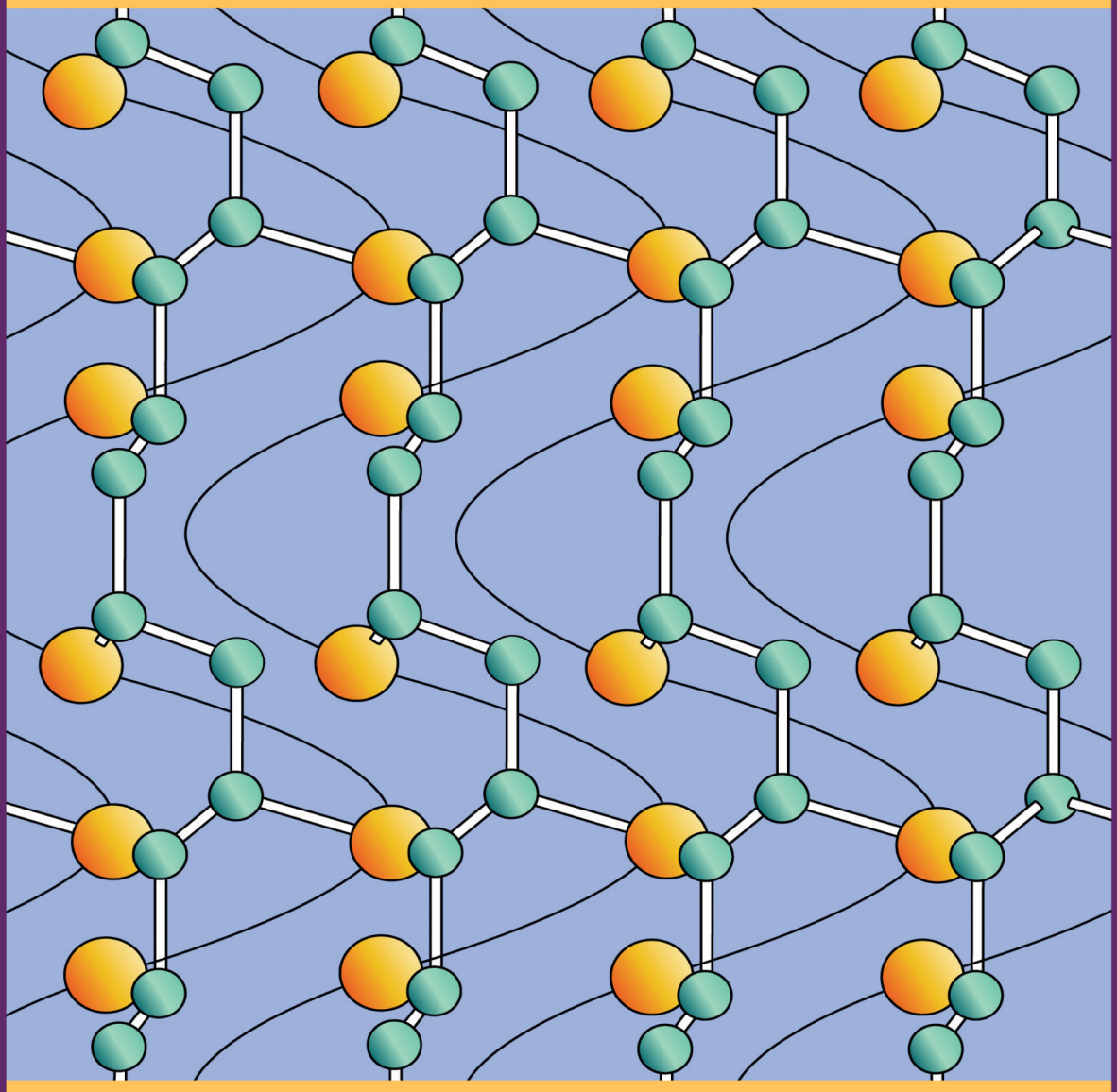
INTRODUCTION TO POLYMERS

Third Edition



Robert J. Young and Peter A. Lovell

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Preface to the Third Edition

