1

Structure of Polymers

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The mechanical properties that form the subject of this book are a consequence of the chemical composition of the polymer and also of its structure at the molecular and supermolecular levels. We shall therefore introduce a few elementary ideas concerning these aspects.

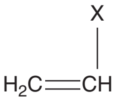
1.1 Chemical Composition

1.1.1 Polymerization

Linear polymers consist of long molecular chains of covalently bonded atoms, each chain being a repetition of much smaller chemical units. One of the simplest polymers is polyethylene, which is an addition polymer made by polymerizing the monomer ethylene, $CH_2{=}CH_2$, to form the polymer.

$$-\!\!\left[CH_2 - CH_2 \right]_n\!\!-$$

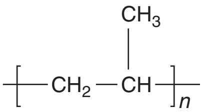
Note that the double bond is removed during the polymerization (Figure 1.1). The well-known vinyl polymers are made by polymerizing compounds of the form



$$H_2C{=}\overset{\displaystyle X \atop |}{CH}$$

where X represents a chemical group; examples are as follows:

Polypropylene



$$-\!\!\left[CH_2 - \overset{\displaystyle CH_3 \atop |}{CH} \right]_n\!\!-$$

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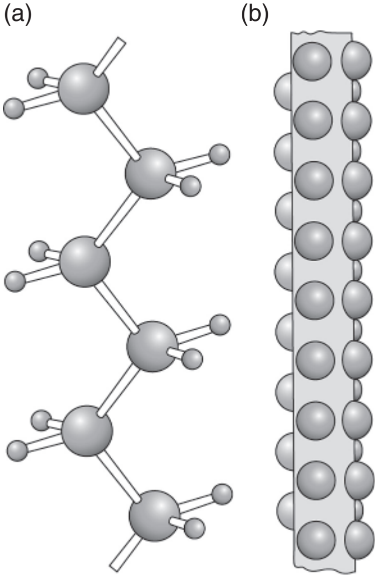
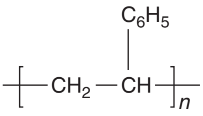


Figure 1.1 (a) The polyethylene chain $(CH_2)_n$ in schematic form (larger spheres, carbon; smaller spheres, hydrogen) and (b) sketch of a molecular model of a polyethylene chain.

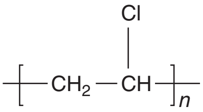
Polystyrene



$$\left[CH_2 - \overset{C_6H_5}{\overset{|}{CH}} \right]_n$$

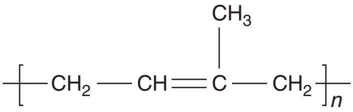
and

poly(vinyl chloride)



$$\left[CH_2 - \overset{Cl}{\overset{|}{CH}} \right]_n$$

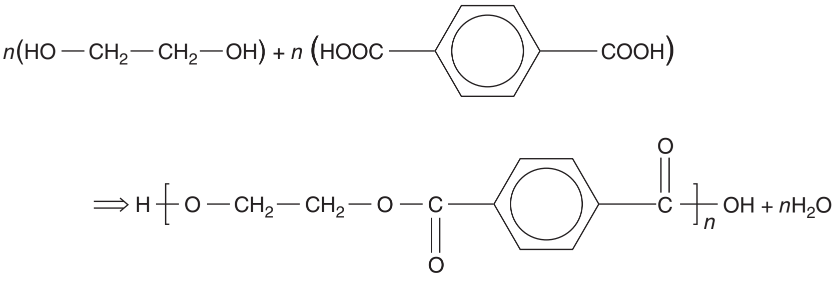
Natural rubber, polyisoprene, is a diene, and its repeat unit



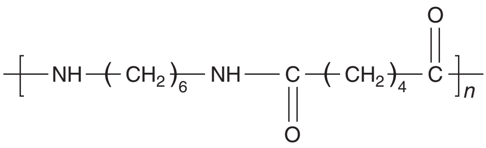
$$\left[CH_2 - CH = \overset{CH_3}{\overset{|}{C}} - CH_2 \right]_n$$

contains a double bond.

A condensation reaction is one in which two or more molecules combine into a larger molecule with or without the loss of a small molecule (such as water). One example is the formation of polyethylene terephthalate (the polyester used for terylene and Dacron fibres and transparent films and bottles) from ethylene glycol and terephthalic acid:



Another common condensation polymer is nylon 6,6.



$$\left[NH - (CH_2)_6 - NH - \underset{O}{\underset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} \right]_n$$

1.1.2 Cross-Linking and Chain-Branching

Linear polymers can be joined by other chains at points along their length to make a cross-linked structure (Figure 1.2). Chemical cross-linking produces a thermosetting polymer, so called because the cross-linking agent is normally activated by heating, after which the material does not soften and melt when heated further, for example Bakelite and epoxy resins. A small amount of cross-linking through sulphur bonds is needed to give natural rubber its characteristic feature of rapid recovery from a large extension.

Very long molecules in linear polymers can entangle to form temporary physical cross-links, and we shall show later that a number of the characteristic properties of solid polymers are explicable in terms of the behaviour of a deformed network.

