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Polymer Materials

an introduction for technologists and scientists

Christopher Hall

Second Edition

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MACMILLAN
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Preface

Some systematic study of materials science now forms a part of many advanced courses in engineering and technology. There is no shortage of introductory textbooks of engineering materials science; yet most show a bias towards metals and ceramics and the treatment of polymers is often less thorough. On the other hand introductory books on polymer science have a preoccupation with polymerisation chemistry which makes them unsuitable for many students.

In this book I have attempted to provide a broad survey of the materials science of polymers for technologists, engineers and scientists, approximately at the level of general one-volume university texts on engineering materials. It is intended to serve both as a self-contained elementary treatment and also as a guide to the extensive specialist literature of polymer materials. I have sought to write a balanced scientific account with a somewhat technological flavour.

Nomenclature for polymers is carefully discussed in an appendix, following BSI and ASTM recommendations. The text makes extensive use of standard abbreviations such as PE, PA, PTFE and so on, but customary names such as acrylic and nylon have not been entirely excised.

In writing a book of broad compass, an author depends heavily on the established research and technical literature and on the indulgence of specialists. A number of such experts have kindly read parts of the manuscript in draft. The book is undoubtedly better for their comments, for which I am most grateful. I am particularly indebted to my colleagues Professor S. F. Bush and Dr W. D. Hoff for their careful reading of the text as it neared completion. I thank Mrs Jennifer Wilding for her help in preparing the typescript.

Manchester, 1980 C. HALL

Prefatory note to second edition

The aim of the second edition is the same as that of the first: to provide a broad scientific introduction to the material properties of polymers. In the seven years since the first edition appeared the specialist literature on polymer materials has grown hugely, increasing rather than reducing the need for introductory texts for students and non-specialists. At the same time, in science and engineering education, the integration of polymers into the main stream of materials teaching is gathering pace. I hope that this new edition will contribute to that process.

Cambridge, 1988 Christopher Hall

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1

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

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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.

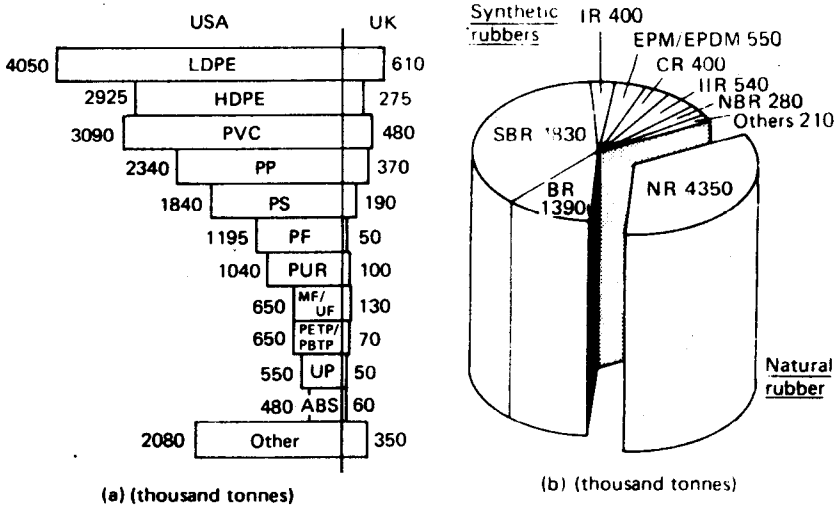

Figure 1.1 (a) United Kingdom and United States production of plastics materials compared, 1985–86 data; US production *per capita* is twice that of the UK. (b) Projected world consumption of rubber (Eastern Europe and parts of Asia excluded) for 1989 (International Institute of Synthetic Rubber Producers)

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.