The second edition of this book was published at the start of a decade during which the discipline of polymer science saw several major developments come to fruition, including methods for effecting 'living' radical polymerization, dendrimer and hyperbranched polymer syntheses, use of metallocene catalysts for the polymerization of olefins, ring-opening methathesis polymerization, methods for the synthesis of inherently conducting polymers and their use in electronic devices, advanced high-performance polymer composites and specialized biomedical applications (both structural and functional). Theoretical understanding of polymers matured further during this time with scaling concepts, reptation theory, mechanisms for toughening polymers, and understanding of phase separation behaviour of multicomponent polymer systems becoming established in mainstream polymer science. Since the beginning of the new millennium, these advances have evolved to the point where they are now routine and used by the many scientists and engineers working on polymers in both academia and industry. Furthermore, during the past 20 years, the significance of developments in polymer science has been recognized by award of several polymer-related Nobel Prizes in both chemistry and physics. Over the same period, the use of polymers has continued to grow and diversify, particularly into medicine, electronics and aerospace applications.

Thus, the content of the second edition had become somewhat dated by midway through the past decade and preparation of a third edition was an imperative. In planning the new edition, we have taken the opportunity not only to include the science which underpins the important new developments and to bring the subject matter up to date, but also to completely reorganize the book into a more visibly coherent form that, we hope, readers will appreciate, whether the book is used as a basis for teaching or for learning the fundamental aspects of contemporary polymer science. The original 5 chapters have been reorganized into 25 self-contained chapters grouped into 4 parts that focus on (1) concepts and synthesis, (2) characterization, (3) structure and morphology, and (4) properties. Whilst retaining the overall balance between these themes, the content of each previous chapter has been reconsidered in detail, revised, reorganized where appropriate and expanded significantly to include the new developments. Anyone who is familiar with the second edition will recognize the previous material, but also should instantly feel the freshness and accessibility of the new structure.

Each of the chapters on polymer synthesis (Part I) has been expanded to include the most important new developments at a depth designed to inform the selection of appropriate method(s) for the synthesis of particular polymer structures and to facilitate the understanding of polymerization mechanisms and kinetics. Some of the more obvious new topics are 'living' radical polymerization, various methods for the synthesis of conducting polymers, strategies for the synthesis of dendrimers and hyperbranched polymers, metallocene polymerization and strategies for block copolymer synthesis. There also are many other less obvious additions, such as modern methods for the evaluation of rate coefficients in radical polymerization, catalytic chain transfer, non-linear radical polymerizations, free-radical ring-opening polymerization, supramolecular polymers and graft copolymer synthesis. Additionally, polymerization mechanisms have been made more explicit by showing electron movements.

The coverage of polymer characterization (Part II) has been expanded to show the complete derivations of the Flory–Huggins theory and the related theory for phase separation behaviour of polymer solutions, and to give a more thorough description of dynamic light scattering. New topics such as diffusion, solution behaviour of polyelectrolytes and field-flow fractionation methods have been added. And there is a major expansion of the coverage of spectroscopic methods, to which is devoted a complete chapter with new topics that include UV-visible spectroscopy, Raman spectroscopy, use

of NMR spectroscopy for the determination of detailed structure, including sequence distributions, and methods of mass spectrometry.

The topics under structure and morphology (Part III) have been rearranged so that the amorphous state is covered (more logically) ahead of the crystalline state. Completely new material on macromolecular dynamics and reptation, on liquid crystalline polymers and on thermal analysis, has been included. In addition, a complete new chapter on multicomponent polymer systems has been added to reflect the growth in importance of polymer blends and block copolymers, and the maturity in the understanding of such materials. Many of the diagrams and micrographs have been updated to more clearly highlight features of polymer morphology.

The topics under polymer properties (Part IV) also benefit from the breakdown into separate chapters and contain the most obvious changes compared to the second edition, with two completely new topics dealt with in chapters on composites and on electrical properties. The previous material has been reorganized into five chapters, which now include topics such as effects of chain entanglements, swelling of elastomers, impact behaviour, ductile fracture and a more thorough coverage of the rubber-toughening of brittle plastics.

Although the new edition expands upon the previous material and adds many new topics and concepts, the philosophy of the book is unchanged and is designed for teaching and learning at both undergraduate and postgraduate levels, as well as for scientists in industry and research. As before, it is written, as far as possible, to be self-contained with most equations derived fully and topics cross-referenced between chapters where appropriate. The new structure should assist learning and the teaching of specific subjects. At the end of each chapter, a list of further reading material is provided to assist the reader in expanding their knowledge of the subject, and sets of problems are given to test understanding, particularly of numerical aspects.

