

Introduction to Polymers

Second Edition

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Preface to the second edition

The decade that has passed since the first edition was written has seen further growth in the uses of polymers. During this time much research effort has been focussed upon the development of speciality polymers for high-performance applications, and this has served to emphasize the importance of polymer chemistry. It is partly for this reason that through the introduction of a second author in the Second Edition, the first three chapters have been reorganized, revised and expanded to give a broader and more thorough coverage of the fundamental aspects of polymer synthesis and polymer characterization. In particular, the sections upon ionic polymerization, Ziegler–Natta polymerization, copolymerization, static light scattering, phase separation, gel permeation chromatography and spectroscopy have been substantially revised and expanded. Additionally, new sections upon ring-opening polymerization, specialized methods of polymerization, dynamic light scattering and small-angle X-ray and neutron scattering have been included to give brief introductions to these topics which are of growing importance. Whilst Chapters 4 and 5 are to a large extent as they appeared in the First Edition, they also have been expanded. A more in-depth treatment of factors affecting glass transition and melting temperatures is given, and new sections have been added to introduce the important topics of thermoplastic elastomers and toughening of brittle polymers.

The approach used, and the design and structure of the book are the same as for the first edition. Thus a modern treatment has been used for presentation of much of the subject matter, and the book seeks to fuse together aspects of the chemistry, structure and mechanical properties of polymers, thereby introducing important relationships between synthesis, structure, and molecular and bulk properties. The book is designed principally for undergraduate and postgraduate students who are studying polymers, but also should be of use to scientists in industry and research who need to become familiar with the fundamentals of Polymer Science. It has been written to be, as far as is possible, self-contained with most equations fully derived and critically discussed. Nevertheless, lists of books are given at the end of each chapter for background and further reading. Together with the problems which have been included, they will enable the

reader to reinforce, extend and test his or her knowledge and understanding of specific subjects.

In addition to the people and organizations who assisted in the preparation of the First Edition, the authors would like to thank Mrs Susan Brandreth and Mrs Jean Smith for typing the new manuscript. They are also grateful to Dr Frank Heatley, Dr Tony Ryan, Dr John Stanford and Dr Bob Stepto for useful comments on aspects of the new material. Finally, they would like to express their sincere gratitude to their families for the understanding and support they have shown during the writing and preparation of the new edition.

ROBERT J. YOUNG
PETER A. LOVELL

Manchester Materials Science Centre
1990

Preface to the first edition

Polymers are a group of materials made up of long covalently-bonded molecules, which include plastics and rubbers. The use of polymeric materials is increasing rapidly year by year and in many applications they are replacing conventional materials such as metals, wood and natural fibres such as cotton and wool. The book is designed principally for undergraduate and postgraduate students of Chemistry, Physics, Materials Science and Engineering who are studying polymers. An increasing number of graduates in these disciplines go on to work in polymer-based industries, often with little grounding in Polymer Science and so the book should also be of use to scientists in industry and research who need to learn about the subject.

A basic knowledge of mathematics, chemistry and physics is assumed although it has been written to be, as far as is possible, self-contained with most equations fully derived and any assumptions stated. Previous books in this field have tended to be concerned primarily with either polymer chemistry, polymer structure or mechanical properties. An attempt has been made with this book to fuse together these different aspects into one volume so that the reader has these different areas included in one book and so can appreciate the relationships that exist between the different aspects of the subject. Problems have also been given at the end of each chapter so that the reader may be able to test his or her understanding of the subject and practise the manipulation of data.

The textbook approaches the subject of polymers from a Materials Science viewpoint, being principally concerned with the relationship between structure and properties. In order to keep it down to a manageable size there have been important and deliberate omissions. Two obvious areas are those of polymer processing (e.g. moulding and fabrication) and electrical properties. These are vast areas in their own right and it is hoped that this book will give the reader sufficient grounding to go on and study these topics elsewhere.

Several aspects of the subject of polymer science have been updated compared with the normal presentation in books at this level. For example, the mechanical properties of polymers are treated from a mechanistic viewpoint rather than in terms of viscoelasticity, reflecting modern developments in the subject. However, viscoelasticity being an important aspect of polymer properties is also covered but with rather less emphasis than it has been given in the past. The presentation of some theories and

experimental results has been changed from the original approach for the sake of clarity and consistency of style.

I am grateful to Professor Bill Bonfield for originally suggesting the book and for his encouragement throughout the project. I am also grateful to my other colleagues at Queen Mary College for allowing me to use some of their material and problems and to many people in the field of Polymers who have contributed micrographs. A large part of the book was written during a period of study leave at the University of the Saarland in West Germany. I would like to thank the Alexander von Humboldt Stiftung for financial support during this period. The bulk of the manuscript was typed by Mrs Rosalie Hillman and I would like to thank her for her help. Finally, my gratitude must go to my wife and family for giving me their support during the preparation of the book.