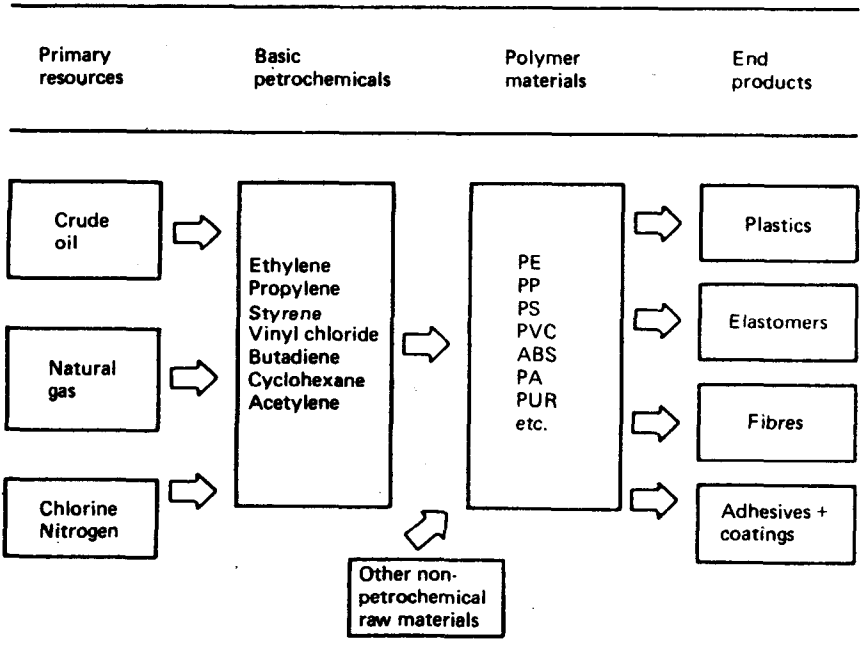

Figure 1.2 Production of polymer-based products from raw materials

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

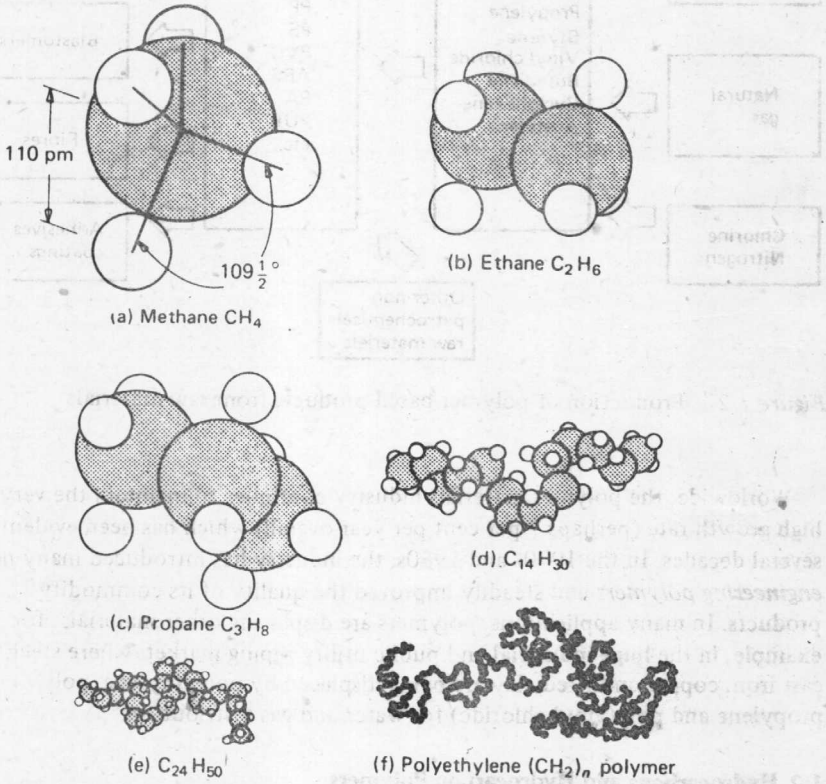

Figure 1.3 (a) Molecular structure of methane CH_4 showing tetrahedral arrangement of C–H bonds, bond angle and bond length. (b) – (f) Molecular structures of other straight-chain hydrocarbons

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.

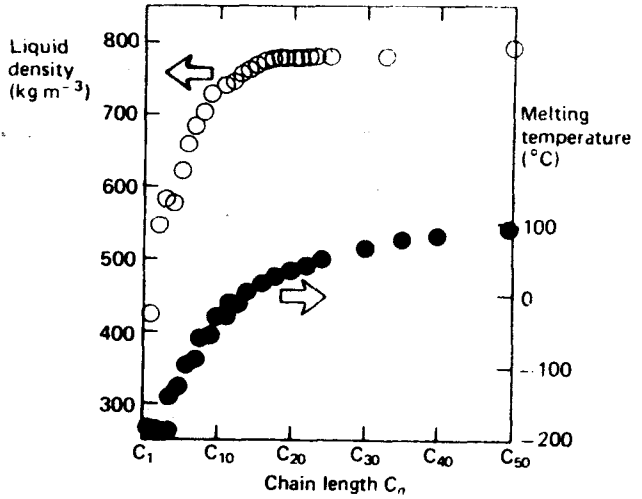

Figure 1.4 Liquid state densities and melting temperatures of normal straight-chain hydrocarbons C_nH_{2n+2} (densities at 20 °C or closest available temperature)

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

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

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.

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

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.)

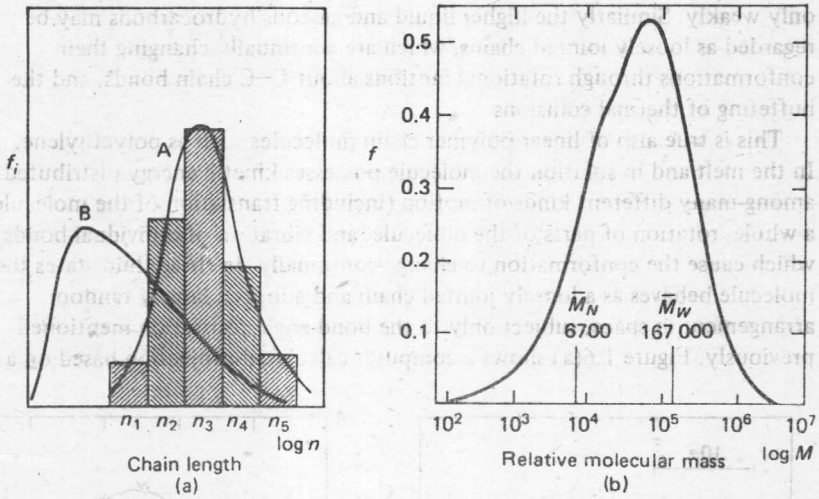

Figure 1.5 (a) Examples of narrow (A) and broad, asymmetric (B) polymer chain length distributions; curve A shown in histogram form (*see* text). (b) Experimental relative molecular mass distribution of an HDPE sample, showing $\bar{M}_N$ and $\bar{M}_W$; $f = n_i f_i / \Sigma(n_i f_i)$, obtained by 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 CC bond angle is fixed at 109.5 degrees. However, a regular coplanar arrangement can be adopted, and is in fact

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