The preparation of the third edition has been a major undertaking that has been fitted in amongst many other conflicting commitments, both private and professional, and its completion would not have been possible without the help and support of other people. The authors would like to thank their colleagues, former students and friends from around the world who have provided material for the new edition and given helpful comments on certain aspects of the manuscript. Finally, they again would like to thank their families for the support they have shown through the long period of time that it has taken to prepare this new edition.

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Part I

Concepts, Nomenclature and Synthesis of Polymers

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1 Concepts and Nomenclature

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 the production of cellophane film.

The polymeric materials described so far are semi-synthetic since they are produced from natural polymers. Leo Baekeland's phenol–formaldehyde 'Bakelite' 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

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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, and as the discipline of polymer science progresses into the twenty-first century there is increasing emphasis on the development of more specialized, functional polymers for biomedical, optical and electronic applications.

Whilst polymer science undoubtedly is now a mature subject, its breadth and importance continue to increase and there remain 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 Figure 1.1.

Cyclic polymers (*ring polymers*) have no chain ends and show properties that are quite different to their linear counterparts. *Branched polymers* have side chains, or *branches*, of significant length which are bonded to the main chain at *branch points* (also known as *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.

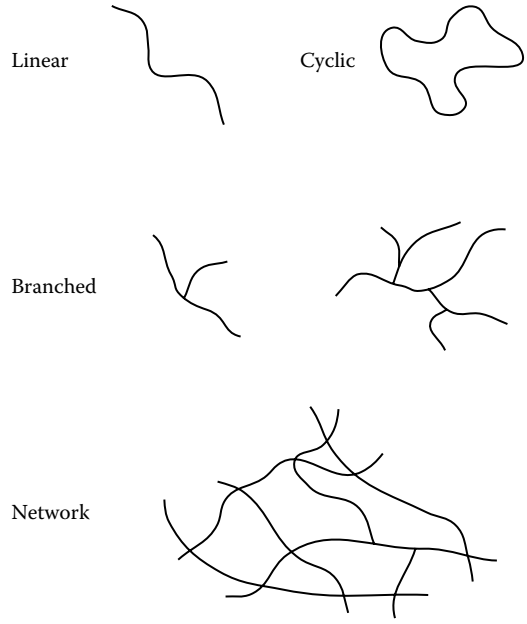


FIGURE 1.1 Skeletal structures representative of linear, cyclic and non-linear polymers.

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

These 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 described 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.

In addition to these more conventional skeletal structures, there has been growing interest in more elaborate skeletal forms of macromolecules. Of particular interest are *dendrimers*, which are highly branched polymers of well-defined structure and molar mass, and *hyperbranched polymers*, which are similar to dendrimers but have a much less well-defined structure and molar mass. Simple depictions of their skeletal structures are shown in Figure 1.2. Research into these types of polymers intensified during the 1990s and they are now beginning to find applications which take advantage of their unusual properties. For example, because of their high level of branching, they are extremely crowded but as a consequence have voids and channels within the molecule and have a

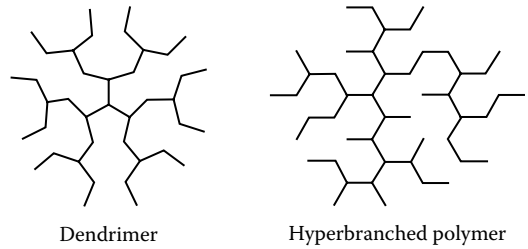


FIGURE 1.2 Skeletal structures representative of dendrimers and hyperbranched polymers.

large number of end groups around their periphery that can be functionalized, leading to therapeutic applications such as in targeted drug delivery.

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 ~~A–A–A–A–A–A–A–A~~ is represented by $-\left[\mathrm{A}\right]_n-$ 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. Entries (9) and (10) in Table 1.1 are examples of homopolymers for which the repeat unit contains two monomer (structural) units; for each of the other examples, the repeat unit and the monomer unit are the same.