ROBERT J. YOUNG

Queen Mary College, London
1980

1 Introduction

1.1 The origins of polymer science and the polymer industry

Polymers have existed in natural form since life began and those such as DNA, RNA, proteins and polysaccharides play crucial roles in plant and animal life. From the earliest times, man has exploited naturally-occurring polymers as materials for providing clothing, decoration, shelter, tools, weapons, writing materials and other requirements. However, the origins of today's polymer industry commonly are accepted as being in the nineteenth century when important discoveries were made concerning the modification of certain natural polymers.

In 1820 Thomas Hancock discovered that when masticated (i.e. subjected repeatedly to high shear forces), natural rubber becomes more fluid making it easier to blend with additives and to mould. Some years later, in 1839, Charles Goodyear found that the elastic properties of natural rubber could be improved, and its tackiness eliminated, by heating with sulphur. Patents for this discovery were issued in 1844 to Goodyear, and slightly earlier to Hancock, who christened the process vulcanization. In 1851 Nelson Goodyear, Charles' brother, patented the vulcanization of natural rubber with large amounts of sulphur to produce a hard material more commonly known as hard rubber, ebonite or vulcanite.

Cellulose nitrate, also called nitrocellulose or gun cotton, first became prominent after Christian Schönbein prepared it in 1846. He was quick to recognize the commercial value of this material as an explosive, and within a year gun cotton was being manufactured. However, more important to the rise of the polymer industry, cellulose nitrate was found to be a hard elastic material which was soluble and could be moulded into different shapes by the application of heat and pressure. Alexander Parkes was the first to take advantage of this combination of properties and in 1862 he exhibited articles made from Parkesine, a form of plasticized cellulose nitrate. In 1870 John and Isaiah Hyatt patented a similar but more easily processed material, named celluloid, which was prepared using camphor as the plasticizer. Unlike Parkesine, celluloid was a great commercial success.

In 1892 Charles Cross, Edward Bevan and Clayton Beadle patented the 'viscose process' for dissolving and then regenerating cellulose. The process was first used to produce viscose rayon textile fibres, and subsequently for production of cellophane film.

The polymeric materials described so far are semi-synthetic since they

are produced from natural polymers. Leo Baekeland's Bakelite phenol-formaldehyde resins have the distinction of being the first fully-synthetic polymers to be commercialized, their production beginning in 1910. The first synthetic rubber to be manufactured, known as methyl rubber, was produced from 2,3-dimethylbutadiene in Germany during World War I as a substitute, albeit a poor one, for natural rubber.

Although the polymer industry was now firmly established, its growth was restricted by the considerable lack of understanding of the nature of polymers. For over a century scientists had been reporting the unusual properties of polymers, and by 1920 the common belief was that they consisted of physically-associated aggregates of small molecules. Few scientists gave credence to the viewpoint so passionately believed by Hermann Staudinger, that polymers were composed of very large molecules containing long sequences of simple chemical units linked together by covalent bonds. Staudinger introduced the word 'macromolecule' to describe polymers, and during the 1920s vigorously set about proving his hypothesis to be correct. Particularly important were his studies of the synthesis, structure and properties of polyoxymethylene and of polystyrene, the results from which left little doubt as to the validity of the macromolecular viewpoint. Staudinger's hypothesis was further substantiated by the crystallographic studies of natural polymers reported by Herman Mark and Kurt Meyer, and by the classic work of Wallace Carothers on the preparation of polyamides and polyesters. Thus by the early 1930s most scientists were convinced of the macromolecular structure of polymers. During the following 20 years, work on polymers increased enormously: the first journals devoted solely to their study were published and most of the fundamental principles of *Polymer Science* were established. The theoretical and experimental work of Paul Flory was prominent in this period, and for his long and substantial contribution to Polymer Science he was awarded the Nobel Prize for Chemistry in 1974. In 1953 Staudinger had received the same accolade in recognition of his pioneering work.

Not surprisingly, as the science of macromolecules emerged, a large number of synthetic polymers went into commercial production for the first time. These include polystyrene, poly(methyl methacrylate), nylon 6.6, polyethylene, poly(vinyl chloride), styrene-butadiene rubber, silicones and polytetrafluoroethylene, as well as many others. From the 1950s onwards regular advances, too numerous to mention here, have continued to stimulate both scientific and industrial progress.

Whilst Polymer Science is now considered to be a mature subject, its breadth is ever increasing and there are many demanding challenges awaiting scientists who venture into this fascinating multidisciplinary science.

1.2 Basic definitions and nomenclature

Several important terms and concepts must be understood in order to discuss fully the synthesis, characterization, structure and properties of polymers. Most of these will be defined and discussed in detail in subsequent chapters. However, some are of such fundamental importance that they must be defined at the outset.

In strict terms, a *polymer* is a *substance* composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary, usually covalent, bonds. The emphasis upon substance in this definition is to highlight that although the words polymer and *macromolecule* are used interchangeably, the latter strictly defines the molecules of which the former is composed.