A less extreme complication is chain-branching, where a secondary chain initiates from a point on the main chain, as is illustrated for polyethylene in Figure 1.3. Low-density

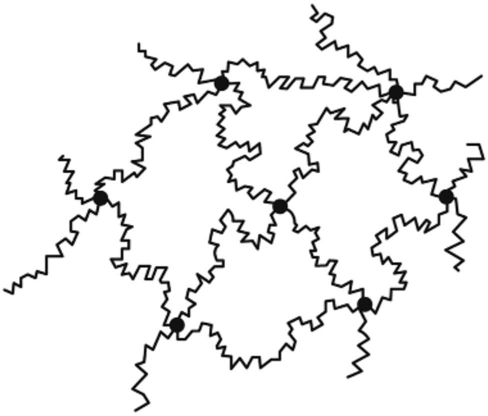


Figure 1.2 Schematic diagram of a cross-linked polymer.

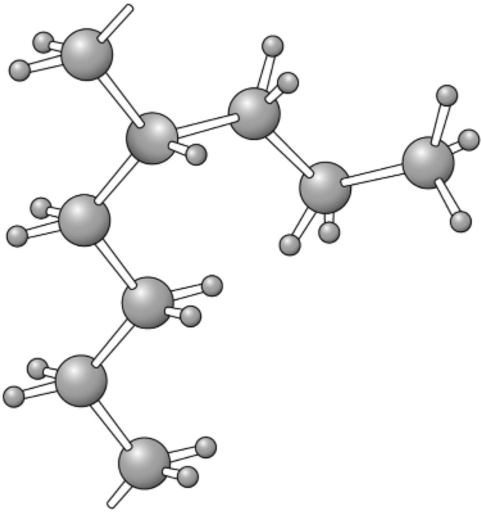


Figure 1.3 A chain branch in polyethylene.

polyethylene, as distinct from the high-density linear polyethylene shown in Figure 1.1, possesses on average one long branch per molecule and a larger number of small branches, mainly ethyl ($—CH_2—CH_3$) or butyl ($—(CH_2)_3—CH_3$) side groups. The presence of these branch points leads to considerable differences in mechanical behaviour compared with linear polyethylene.

1.1.3 Average Molecular Mass and Molecular Mass Distribution

Each sample of a polymer contains molecular chains of varying lengths, that is of varying molecular mass (Figure 1.4). The mass (length) distribution is of importance in determining the properties of the polymer, but until the advent of gel permeation chromatography (Vaughan 1960; Moore 1964), it could be determined only by tedious fractionation procedures. Most investigations therefore quoted different types of average molecular mass, the commonest being the number average $\overline{M}_n$ and the weight average $\overline{M}_n$, defined as

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} \qquad \overline{M}_w = \frac{\sum (N_i M_i) M_i}{\sum N_i M_i},$$

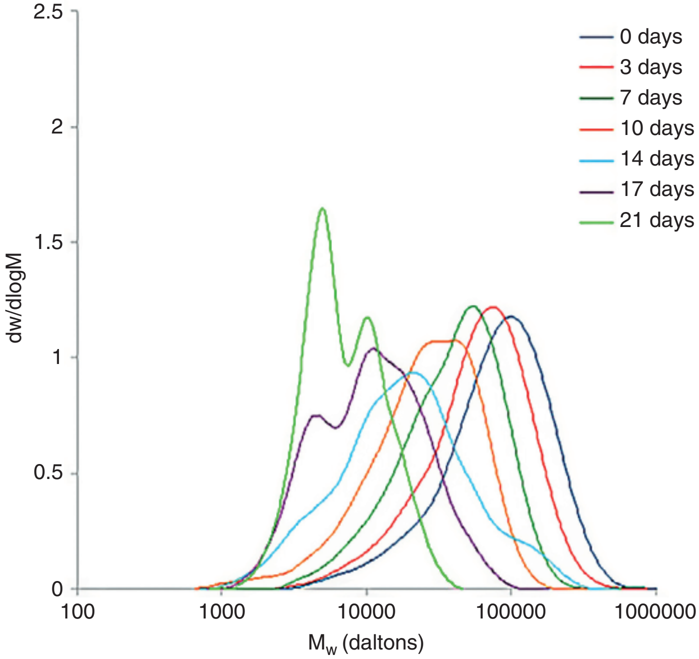


Figure 1.4 The gel permeation chromatograph traces give a direct indication of the molecular mass distribution. Results are for polylactic acid (PLA) undergoing degradation for periods up to 21 days; note the generally decreasing molecular mass with time. Stloukl et al., 2016 / with permission of Elsevier.

where N_i is the number of molecules of molecular mass M_i and Σ denotes summation over all i molecular masses.

The weight average molecular mass is always higher than the number average, as the former is strongly influenced by the relatively small number of very long (massive) molecules. The ratio of the two averages gives a general idea of the width of the molecular mass distribution.

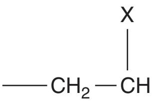
Fundamental measurements of average molecular mass must be performed on solutions so dilute that intermolecular interactions can be ignored or compensated for. The commonest techniques are osmotic pressure for the number average and light scattering for the weight average. Both methods are rather lengthy, so in practice an average molecular mass was often deduced from viscosity measurements of either a dilute solution of the polymer (which relates to M_n) or a polymer melt (which relates to M_w). Each method yielded a different average value, which made it difficult to correlate specimens characterized by different groups of workers.