The naming of polymers, or envisaging of 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 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 (9) and (10) 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 the 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 (9) and (10) 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 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

~~B–B–B–A–B–B–A–B–A–A~~

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

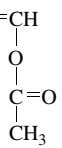
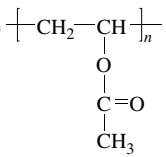
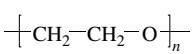
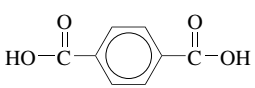
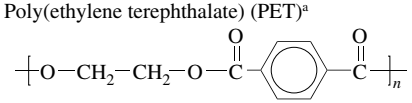
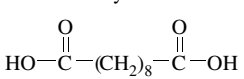
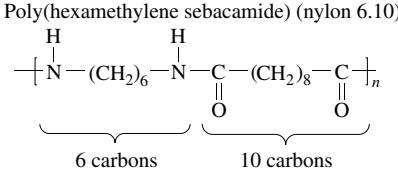
~~A–B–A–B–A–B–A–B–A–B~~

TABLE 1.1
Some Common Homopolymers

Monomers	Polymer	Comments
1. Ethylene $CH_2{=}CH_2$	Polyethylene (PE) $\left[CH_2{-}CH_2\right]_n$	Moulded objects, tubing, film, electrical insulation, e.g. ‘Alkathene’, ‘Lupolen’.
2. Propylene $CH_2{=}CH(CH_3)$	Polypropylene (PP) $\left[CH_2{-}CH(CH_3)\right]_n$	Similar uses to PE; lower density, stiffer, e.g. ‘Propathene’, ‘Novolen’.
3. Tetrafluoroethylene $CF_2{=}CF_2$	Polytetrafluoroethylene (PTFE) $\left[CF_2{-}CF_2\right]_n$	Mouldings, film, coatings; high temperature resistance, chemically inert, excellent electrical insulator, very low coefficient of friction; expensive, e.g. ‘Teflon’, ‘Fluon’.
4. Styrene $CH_2{=}CH(C_6H_5)$	Polystyrene (PS) $\left[CH_2{-}CH(C_6H_5)\right]_n$	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.
5. Methyl methacrylate $CH_2{=}C(CH_3)C(=O)OCH_3$	Poly(methyl methacrylate) (PMMA) $\left[CH_2{-}C(CH_3)(C(=O)OCH_3)\right]_n$	Transparent sheets and mouldings; used for aeroplane windows; more expensive than PS, e.g. ‘Perspex’, ‘Diakon’, ‘Lucite’, ‘Oroglass’, ‘Plexiglas’.
6. Vinyl chloride $CH_2{=}CH(Cl)$	Poly(vinyl chloride) (PVC) $\left[CH_2{-}CH(Cl)\right]_n$	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’.

(*continued*)

TABLE 1.1 (continued)
Some Common Homopolymers

Monomers	Polymer	Comments
7. Vinyl acetate 	Poly(vinyl acetate) 	Surface coatings, adhesives, chewing gum.
8. Ethylene oxide 	Poly(ethylene oxide) (PEO) 	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)[a] 	Textile fibres, film, bottles, e.g. ‘Terylene’, ‘Dacron’, ‘Melinex’, ‘Mylar’.
10. Hexamethylene diamine H_2N—$(CH_2)_6$—NH_2 and sebacic acid 	Poly(hexamethylene sebacamide) (nylon 6.10)[a] 	Mouldings, fibres, e.g. ‘Ultramid 6.10’.

[a] The polymer has two monomer units in the repeat unit.

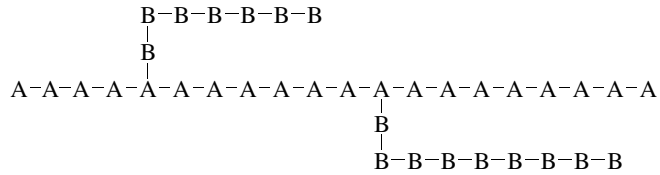
Statistical, random and alternating copolymers generally have properties which are intermediate to those of the corresponding homopolymers. Thus by preparing such copolymers, it is possible to combine the desirable properties of the homopolymers into a single material. This is not normally possible by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

A–A–A–A–A–A–A–A–A–A–B–B–B–B–B–B–B–B–B–B

A–A–A–A–A–A–A–A–B–B–B–B–B–B–B–B–A–A–A–A–A–A–A–A

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 copolymers described earlier, block and graft copolymers usually show properties characteristic of each of the constituent homopolymers. They also have some unique properties that arise because the chemical linkage(s) between the homopolymer sequences prevent 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 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 Figure 1.3 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 become liquid 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 in commercial production. Generally, thermoplastics do not crystallize easily upon cooling to the solid state because this

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[a]	PolyA-*graft*-polyB

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

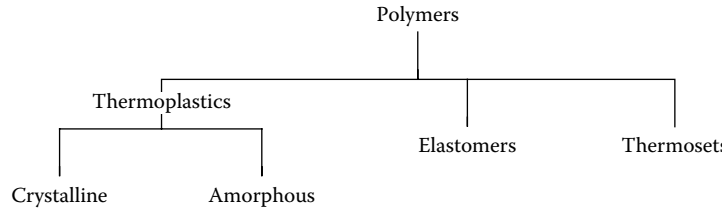


FIGURE 1.3 Classification of polymers.