Macromolecules are formed by linking together *monomer* molecules through chemical reactions, the process by which this is achieved being known as *polymerization*. For example, polymerization of ethylene yields polyethylene, a typical sample of which may contain molecules with 50 000 carbon atoms linked together in a chain. It is this long chain nature which sets polymers apart from other materials and gives rise to their characteristic properties.

1.2.1 Skeletal structure

The definition of macromolecules presented up to this point implies that they have a *linear* skeletal structure which may be represented by a chain with two ends. Whilst this is true for many macromolecules, there are also many with *non-linear* skeletal structures of the type shown in Fig. 1.1.

Branched polymers have side chains, or *branches*, of significant length which are bonded to the main chain at *branch points* (also known as

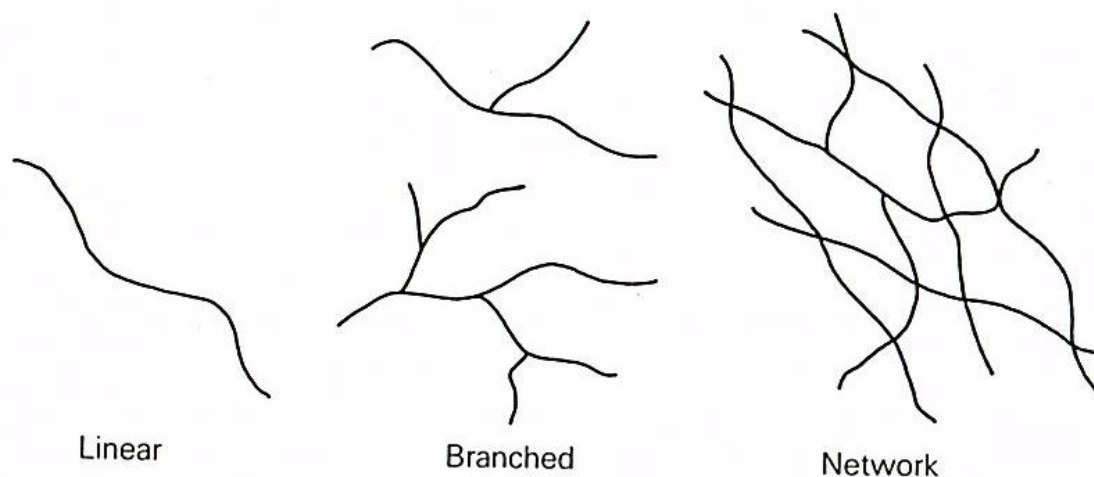


Fig 1.1 Representative skeletal structures of linear and non-linear polymers.

junction points), and are characterized in terms of the number and size of the branches. *Network polymers* have three-dimensional structures in which each chain is connected to all others by a sequence of junction points and other chains. Such polymers are said to be *crosslinked* and are characterized by their *crosslink density*, or *degree of crosslinking*, which is related directly to the number of junction points per unit volume.

Non-linear polymers may be formed by polymerization, or can be prepared by linking together (i.e. *crosslinking*) pre-existing chains.

Variations in skeletal structure give rise to major differences in properties. For example, linear polyethylene has a melting point about 20°C higher than that of branched polyethylene. Unlike linear and branched polymers, network polymers do not melt upon heating and will not dissolve, though they may swell considerably in compatible solvents. The importance of crosslink density has already been encountered in terms of the vulcanization (i.e. sulphur-crosslinking) of natural rubber. With low crosslink densities (i.e. low levels of sulphur) the product is a flexible elastomer, whereas it is a rigid material when the crosslink density is high.

1.2.2 *Homopolymers*

The formal definition of a homopolymer is a polymer derived from one species of monomer. However, the word *homopolymer* often is used more broadly to describe polymers whose structure can be represented by multiple repetition of a single type of *repeat unit* which may contain one or more species of *monomer unit*. The latter is sometimes referred to as a structural unit.

The chemical structure of a polymer usually is represented by that of the repeat unit enclosed by brackets. Thus the hypothetical homopolymer $\sim\text{A}-\text{A}-\text{A}-\text{A}-\text{A}-\text{A}-\text{A}-\text{A}\sim$ is represented by $[\text{A}]_n$ where n is the number of repeat units linked together to form the macromolecule. Table 1.1 shows the chemical structures of some common homopolymers together with the monomers from which they are derived and some comments upon their properties and uses. It should be evident that slight differences in chemical structure can lead to very significant differences in properties.

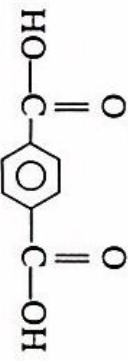
The naming of polymers or envisaging the chemical structure of a polymer from its name is often an area of difficulty. At least in part this is because most polymers have more than one correct name, the situation being further complicated by the variety of trade-names which also are used to describe certain polymers. The approach adopted here is to use names which most clearly and simply indicate the chemical structures of the polymers under discussion.