The molecular mass distribution is important in determining flow properties and so may affect the mechanical properties of a solid polymer indirectly by influencing the final physical state. Direct correlations of molecular mass to viscoelastic behaviour and brittle strength have also been obtained.

1.1.4 Chemical and Steric Isomerism and Stereoregularity

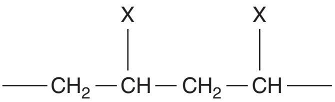
A further complication of the chemical structure of polymers lies in the possibility of different chemical isomeric forms within a repeat unit or between a series of repeat units. Both natural rubber and gutta percha are chemically polyisoprene, but the former is the *cis* form and the latter is the *trans* form (see Figure 1.5). The characteristic properties of rubber are a consequence of the loose packing of molecules (i.e. large *free volume*) that arises from its structure.

Vinyl monomer units



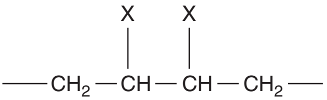
$$-CH_2-\overset{\overset{X}{|}}{CH}$$

can be added to a growing chain either head-to-tail:

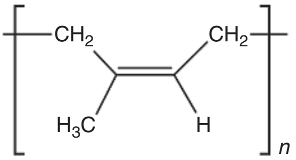


$$-CH_2-\overset{\overset{X}{|}}{CH}-CH_2-\overset{\overset{X}{|}}{CH}-$$

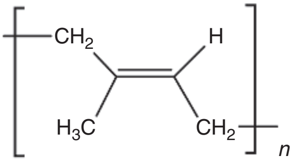
or head-to-head:



$$-CH_2-\overset{\overset{X}{|}}{CH}-\overset{\overset{X}{|}}{CH}-CH_2-$$



cis-1,4 Polyisoprene



trans-1,4 Polyisoprene

Figure 1.5 cis-1,4-Polyisoprene and trans-1,4-polyisoprene.

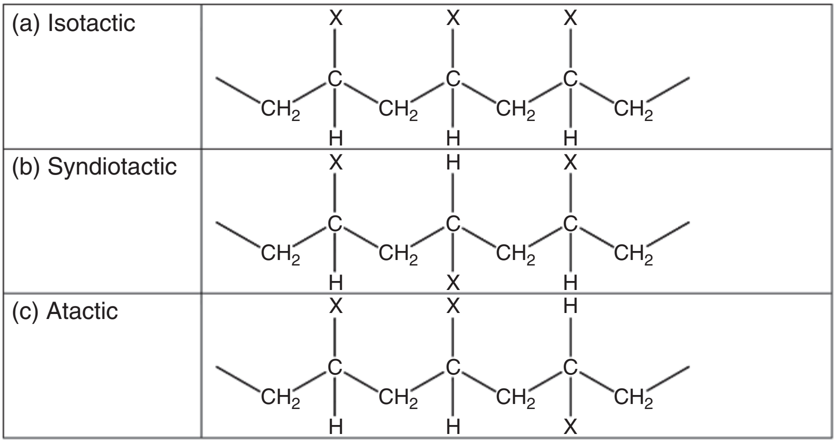


Figure 1.6 A substituted α-olefin can take three stereosubstituted forms.

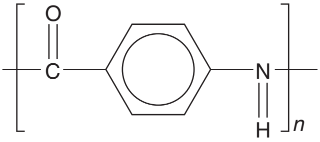
Head-to-tail substitution is usual, and only a small proportion of head-to-head linkages can produce a reduction in the tensile strength because of the loss of regularity.

Stereoregularity provides a more complex situation, which we will examine in terms of the simplest type of vinyl polymer (Figure 1.6) and for which we shall suppose that the polymer chain is a planar zigzag. Two very simple regular polymers can be constructed. In the first (Figure 1.6(a)) the substituent groups are all added in an identical manner to give an *isotactic* polymer. In the second regular polymer (Figure 1.6(b)) there is an inversion of the manner of substitution between consecutive units, giving a *syndiotactic* polymer for which the substituent groups alternate regularly on opposite sides of the chain. The regular sequence of units is called *stereoregularity*, and stereoregular polymers are crystalline and can possess high melting temperatures. The working range of a polymer is thereby extended compared with the amorphous atactic form, whose range is limited by the lower softening point. The final alternative structure is formed when the orientation of successive substituents takes place randomly (Figure 1.6(c)) to give an irregular *atactic* polymer that is incapable of crystallizing. Polypropylene $(\text{—}CH_2CHCH_3\text{—})_n$ was for many years obtainable only as an atactic polymer, and its widespread use began only when stereospecific catalysts were developed to produce the isotactic form. Even so, some faulty substitution occurs and atactic chains can be separated from the rest of the polymer by solvent extraction.

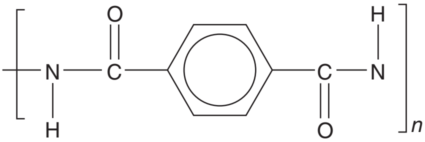
1.1.5 Liquid Crystalline Polymers

Liquid crystals (or plastic crystals as they are sometimes called) are materials that show molecular alignment in one direction but not three-dimensional crystalline order. During the last 20 years, liquid crystalline polymers have been developed where the polymer chains are so straight and rigid that small regions of almost uniform orientation (domains) separated by distinct boundaries are produced. In the case where these domains occur in solution, polymers are termed *lyotropic*. Where the domains occur in the melt, the polymers are termed *thermotropic*.

