier that such important properties of the polymer product as chain length (and its distribution) and stereoregularity are determined by details of the synthetic method employed. Other variables which we have not

TABLE 1.9

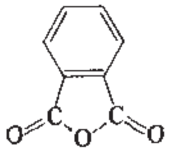
Preparation and curing of unsaturated polyesters

Typical starting materials:

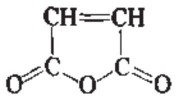


$HO-CH(CH_3)-CH_2-OH$

propylene glycol



phthalic anhydride

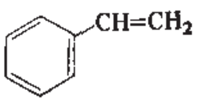


maleic anhydride

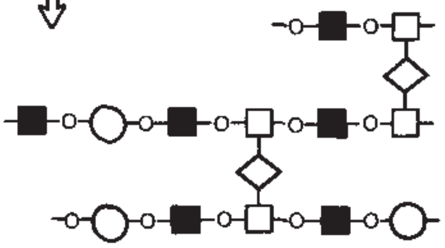
We represent these molecules by the symbols

Polymerisation produces a linear unsaturated polyester with a structure like this:

The addition of a vinyl monomer such as styrene makes a liquid resin which can be crosslinked by a free-radical initiator (*curing agent*)



styrene

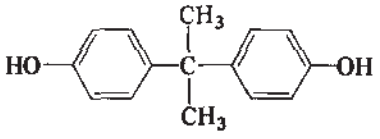


Schematic crosslinked polyester structure

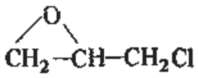
TABLE 1.10

Preparation and crosslinking of an epoxy resin

Starting materials:

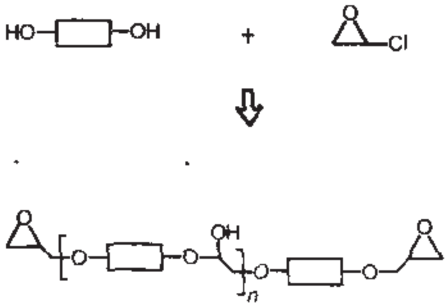


phenol (bisphenol A)



$CH_2-CH-CH_2Cl$ (with O bridging CH_2 and CH)

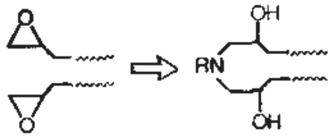
epoxide (epichlorhydrin)



$n = 1–12$

Crosslinking occurs through the terminal epoxy groups:

Crosslinking agent,
e.g. amine RNH_2



discussed are important determinants of the product as well – parameters such as temperature, pressure and the concentrations of the reactants and catalysts. On both the industrial and the laboratory scale the polymerisation conditions may be chosen in order to optimise the product for certain properties. Consider the commercial processes for the production of PS and its copolymers.

The monomer styrene is a liquid which boils at 146 °C. Addition of an initiator to a batch of pure styrene starts polymerisation of the entire mass of liquid. Styrene acts as a solvent for the PS formed. As polymerisation proceeds, the viscosity of the system rises steeply. This may interfere with heat loss to the walls of the reaction vessel (usually assisted by stirring) and cause local hot spots to develop. In these regions the reaction occurs in an uncontrolled fashion and this may give rise to undesirable changes in the quality of the product. This method of producing PS is an example of a *bulk polymerisation* operated batchwise. It has some commercial application in the production of PS in block form in special reactors designed for efficient heat removal. Since the monomer is used in pure form the product is of high purity. Bulk polymerisation of styrene is more commonly carried out in flow reactors which receive unpolymerised styrene feed at about 100 °C. Polymerisation occurs as the styrene passes through the reactor, and to control the rising viscosity the temperature is increased steadily to about 200 °C at the PS outlet. (Polymers are not invariably soluble in their monomers; for example, the bulk polymerisation of PVC leads to precipitation of polymer as the reaction progresses.)

A solvent such as ethylbenzene may be added to the styrene feed, converting the bulk process to a *solution polymerisation.* Commercial processes for the solution polymerisation of PS or copolymers such as SAN use only small amounts of solvent. Solution processes are used in producing many polymers, since good control of viscosity and heat transfer can be obtained. The polymer product may be either soluble or insoluble in the selected solvent. It is necessary to remove the solvent to obtain the pure polymer but this is often difficult to do completely. If the polymer is insoluble in the solvent, it is precipitated as it is formed. Such methods lend themselves to continuous production processes, for the solid polymer can be continuously removed from the reaction medium and the monomer and initiator replenished. However, the presence of large amounts of solvent increases the risk of side reactions, such as chain transfer, which prematurely terminate chain growth – a factor which influences the choice of solvent.

Two principal alternatives to the single-phase polymerisations exist. Styrene is not appreciably soluble in water. A mechanically agitated mixture of water and styrene (2 + 1) forms a dispersion of styrene droplets in water, which may be stabilised by a small amount of a colloidal additive. In the *suspension* process, initiator is added and polymerisation begins within each droplet, eventually forming a water–polymer slurry (or suspension), from which PS may easily be recovered, for example by centrifugation.

Emulsion polymerisation resembles suspension polymerisation in several ways. Both are heterophase processes in which the monomer and polymer are dispersed in water. In the emulsion process, however, polymerisation occurs not in the monomer disperse phase but in microscopic clusters or *micelles* of soap molecules in the aqueous phase. The micelles and the solid polymer particles to which they give rise are several orders of magnitude smaller than the particles formed in suspension polymerisation.

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