The names given to the polymers in Table 1.1 exemplify elementary

TABLE 1.1 Some common homopolymers

Monomers	Polymer	Comments
(1) Ethylene $\text{CH}_2=\text{CH}_2$	Polyethylene (PE) $\text{-(CH}_2\text{--CH}_2\text{)}_n$	Moulded objects, tubing, film, electrical insulation, e.g. 'Alkathene', 'Lupolen'.
(2) Propylene $\text{CH}_2=\text{CH}-\text{CH}_3$	Polypropylene (PP) $\text{-(CH}_2\text{--CH(CH}_3\text{))}_n$	Similar uses to PE; lower density, stiffer, e.g. 'Propathene', 'Novolen'.
(3) Tetrafluoroethylene $\text{CF}_2=\text{CF}_2$	Polytetrafluoroethylene (PTFE) $\text{-(CF}_2\text{--CF}_2\text{)}_n$	Mouldings, film, coatings; high temperature resistance, chemically inert, excellent electrical insulator, very low coefficient of friction; expensive, e.g. 'Teflon', 'Fluon'.
(4) Styrene $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	Polystyrene (PS) $\text{-(CH}_2\text{--CH(C}_6\text{H}_5\text{))}_n$	Cheap moulded objects, e.g. 'Styron', 'Hostyren'. Modified with rubbers to improve toughness, e.g. high-impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene copolymer (ABS). Expanded by volatilization of a blended blowing agent (e.g. pentane) to produce polystyrene foam.

TABLE 1.1 *continued*

Monomers	Polymer	Comments
(8) Ethylene glycol HO—CH ₂ —CH ₂ —OH	Poly(ethylene glycol) (PEG) $\text{+CH}_2\text{—CH}_2\text{—O+}_n$	Water-soluble packaging films, textile sizes, thickeners, e.g. 'Carbowax'.
(9) Ethylene glycol HO—CH ₂ —CH ₂ —OH and terephthalic acid 	Poly(ethylene terephthalate) (PET)* $\text{+O—CH}_2\text{—CH}_2\text{—O—C(=O)—C}_6\text{H}_4\text{—C(=O)—C+}_n$	Textile fibres, film, bottles, e.g. 'Terylene', 'Dacron', 'Melinex', 'Mylar'.
(10) Hexamethylene diamine H ₂ N—(CH ₂) ₆ —NH ₂ and sebacic acid 	Poly(hexamethylene sebacate) (nylon 6.10)* $\text{+N(CH}_2\text{)}_6\text{N—C(=O)—(CH}_2\text{)}_{10}\text{C(=O)—C+}_n$  	Mouldings, fibres, e.g. 'Ultramid 6.10'.

* The polymer has two monomer units in the repeat unit.

TABLE 1.1 *continued*

Monomers	Polymer	Comments
(5) Methyl methacrylate $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array}$	Poly(methyl methacrylate) (PMMA) $\begin{array}{c} \text{CH}_3 \\ \\ +\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array}$	Transparent sheets and mouldings; used for aeroplane windows; more expensive than PS, e.g. 'Perspex', 'Diakon', 'Lucite', 'Oroglas', 'Plexiglas'.
(6) Vinyl chloride $\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{Cl} \end{array}$	Poly(vinyl chloride) (PVC) $\begin{array}{c} +\text{CH}_2-\text{CH}- \\ \\ \text{Cl} \end{array}$	Water pipes and gutters, bottles, gramophone records; plasticized to make PVC leathercloth, raincoats, flexible pipe and hose, toys, sheathing on electrical cables, e.g. 'Darvic', 'Welvic', 'Vinoflex', 'Hostalit'.
(7) Vinyl acetate $\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$	Poly(vinyl acetate) (PVAc) $\begin{array}{c} +\text{CH}_2-\text{CH}- \\ \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$	Surface coatings, adhesives, chewing gum.

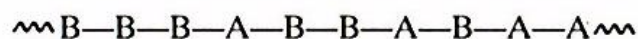
aspects of nomenclature. Thus source-based nomenclature places the prefix 'poly' before the name of the monomer, the monomer's name being contained within parentheses unless it is a simple single word. In structure-based nomenclature the prefix poly is followed in parentheses by words which describe the chemical structure of the repeat unit. This type of nomenclature is used for polymers nine and ten in Table 1.1.

1.2.3 Copolymers

The formal definition of a *copolymer* is a polymer derived from more than one species of monomer. However, in accordance with use of the word homopolymer, it is common practice to use a structure-based definition. Thus the word copolymer more commonly is used to describe polymers whose molecules contain two or more different types of repeat unit. Hence polymers nine and ten in Table 1.1 usually are considered to be homopolymers rather than copolymers.