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, above which such polymers can be converted into artefacts by conventional polymer-processing techniques such as extrusion, injection moulding and compression moulding.

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.

It is a common misnomer that completely amorphous polymers 'melt'; they do not (because they have no ordered phases, there is nothing to melt!) and may simply be considered as reducing steadily in viscosity as temperature increases above T_g until the viscosity becomes low enough for so-called melt processing.

Elastomers are crosslinked rubbery polymers (i.e. rubbery networks) that can be stretched easily to high extensions (e.g. 3× to 10× 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 that 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 become fluid upon the application of heat. Hence, their processing into artefacts is often done using processes, such as compression moulding, that require minimum amounts of flow.

1.3 MOLAR MASS AND DEGREE OF POLYMERIZATION

Many properties of polymers show a strong dependence upon the size of the polymer chains, so 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 mol 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. ~10^{-19} to ~10^{-18} 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 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

$$M = xM_0 \tag{1.1}$$

where M_0 is the molar mass of the repeat unit. Equation 1.1 also can be used for copolymers, but M_0 needs to be replaced by M_0^{cop}, which is the mean repeat unit molar mass of the copolymer taking into account its composition

$$M_0^{\text{cop}} = \sum X_j M_0^j \tag{1.2}$$

where

X_j is the mole fraction, and

M_0^j the molar mass of repeat units of type 'j' in the copolymer.

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 Figure 1.4.

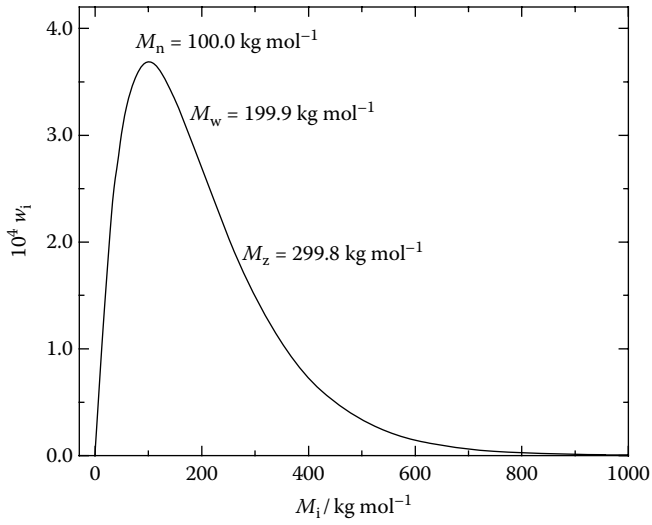


FIGURE 1.4 A typical weight-fraction molar mass distribution curve (for a polymer with the most probable distribution of molar mass and a repeat unit molar mass of 100 g mol^{-1}).

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, i.e.

$$\bar{M}_n = \sum X_i M_i \tag{1.3}$$

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

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \tag{1.4}$$

showing this average to be the arithmetic mean of the molar mass distribution. It often is 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, i.e.

$$w_i = \frac{N_i M_i}{\sum N_i M_i} \tag{1.5}$$

from which it can be deduced that

$$\sum \left(\frac{w_i}{M_i} \right) = \frac{\sum N_i}{\sum N_i M_i} \tag{1.6}$$

Combining Equations 1.4 and 1.6 gives $\bar{M}_n$ in terms of weight fractions

$$\bar{M}_n = \frac{1}{\sum \left(w_i / M_i \right)} \tag{1.7}$$

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, i.e.

$$\bar{M}_w = \sum w_i M_i \tag{1.8}$$

By combining this equation with Equation 1.5, $\bar{M}_w$ can be expressed in terms of the numbers of molecules

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{1.9}$$

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* (often referred to as *PDI*). 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 $\bar{M}_w/\bar{M}_n = 1.00$.