An important class of lyotropic liquid crystal polymers are the aramid polymers such as polyparabenzamide

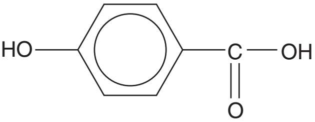


and polyparaphenylene terephthalamide

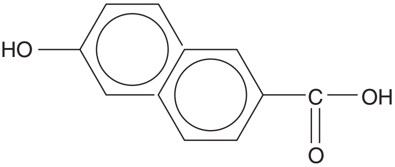


better known as Kevlar, which is a commercially produced high stiffness and high strength fibre. It is important to emphasize that although Kevlar fibres are prepared by spinning a lyotropic liquid crystalline phase, the final fibre shows clear evidence of three-dimensional order.

Important examples of thermotropic liquid crystalline polymers are copolyesters produced by condensation of hydroxybenzoic acid (HBA)



and 2,6-hydroxynaphthoic acid (HNA)



most usually in the proportions HBA:HNA = 73:27.

In addition to these main-chain liquid crystalline polymers, there are also side-chain liquid crystalline polymers, where the liquid crystalline nature arises from the presence of rigid straight side-chain units (called the mesogens) chemically linked to an existing polymer backbone either directly or via flexible spacer units.

The review by Noël and Navard (1991) gives further information on liquid crystalline polymers, including methods of preparation.

1.1.6 Naturally Occurring Polymers

While a significant number of published works and interest over the last 90 years (since polyethylene was invented in 1933) have concentrated on what are termed synthetic

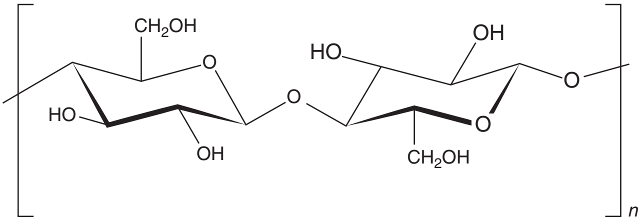


Figure 1.7 The chemical structure of cellulose.

polymers, there is also another class of polymers which are termed natural polymers. These are defined as being found naturally in the environment and produced via a biological process, as opposed to the synthetic polymers that are human created. This class of natural polymers includes two major groups: polysaccharides (long-chain carbohydrate-based molecules) such as cellulose and starch; and proteins (based on amino acids) such as keratin (wool, leather), silk and collagen. The renewed interest in these natural polymers (which were used long before synthetic polymers were invented – for example cotton and paper) comes from their combination of deriving from renewable sources, biocompatibility and their ability to biodegrade (in contrast to most synthetic polymers). Hence these natural polymers are finding increasingly wide usage in a range of fields such as construction, biomedical and general engineering (automotive, etc.).

Of all the naturally produced polymers, cellulose is the most abundant and most widely used. Cellulose is the main structural component of all plant walls and so forms a major part of the world's biomass. The repeat unit of cellulose is shown in Figure 1.7 and comprises two glucose monomers linked by an oxygen atom which is termed a glycosidic linkage. For each repeat unit, one glucose unit is rotated by 180° leading to a straight linear chain when these are connected together by nature to form a natural polymer.

An important aspect is that the cellulose chains form a dense network of hydrogen bonds (both intramolecular and intermolecular) which then allows the molecules to stack and form strong and stiff meso-structures (with a significant crystallinity) that are resistant to most solvents. The hydrogen bond network has the result that cellulose polymer does not melt like a synthetic thermoplastic polymer, and so chemical process is required if further processing is necessary, but giving excellent temperature resistance.

A further subset of natural cellulosic polymers is termed semi-synthetic natural polymers which are formed by the chemical modification of cellulose. In these polymers, acid treatment substitutes some or all of the OH groups of cellulose, leading to increased solubility and thermal processing depending on the level of substitution. Two important polymers resulting from this are cellulose acetate (from treating natural cellulose with acetic acid) and cellulose nitrate (by treating with nitric acid).

1.1.7 Polymers from Renewable Sources

A third group of polymers that fits between the two groups of synthetic and naturally occurring polymers are those that are human produced but derived from renewable biomass sources such as sugar cane or corn starch; these are often termed biopolymers. Poly lactic acid (PLA) is one of the most common of these and is currently the most widely used polymer made from biomass.

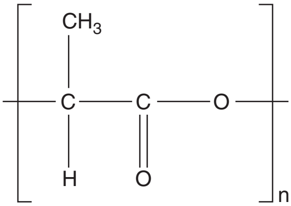


Figure 1.8 The chemical structure of poly lactic acid.