There are several categories of copolymer, each being characterized by a particular form of arrangement of the repeat units along the polymer chain. For simplicity, the representation of these categories will be illustrated by copolymers containing only two different types of repeat unit (A and B).

Statistical copolymers are copolymers in which the sequential distribution of the repeat units obeys known statistical laws (e.g. Markovian). *Random copolymers* are a special type of statistical copolymer in which the distribution of repeat units is truly random (some words of caution are necessary here because older textbooks and scientific papers often use the term random copolymer to describe both random and non-random statistical copolymers). A section of a truly random copolymer is represented below



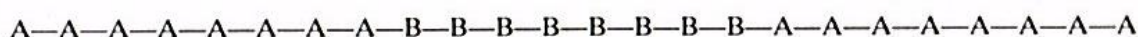
Alternating copolymers have only two different types of repeat unit and these are arranged alternately along the polymer chain



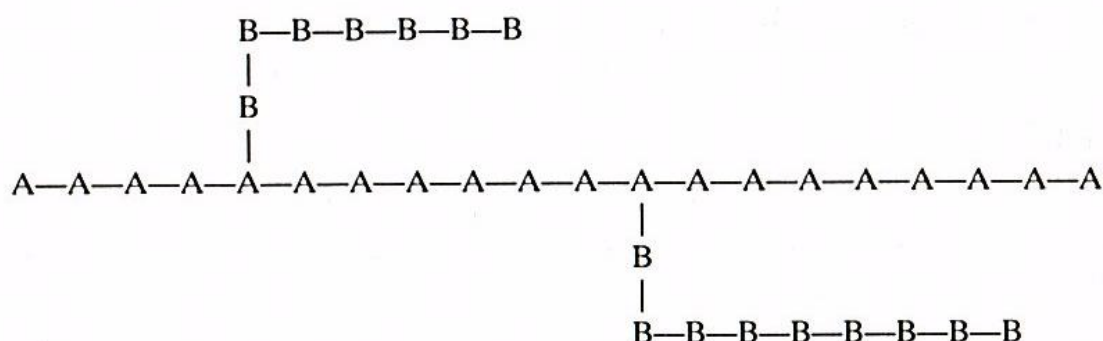
Statistical, random and alternating copolymers generally have properties which are intermediate to those of the corresponding homopolymers. Thus by preparing such copolymers it is possible to combine the desirable properties of the homopolymers into a single material. This is not normally possible by blending because most homopolymers are immiscible with each other.

Block copolymers are linear copolymers in which the repeat units exist only in long sequences, or *blocks*, of the same type. Two common block

copolymer structures are represented below and usually are termed AB di-block and ABA tri-block copolymers



Graft copolymers are branched polymers in which the branches have a different chemical structure to that of the main chain. In their simplest form they consist of a main homopolymer chain with branches of a different homopolymer



In distinct contrast to the types of copolymer described earlier, block and graft copolymers usually show properties characteristic of each of the constituent homopolymers. They also have some unique properties arising from the chemical linkage(s) between the homopolymer sequences preventing them from acting entirely independently of each other.

The current principles of nomenclature for copolymers are indicated in Table 1.2 where A and B represent source- or structure-based names for these repeat units. Thus a statistical copolymer of ethylene and propylene

TABLE 1.2 *Principles of nomenclature for copolymers*

Type of copolymer	Example of nomenclature
Unspecified	Poly(A-co-B)
Statistical	Poly(A-stat-B)
Random	Poly(A-ran-B)
Alternating	Poly(A-alt-B)
Block	PolyA-block-polyB
Graft*	PolyA-graft-polyB

* The example is for polyB branches on a polyA main chain.

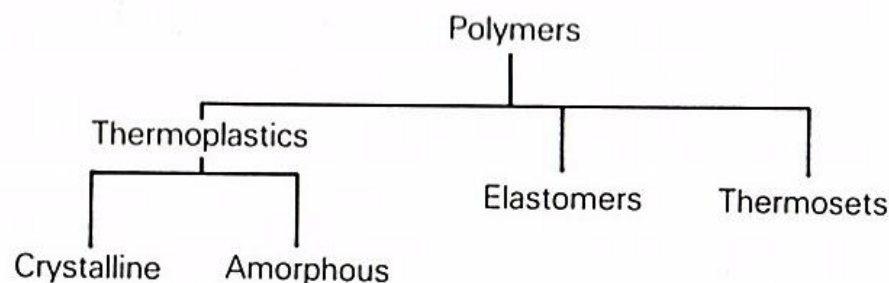


Fig. 1.2 Classification of polymers.

is named poly(ethylene-*stat*-propylene), and an ABA tri-block copolymer of styrene (A) and isoprene (B) is named polystyrene-*block*-polyisoprene-*block*-polystyrene. In certain cases, additional square brackets are required. For example, an alternating copolymer of styrene and maleic anhydride is named poly[styrene-*alt*-(maleic anhydride)].