It should be noted that in 2009 IUPAC (the international organization which defines nomenclature and terminology in pure and applied fields of chemistry) criticized use of the long-established terms 'monodisperse' (because it is a self-contradictory word) and 'polydisperse'/'polydispersity' (because they are tautologous). Paraphrasing their comments, they recommended that a polymer sample composed of a single macromolecular species should be called a *uniform polymer* (instead of monodisperse) and a polymer sample composed of macromolecular species of differing molar masses a *non-uniform polymer* (instead of polydisperse). They further recommended that polydispersity should be replaced by a new term, *dispersity* (given the symbol $Đ$), such that $Đ_M$ is the molar mass dispersity (= $\bar{M}_w/\bar{M}_n$), $Đ_X$ is the degree-of-polymerization dispersity (= $\bar{x}_w/\bar{x}_n$) and for most polymers $Đ = Đ_M = Đ_X$. It is much too early to know whether these new terms will become embedded in the vocabulary of, and future publications from, the world polymer community, but they are used from here onwards in this book because the recommendations are sensible and based on use of good English.

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

$$\bar{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum w_i M_i^2}{\sum w_i M_i} \tag{1.10}$$

In addition, averages with more complex exponents are obtained from other methods of polymer characterization (e.g. from 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

$$\bar{x}_n = \frac{\bar{M}_n}{M_0} \tag{1.11}$$

and

$$\bar{x}_w = \frac{\bar{M}_w}{M_0} \tag{1.12}$$

The same equations can be applied to calculate $\bar{x}_n$ and $\bar{x}_w$ for copolymers by replacing M_0 with M_0^{cop}.

PROBLEMS

1.1 A sample of polystyrene is found to have a number-average molar mass of 89,440 g mol^{-1}. Neglecting contributions from end groups, calculate the number-average degree of polymerization of this sample.

Assuming that the sample has a molar mass dispersity of 1.5, calculate its weight-average molar mass.

1.2 Calculate the mean repeat unit molar mass for a sample of poly[ethylene-*stat*-(vinyl acetate)] that comprises 12.9 wt% vinyl acetate repeat units. Given that its number-average molar mass is 39,870 g mol^{-1}, calculate the number-average degree of polymerization of the copolymer.

1.3 Three mixtures were prepared from three very narrow molar mass distribution polystyrene samples with molar masses of 10,000, 30,000 and 100,000 g mol^{-1} as indicated below:

(a) Equal numbers of molecules of each sample
(b) Equal masses of each sample
(c) By mixing in the mass ratio 0.145:0.855 the two samples with molar masses of 10,000 and 100,000 g mol^{-1}

For each of the mixtures, calculate the number-average and weight-average molar masses and comment upon the meaning of the values.

FURTHER READING

General Historical and Introductory Reading

Note that although many of these textbooks use old terminology and are out of print, they do provide very good, simple introductions to polymer science and can be found in libraries.

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Jenkins, A.D. and Loening, K.L., Nomenclature, in *Comprehensive Polymer Science*, Allen, G. and Bevington, J.C. (eds), Chap. 2, Vol. 1 (Booth, C. and Price, C., eds), Pergamon Press, Oxford, U.K., 1989.
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2 Principles of Polymerization

2.1 INTRODUCTION

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. Consequently, the number of different synthetic polymers that have been prepared is extremely large and many can be formed by more than one type of polymerization. Hence, the number of individually different polymerization reactions that have been reported is extraordinarily large. To discuss each of these would be an enormous task which fortunately is not necessary since it is possible to categorize most polymerization reactions into a relatively small number of classes of polymerization, each class having distinctive characteristics.

The purpose of this chapter is to set out some of the most important guiding principles of polymerization. These principles are built upon in the following chapters on polymerization, which give details of the chemistry and kinetics of the most important types of polymerization in use today.

2.2 CLASSIFICATION OF POLYMERIZATION REACTIONS

The classification of polymerization reactions 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 are 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 contains examples of each class: the latter two 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.

The modern preference is to simplify these names to *step polymerization* and *chain polymerization*, and this practice will be used here. The essential differences between these classes of polymerization are highlighted in Table 2.1 which illustrates for each mechanism the reactions involved in growth of the polymer chains to a degree of polymerization equal to eight.