PLA is a linear thermoplastic polyester with a repeat unit as shown in Figure 1.8. It has a glass transition temperature around 60°C and a melting temperature around 160°C. PLA refers to a family of polymers with differing isomeric forms. PLLA is a polymer of L-lactide and PDLA is a polymer of D-lactide, and there is a co-polymer form PLDLA and other variations. PLAs are biocompatible and degrade hydrolytically, i.e. in response to the ingress of water molecules; PLLA is semi-crystalline and therefore least permeable to water and less degradable than the effectively amorphous PLDA and PLDLA. These characteristics have resulted in the widespread use of PLAs in medical applications, such as implants (pins, screws, plates, etc.), due to the ability to degrade over the timescale of a year. It is non-toxic and biocompatible with good mechanical properties at body temperature. They are also used to make disposable items such as drinking cups, as they are biodegradable. However, this capability is only realized via an industrial composting process, and if released into the environment PLA may persist over decades and form microparticles in seawater (Haider et al. 2019).

1.1.8 Blends, Grafts and Copolymers

A *blend* is a physical mixture of two or more polymers. A *graft* is formed when long side chains of a second polymer are chemically attached to the base polymer. A *copolymer* is formed when chemical combination exists in the main chain between two or more polymers, $_n$, $[B]_n$ and so on. The two principal forms are block copolymers ([AAAA. . .] [BBB. . .]) and *random* copolymers, the latter having no long sequences of A or B units.

All these processes are commonly used to enhance the ductility and toughness of brittle homopolymers or increase the stiffness of rubbery polymers. An example of a blend is acrylonitrile–butadiene–styrene copolymer (ABS), where the separate rubber phase gives much improved impact resistance.

The basic properties of polymers may be enhanced by physical as well as chemical means. An important example is the use of finely divided carbon black as a filler in rubber compounds. Polymers may be combined with stiffer filaments, such as glass and carbon fibres, to form a composite. We shall show later that some semi-crystalline polymers may be treated as composites at a molecular level.

It must not be forgotten that all useful polymers contain small quantities of additives to aid processing and increase the resistance to degradation. The physical properties of the base polymer may be modified by the presence of such additives.

1.2 Physical Structure

The physical properties of a polymer of a given chemical composition are dependent on two distinct aspects of the arrangement of the molecular chains in space.

1) The arrangement of a single chain without regard to its neighbour: rotational isomerism.
2) The arrangement of chains with respect to each other: orientation and crystallinity.

1.2.1 Rotational Isomerism

Rotational isomerism arises because of the alternative conformations of a molecule that can result from the possibility of hindered rotation about the many single bonds in the structure. Spectroscopic techniques (Mizushima 1954) developed in small molecules have been extended to polymers, and as an example we illustrate (Figure 1.9) the alternative trans and gauche conformations in the glycol residue of polyethylene terephthalate (Grime and Ward 1958): the former is a crystalline conformation, but the latter is present in amorphous regions.

To pass from one rotational isomeric form to another requires that an energy barrier be surmounted (Figure 1.10), so that the possibility of the chain molecules changing their conformations depends on the relative magnitude of the energy barrier compared with thermal energies and the perturbing effects of applied stress. Hence, arises the possibility of linking molecular flexibility to deformation mechanisms, a theme to which we will return on several occasions.

1.2.2 Orientation and Crystallinity

When we consider the arrangement of molecular chains with respect to each other, there are again two largely separate aspects, those of molecular orientation and crystallinity. In semi-crystalline polymers, this distinction may at times be an artificial one.

Figure 1.9 Polyethylene terephthalate in the crystalline trans conformation (a) and in the gauche conformation present in ‘amorphous’ regions (b). Grime, D. and Ward, I.M. (1958) / Royal Society of Chemistry.

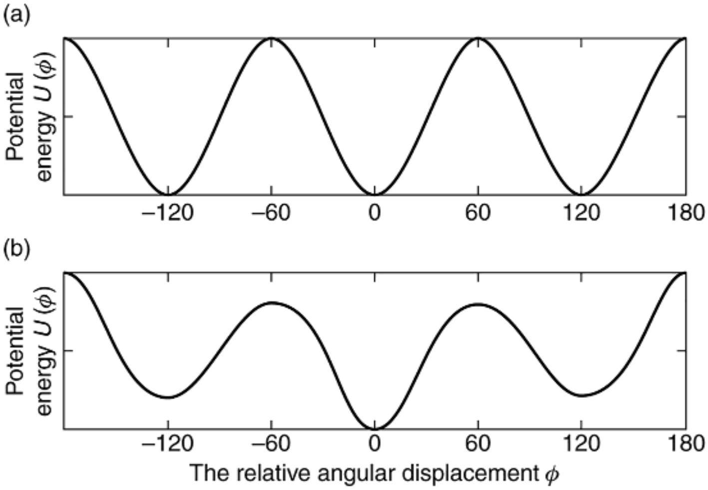


Figure 1.10 Potential energy for rotation (a) around the C—C bond in ethane and (b) around the central C—C bond in n-butane. Adapted from McCrum et al., 1991.