1.2.4 Classification of polymers

The most common way of classifying polymers is outlined in Fig. 1.2 where they are first separated into three groups: *thermoplastics*, *elastomers* and *thermosets*. Thermoplastics are then further separated into those which are crystalline and those which are amorphous (i.e. non-crystalline). This method of classification has an advantage in comparison to others since it is based essentially upon the underlying molecular structure of the polymers.

Thermoplastics, often referred to just as plastics, are linear or branched polymers which can be melted upon the application of heat. They can be moulded (and remoulded) into virtually any shape using processing techniques such as injection moulding and extrusion, and now constitute by far the largest proportion of the polymers used in industry. Generally, thermoplastics do not crystallize easily upon cooling to the solid state because this requires considerable ordering of the highly coiled and entangled macromolecules present in the liquid state. Those which do crystallize invariably do not form perfectly crystalline materials but instead are *semi-crystalline* with both crystalline and amorphous regions. The crystalline phases of such polymers are characterized by their *melting temperature* (T_m). Many thermoplastics are, however, completely amorphous and incapable of crystallization, even upon annealing. Amorphous polymers (and amorphous phases of semi-crystalline polymers) are characterized by their *glass transition temperature* (T_g), the temperature at which they transform abruptly from the *glassy state* (hard) to the *rubbery state* (soft). This transition corresponds to the onset of chain motion; below T_g the polymer chains are unable to move and are 'frozen' in position. Both T_m and T_g increase with increasing chain stiffness and increasing forces of intermolecular attraction.

Elastomers are crosslinked rubbery polymers (i.e. rubbery networks) that can be stretched easily to high extensions (e.g. $3\times$ to $10\times$ their original dimensions) and which rapidly recover their original dimensions when the applied stress is released. This extremely important and useful property is a reflection of their molecular structure in which the network is of low crosslink density. The rubbery polymer chains become extended upon deformation but are prevented from permanent flow by the crosslinks, and driven by entropy, spring back to their original positions on removal of the stress. The word rubber, often used in place of elastomer, preferably should be used for describing rubbery polymers which are not crosslinked.

Thermosets normally are rigid materials and are network polymers in which chain motion is greatly restricted by a high degree of crosslinking. As for elastomers, they are intractable once formed and degrade rather than melt upon the application of heat.

1.3 Molar mass and degree of polymerization

Many properties of polymers show a strong dependence upon the size of the polymer chains, so that it is essential to characterize their dimensions. This normally is done by measuring the *molar mass* (M) of a polymer which is simply the mass of 1 mole of the polymer and usually is quoted in units of g mol^{-1} or kg mol^{-1} . The term 'molecular weight' is still often used instead of molar mass, but is not preferred because it can be somewhat misleading. It is really a dimensionless quantity, the relative molecular mass, rather than the weight of an individual molecule which is of course a very small quantity (e.g. $\sim 10^{-19} - \sim 10^{-18} \text{ g}$ for most polymers). By multiplying the numerical value of molecular weight by the specific units g mol^{-1} it can be converted into the equivalent value of molar mass. For example, a molecular weight of 100 000 is equivalent to a molar mass of $100\,000 \text{ g mol}^{-1}$ which in turn is equivalent to a molar mass of 100 kg mol^{-1} .

For network polymers the only meaningful molar mass is that of the polymer chains existing between junction points (i.e. *network chains*), since the molar mass of the network itself essentially is infinite.

The molar mass of a homopolymer is related to the *degree of polymerization* (x), which is the number of repeat units in the polymer chain, by the simple relation

$$M = xM_0 \quad (1.1)$$

where M_0 is the molar mass of the repeat unit. For copolymers the sum of the products xM_0 for each type of repeat unit is required to define the molar mass.