In step polymerizations the degree of polymerization increases steadily throughout the reaction, but the monomer is rapidly consumed in its early stages (e.g. when $\bar{x}_n = 10$ only 1% of the monomer

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TABLE 2.1
A Schematic Illustration of the Fundamental Differences in Reaction Mechanism between Step Polymerization and Chain Polymerization[a]

Formation of	Step Polymerization	Chain Polymerization
Dimer	o+o → o–o	I+o → I–o
		I–o+o → I–o–o
Trimer	o–o+o → o–o–o	I–o–o+o → I–o–o–o
Tetramer	o–o–o+o → o–o–o–o	I–o–o–o+o → I–o–o–o–o
	o–o+o–o → o–o–o–o	
Pentamer	o–o–o–o+o → o–o–o–o–o	I–o–o–o–o+o → I–o–o–o–o–o
	o–o+o–o–o → o–o–o–o–o	
Hexamer	o–o–o–o–o+o → o–o–o–o–o–o	I–o–o–o–o–o+o → I–o–o–o–o–o–o
	o–o+o–o–o–o → o–o–o–o–o–o	
	o–o–o+o–o–o → o–o–o–o–o–o	
Heptamer	o–o–o–o–o–o+o → o–o–o–o–o–o–o	I–o–o–o–o–o–o+o → I–o–o–o–o–o–o–o
	o–o+o–o–o–o–o → o–o–o–o–o–o–o	
	o–o–o+o–o–o–o → o–o–o–o–o–o–o	
Octomer	o–o–o–o–o–o–o+o → o–o–o–o–o–o–o–o	I–o–o–o–o–o–o–o+o → I–o–o–o–o–o–o–o–o
	o–o+o–o–o–o–o–o → o–o–o–o–o–o–o–o	
	o–o–o+o–o–o–o–o → o–o–o–o–o–o–o–o	
	o–o–o–o+o–o–o–o → o–o–o–o–o–o–o–o	

[a] I = initiator species, o = molecule of monomer and repeat unit, – = chemical link.

remains unreacted). All the polymer chains continue to grow throughout the reaction as the conversion of functional groups into chain links increases. Carothers was quick to recognize that in order to attain even moderately high degrees of polymerization ($\bar{x}_n > 100$), the extent of reaction of functional groups needs to be extremely high (greater than 99.9%), something that he set about achieving by careful design of laboratory apparatus. This key feature of step polymerizations also highlights the importance of using *clean* reactions in which contributions from side reactions are completely absent or negligibly small.

By contrast, in chain polymerizations, high degrees of polymerization are attained at low monomer conversions, the monomer being consumed steadily throughout the reaction. After its growth has been initiated, each polymer chain forms rapidly by successive additions of molecules of monomer to the reactive site at the chain end. In many chain polymerizations, more than 1000 repeat units are added to a single propagating chain in less than a second and the activity of the chain is lost (i.e. its activity dies and it can no longer propagate) after only a fraction of a second or a few seconds of chain growth. As the percentage conversion of monomer into polymer increases, it is simply the number of polymer molecules formed that increases; the degree of polymerization of those polymer molecules already formed does not change.

2.3 MONOMER FUNCTIONALITY AND POLYMER SKELETAL STRUCTURE

The *functionality* of a monomer is best defined as the number of chain links it can give rise to, because it is not necessarily equal to the number of functional groups present in the monomer, i.e. it is not always immediately obvious from the chemical structure of the monomer. The first seven examples in Table 1.1 are of polymers formed by chain polymerizations of olefinic monomers which contain a single C=C double bond; these monomers have a functionality of two because each C=C

double bond gives rise to two chain links. The eighth example is of a ring-opening chain polymerization of an epoxide group which also gives rise to two chain links; hence ethylene oxide also has a functionality of two. The remaining two examples in Table 1.1 are step polymerizations of monomers that have functional groups which are mutually reactive towards each other; in these examples, each monomer possesses two functional groups and has a functionality of two because each functional group can give rise to only a single chain link by reaction with the complementary functional group (e.g. in example (9) of Table 1.1, a $-CO_2H$ group reacts with a –OH group to give a single ester chain link with loss of H_2O). Thus all the examples in Table 1.1 are of *linear polymerizations* of monomers with a functionality of two.