When cooled from the melt, many polymers form a disordered structure called the amorphous state. Some of these materials, such as polymethyl methacrylate, polystyrene and rapidly cooled (melt-quenched) polyethylene terephthalate, have a comparatively high modulus at room temperature, but others, such as natural rubber and atactic polypropylene, have a low modulus. These two types of polymer are often termed glassy and rubberlike, respectively, and we shall see that the form of behaviour exhibited depends on the temperature relative to a glass–rubber transition temperature (T_g) that is dependent on the material and the test method employed. Although an amorphous polymer may be modeled as a random tangle of molecules (Figure 1.11(a)), features such as the comparatively high density (Robertson 1965) show that the packing cannot be completely random. X-ray diffraction techniques indicate no distinct structure, rather a broad diffuse maximum (the amorphous halo) that indicates a preferred distance of separation between the molecular chains.

When an amorphous polymer is stretched, the molecules may be preferentially aligned along the stretch direction. In polymethyl methacrylate and polystyrene, such molecular orientation may be detected by optical methods, which measure the small difference between the refractive index in the stretch direction and that in the perpendicular direction. X-ray diffraction methods for relaxed amorphous polymers still reveal no evidence of three-dimensional order, so the structure may be regarded as a somewhat oriented tangled skein (Figure 1.11(b)) that is oriented amorphous but not crystalline.

In polyethylene terephthalate, however, stretching produces both molecular orientation and small regions of three-dimensional order, termed crystallites, because the orientation processes have brought the molecules into adequate juxtaposition for regions of three-dimensional order to form.

Many polymers, including polyethylene terephthalate, also crystallize if they are cooled slowly from the melt. In this case, we may say that they are crystalline but unoriented.

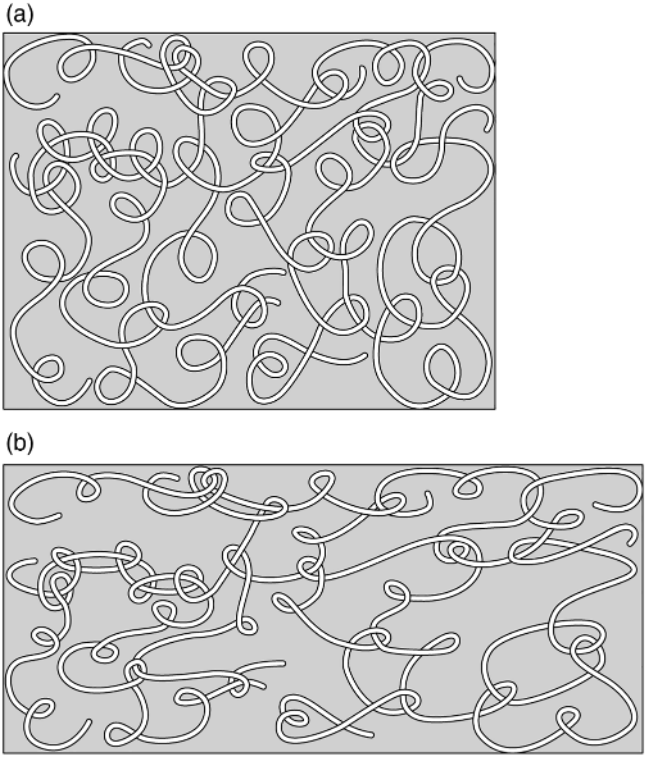


Figure 1.11 Schematic diagrams of (a) unoriented amorphous polymer and (b) oriented amorphous polymer.

Although such specimens are unoriented in the macroscopic sense, that is, they possess isotropic bulk mechanical properties, they are not homogeneous in the microscopic sense and often show a spherulitic structure under a polarizing microscope.

In summary, it may be said that for a polymer to crystallize the molecule must have a regular structure, the temperature must be below the crystal melting point and sufficient time must be available for the long molecules to become ordered in the solid state.

The structure of the crystalline regions of polymers can be deduced from wide-angle X-ray diffraction patterns of highly stretched specimens. When the stretching is uniaxial, the patterns are related to those obtained from fully oriented single crystals. The crystal structure of polyethylene is well established as determined by Bunn (1939) (Figure 1.12).

In addition to the discrete reflections from the crystallites, the diffraction pattern of a polymer shows diffuse scattering attributed to amorphous regions. Such polymers are said to be semi-crystalline, with the crystalline fraction being controlled by molecular regularity. By comparing the relative amounts of crystalline and amorphous scattering of X-rays, the crystallinity has been found to vary from more than 90% for linear polyethylene to about 30% for oriented polyethylene terephthalate.

The first model (Hill 1953) to describe the structure of a semi-crystalline polymer was the so-called fringed micelle model (Figure 1.13), which is a natural development of the

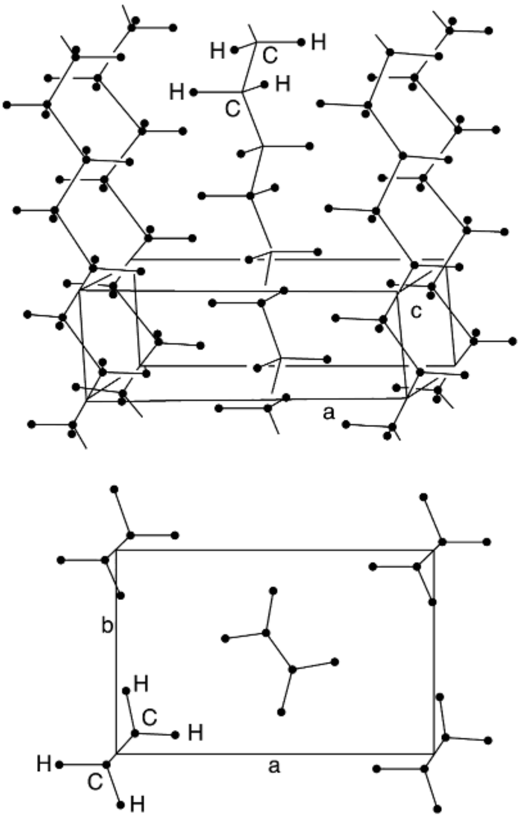


Figure 1.12 Arrangement of molecules in polyethylene crystallites. Adapted from Hill, 1953.