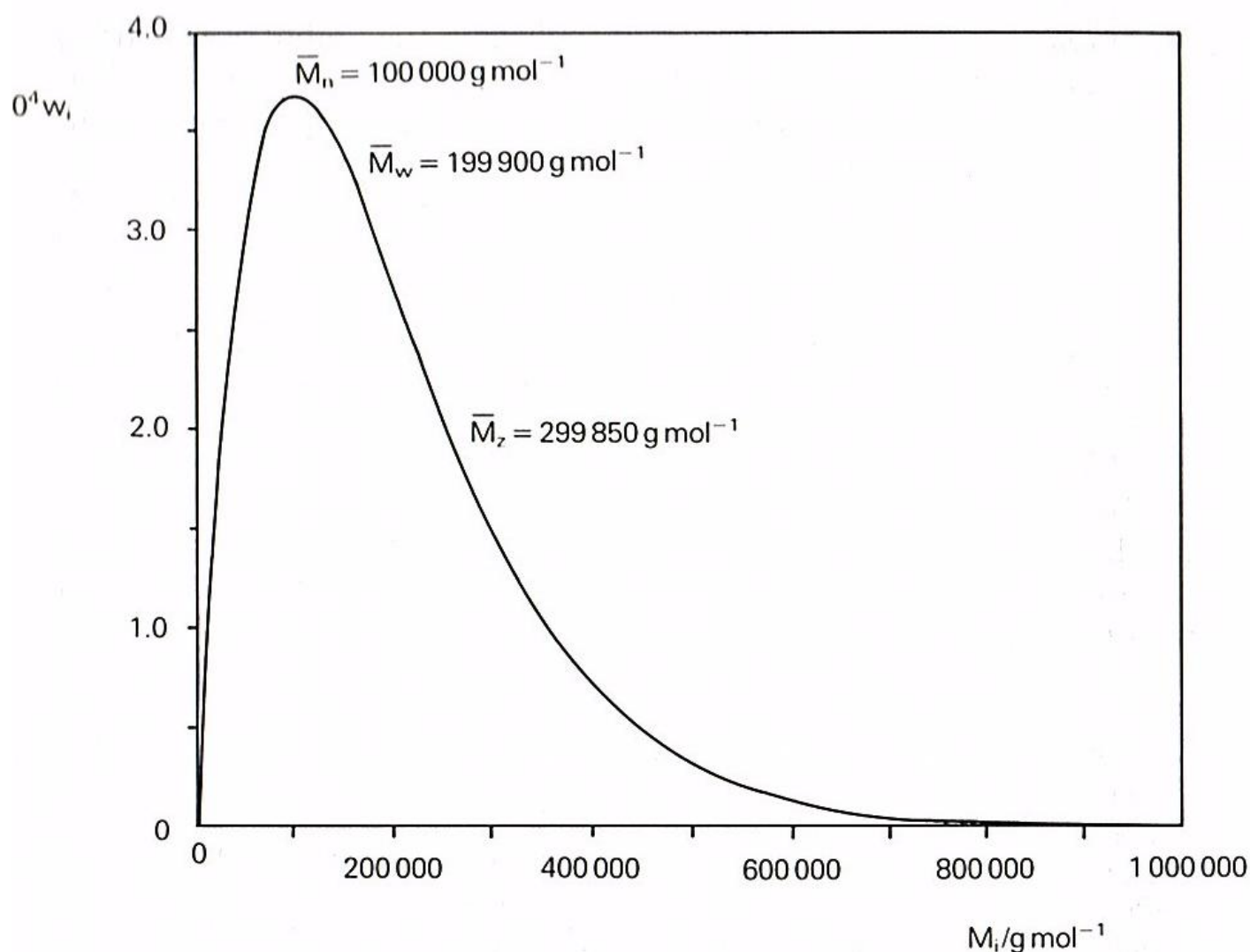


Fig. 1.3 A typical molar mass distribution curve.

1.3.1 Molar mass distribution

With very few exceptions, polymers consist of macromolecules (or network chains) with a range of molar masses. Since the molar mass changes in intervals of M_0 , the distribution of molar mass is discontinuous. However, for most polymers these intervals are extremely small in comparison to the total range of molar mass and the distribution can be assumed to be continuous, as exemplified in Fig. 1.3.

1.3.2 Molar mass averages

Whilst a knowledge of the complete molar mass distribution is essential in many uses of polymers, it is convenient to characterize the distribution in terms of molar mass averages. These usually are defined by considering the discontinuous nature of the distribution in which the macromolecules exist in discrete fractions i containing N_i molecules of molar mass M_i .

The *number-average molar mass* ($\bar{M}_n$) is defined as ‘the sum of the products of the molar mass of each fraction multiplied by its mole fraction’

$$\text{i.e. } \bar{M}_n = \sum X_i M_i \quad (1.2)$$

where X_i is the mole fraction of molecules of molar mass M_i and is given by the ratio of N_i to the total number of molecules. Therefore it follows that

$$\bar{M}_n = \sum N_i M_i / \sum N_i \quad (1.3)$$

showing this average to be the arithmetic mean of the molar mass distribution. It is often more convenient to use weight fractions rather than numbers of molecules. The weight fraction w_i is defined as the mass of molecules of molar mass M_i divided by the total mass of all the molecules present

$$\text{i.e. } w_i = N_i M_i / \sum N_i M_i \quad (1.4)$$

from which it can be deduced that

$$\sum (w_i / M_i) = \sum N_i / \sum N_i M_i \quad (1.5)$$

Combining Equations (1.3) and (1.5) gives $\bar{M}_n$ in terms of weight fractions

$$\bar{M}_n = 1 / \sum (w_i / M_i) \quad (1.6)$$

The *weight-average molar mass* ($\bar{M}_w$) is defined as 'the sum of the products of the molar mass of each fraction multiplied by its weight fraction'

$$\text{i.e. } \bar{M}_w = \sum w_i M_i \quad (1.7)$$

By combining this equation with Equation (1.4) $\bar{M}_w$ can be expressed in terms of the numbers of molecules