Figure 1.13 The fringed micelle representation of crystalline polymers. Adapted from Hill, 1953.

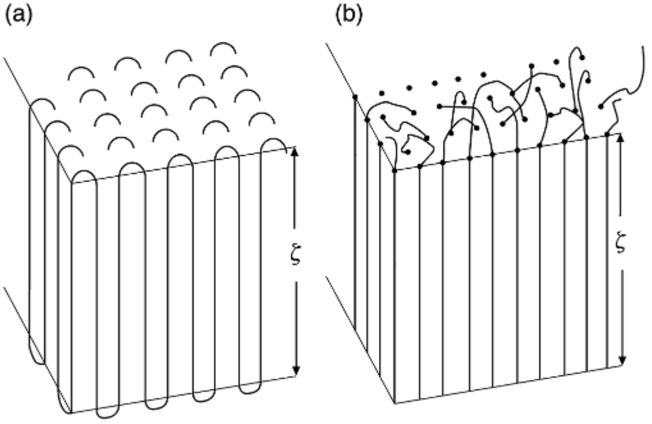


Figure 1.14 Crystallites with folded lamellar crystals of thickness ζ in the direction of the c axis for (a) regular folding and (b) irregular folding of the chain molecules.

imagined situation in an amorphous polymer. The molecular chains alternate between regions of order (the crystallites) and disorder (the amorphous regions).

The fringed micelle model was called into question by the discovery of polymer single crystals grown from solution (Fischer 1957; Keller 1957; Till 1957). Linear polyethylene, for example forms single-crystal lamellae with lateral dimensions of the order of 10–20 μm and thickness of 10 nm. Electron diffraction shows that the molecular chains are oriented approximately normal to the lamellar surface. As the molecules are typically about 1 μm in length, it follows that they must be folded back and forth within the crystals. The simplest geometric arrangement is that the folds are sharp and regular producing the adjacent re-entry model shown in Figure 1.14(a). This model provoked controversy, and an alternative switchboard model shown schematically in Figure 1.14(b) was proposed (Flory 1962).

The crystallization of polymers from the melt has proved even more controversial, as a single molecule is unlikely to be laid down on a crystalline substrate without interference from its neighbours, and it might be expected that the highly entangled topology of the chains that exists in the melt would be substantially retained in the crystalline state. These issues were explored to great effect by neutron-scattering measurements, notably by Fischer (1978), Stamm *et al.* (1979, 1981). The neutron-scattering measurements showed that the radii of gyration in the melt and in the semi-crystalline state for polyethylene quenched from the melt, for polyethylene oxide crystallized by slow cooling and for isotactic polypropylene, isothermally crystallized, were almost identical. On the basis of these results, Fischer (1978) proposed the solidification model shown in Figure 1.15, where straight sequences of the original melt are incorporated into the growing lamellae without long-range diffusional motion.

Although it is accepted that kinetic factors determine the growth rate of crystallization and the morphology, there is still debate in this area also. The theory proposed by Lauritzen and Hoffman (1960) led the field and predicted the growth rate as the function of the degree of supercooling, the temperature difference between the crystallization temperature and the melting point. It was assumed that the free-energy barrier associated with nucleation of the

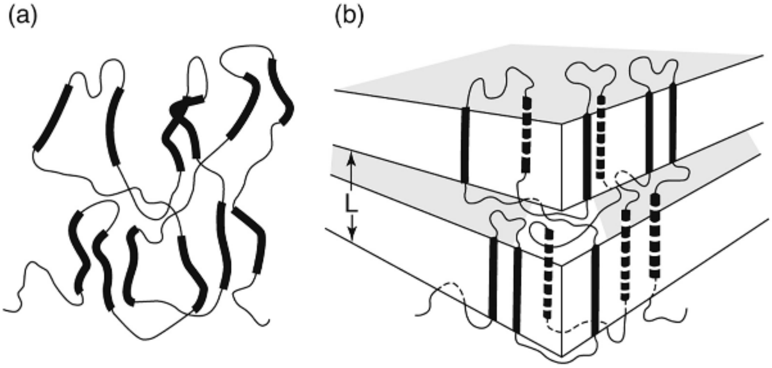


Figure 1.15 Chain conformation (a) in the melt and (b) in the crystal according to the solidification model. Stamm et al. (1979) / Royal Society of Chemistry.

crystallization was energetic in origin. An alternative model for chain folding in polymer crystals has been proposed by Sadler and Gilmer (1984), which assumes that the free-energy barrier for nucleation is predominantly entropic. For a comprehensive review of these theories and related issues, the reader is referred to an excellent review by Gedde (1995) and also to Strobl (1997).

There is, of course, much evidence to support the existence of a lamellar morphology in crystalline polymers. Typically, spherulites 1–10 μm in diameter are formed, which grow outwards until they impinge upon neighbouring spherulites (Figure 1.16). The spherulitic textures are formed by the growth of dominant lamellae from a central nucleus in all directions by a twisting of these lamellae along the fibrils, the intervening spaces being filled in by subsidiary lamellae, possibly due to low-molecular-weight material. This is shown schematically in Figure 1.17, where, for ease of illustration, regular chain folding is sketched (Takayanagi 1963). For a good review of polymer morphology, see the text by Bassett (1981) and also more recent work directed by the same author.

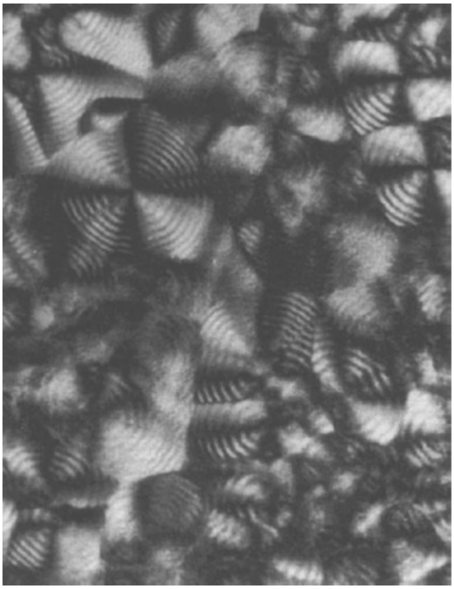


Figure 1.16 A photograph of typical spherulitic structure under a polarizing microscope.

Orientation through plastic deformation (drawing) destroys the spherulitic structure. What remains is determined to a large extent by the degree of crystallinity. Mechanical testing, described in the subsequent chapters, has helped to establish several models. At one extreme, some highly oriented, highly

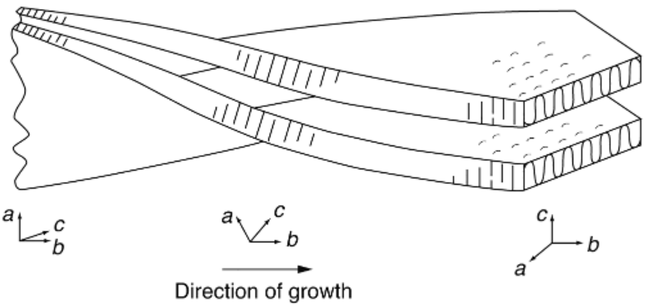


Figure 1.17 A model of the lamellar arrangement in a polyethylene spherulite. The small diagrams of the *a*, *b*, *c* axes show the orientation of the unit cell at various points. Adapted from Takayanagi, 1963.

crystalline specimens of linear polyethylene behave as blocks or lamellae of crystalline material, connected together by tie molecules or crystalline bridges and separated by the amorphous component. Such materials in some respects can be treated as microscopic composites. At the other extreme one has materials such as polyethylene terephthalate in which the crystalline and amorphous components are so intermixed that a single-phase model appears to be more appropriate.

The current state of knowledge suggests that both chain folding and the threading of molecules through the crystalline region occur in typical polymers.

A schematic attempt (Hosemann 1962) to illustrate this situation, and other types of irregularity, is given in Figure 1.18.

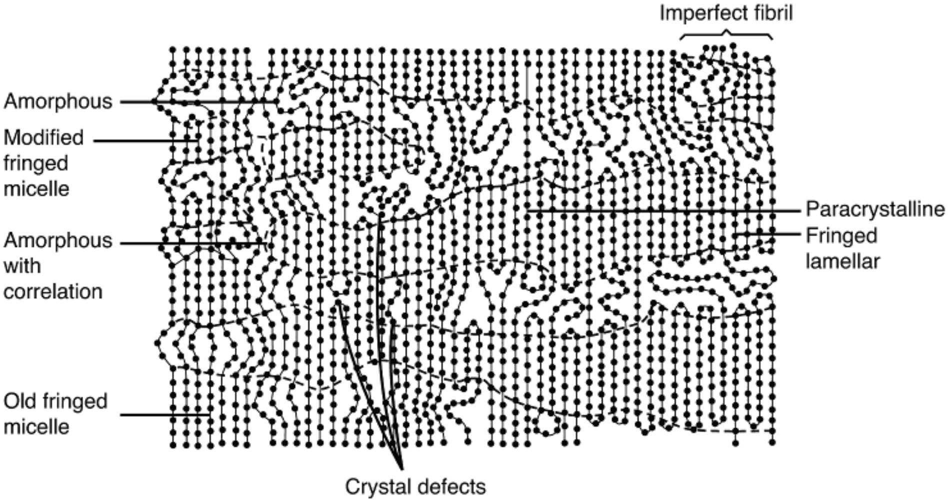


Figure 1.18 Schematic composite diagram of different types of order and disorder in oriented polymers. Adapted from Hosemann, 1962.

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