$$\bar{M}_w = \sum N_i M_i^2 / \sum N_i M_i \quad (1.8)$$

The ratio $\bar{M}_w / \bar{M}_n$ must by definition be greater than unity for a *polydisperse* polymer and is known as the *polydispersity* or *heterogeneity index*. Its value often is used as a measure of the breadth of the molar mass distribution, though it is a poor substitute for knowledge of the complete distribution curve. Typically $\bar{M}_w / \bar{M}_n$ is in the range 1.5–2.0, though there are many polymers which have smaller or very much larger values of polydispersity index. A perfectly *monodisperse* polymer would have $\bar{M}_w / \bar{M}_n = 1.00$.

Higher molar mass averages sometimes are quoted. For example, certain methods of molar mass measurement (e.g. sedimentation equilibrium) yield the *z-average molar mass* ($\bar{M}_z$) which is defined as follows

$$\bar{M}_z = \sum N_i M_i^3 / \sum N_i M_i^2 = \sum w_i M_i^2 / \sum w_i M_i \quad (1.9)$$

In addition, more complex exponent averages can be obtained (e.g. by dilute solution viscometry and sedimentation measurements).

Degree of polymerization averages are of more importance than molar mass averages in the theoretical treatment of polymers and polymerization, as will be highlighted in the subsequent chapters. For homopolymers they may be obtained simply by dividing the corresponding molar mass average by M_0 . Thus the *number-average* and *weight-average degrees of polymerization* are given by

$$\bar{x}_n = \bar{M}_n / M_0 \quad (1.10)$$

$$\text{and } \bar{x}_w = \bar{M}_w / M_0 \quad (1.11)$$

Further reading

- Billmeyer, F.W. (1984), *Textbook of Polymer Science*, 3rd edn, Wiley-Interscience, New York.
- Cowie, J.M.G. (1973), *Polymers: Chemistry and Physics of Modern Materials*, International Textbook Company, Aylesbury, UK.
- Elias, H-G. (1987), *Mega Molecules*, Springer-Verlag, Berlin.
- ICI Plastics Division (1962), *Landmarks of the Plastics Industry*, Kynoch Press, Birmingham.
- Jenkins, A.D. and Loening, K.L. (1989), 'Nomenclature' in *Comprehensive Polymer Science*, Vol. 1 (ed. C. Booth and C. Price), Pergamon Press, Oxford.
- Kaufman, M. (1963), *The First Century of Plastics — Celluloid and its Sequel*, The Plastics Institute, London.
- Mandelkern, L. (1983), *An Introduction to Macromolecules*, 2nd edn, Springer-Verlag, New York.
- Mark, H.F. (1970), *Giant Molecules*, Time-Life Books, New York.
- Morawetz, H. (1985), *Polymers — The Origins and Growth of a Science*, John Wiley, New York.
- Treloar, L.R.G. (1970), *Introduction to Polymer Science*, Wykeham Publications, London.

2 Synthesis

2.1 Classification of polymerization reactions

The most basic requirement for polymerization is that each molecule of monomer must be capable of being linked to two (or more) other molecules of monomer by chemical reaction, i.e. monomers must have a *functionality* of two (or higher). Given this relatively simple requirement, there are a multitude of chemical reactions and associated monomer types that can be used to effect polymerization. To discuss each of these individually would be a major task which fortunately is not necessary since it is possible to place most polymerization reactions in one of two classes, each having distinctive characteristics.

The classification used in the formative years of polymer science was due to Carothers and is based upon comparison of the molecular formula of a polymer with that of the monomer(s) from which it was formed. *Condensation polymerizations* are those which yield polymers with repeat units having fewer atoms than present in the monomers from which they are formed. This usually arises from chemical reactions which involve the elimination of a small molecule (e.g. H_2O , HCl). *Addition polymerizations* are those which yield polymers with repeat units having identical molecular formulae to those of the monomers from which they are formed. Table 1.1 (Section 1.2.2) contains examples of each class: the latter three examples are condensation polymerizations involving elimination of H_2O , whereas the others are addition polymerizations.

Carothers' method of classification was found to be unsatisfactory when it was recognized that certain condensation polymerizations have the characteristic features of typical addition polymerizations and that some addition polymerizations have features characteristic of typical condensation polymerizations. A better basis for classification is provided by considering the underlying polymerization mechanisms, of which there are two general types. Polymerizations in which the polymer chains grow step-wise by reactions that can occur between any two molecular species are known as *step-growth* polymerizations. Polymerizations in which a polymer chain grows only by reaction of monomer with a reactive end-group on the growing chain are known as *chain-growth* polymerizations, and usually require an initial reaction between the monomer and an *initiator* to start the growth of the chain. There has been a tendency in recent years to change these names to *step polymerization* and *chain polymerization*, and this practice will be used here. The essential