If a monomer has a functionality greater than two, then this will lead to the formation of branches and possibly to the formation of a network polymer, depending on the particular polymerization and

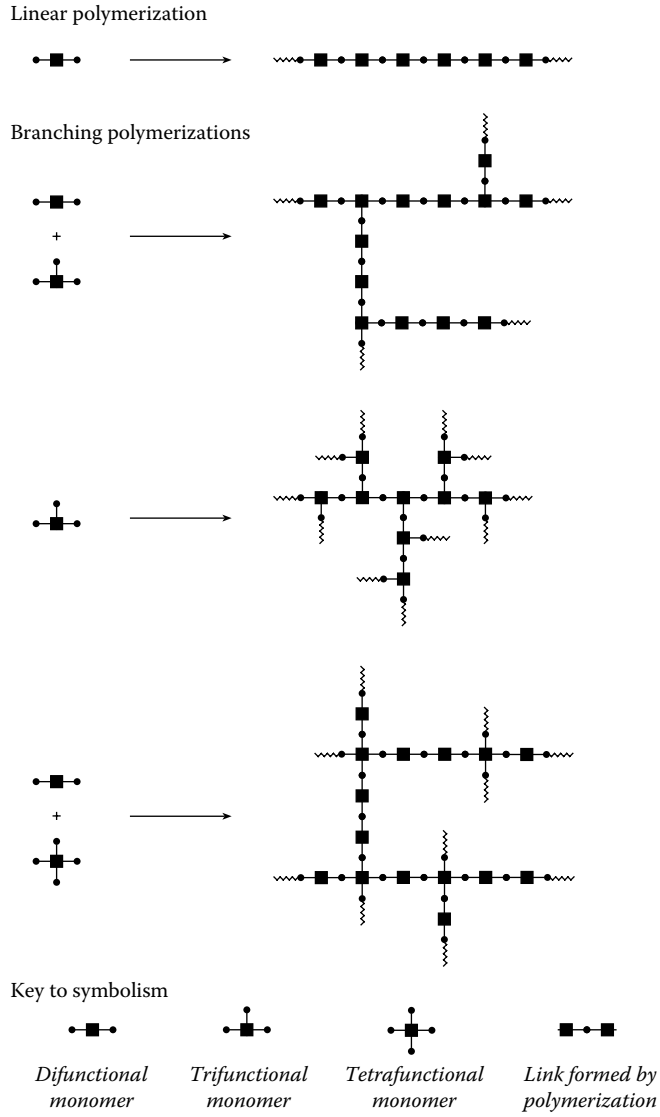


FIGURE 2.1 Schematic representations of how polymer skeletal structure is affected by monomer functionality.

reactant stoichiometry. The effect of monomer functionality is illustrated schematically in Figure 2.1. Although this depiction of the effect of monomer functionality is very much an oversimplification, it nevertheless demonstrates the importance of functionality. The formation of dendrimers and hyperbranched polymers is achieved using monomers with functionalities of three or higher, but in a way that is controlled so that a network polymer cannot form.

2.4 FUNCTIONAL GROUP REACTIVITY AND MOLECULAR SIZE: THE PRINCIPLE OF EQUAL REACTIVITY

Chemical reactions proceed as a consequence of collisions during encounters between mutually-reactive functional groups. At each encounter, the functional groups collide repeatedly until they either diffuse apart or, far more rarely, react. Under normal circumstances, the reactivity of a functional group depends upon its collision frequency and not upon the collision frequency of the molecule to which it is attached. As molecular size increases, the rate of molecular diffusion decreases, leading to larger time intervals between encounters (i.e. to fewer encounters per unit time). This effect is compensated by the greater duration of each encounter giving rise to a larger number of functional group collisions per encounter. Hence the reactivity of a functional group can be expected to be approximately independent of molecular size.

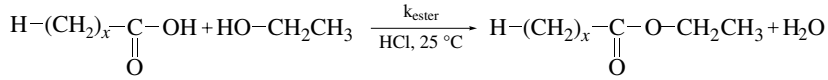
Mathematical analysis of polymerizations is simplified greatly by assuming that the intrinsic reactivity of a functional group is independent of molecular size and unaffected by the reaction of other functional group(s) in the molecule of monomer from which it is derived. This principle of *equal reactivity of functional groups* was proposed by Flory who demonstrated its validity for functional groups in many step polymerizations by examining the kinetics of model reactions. Similarly, analysis of the kinetics of chain polymerizations shows that it is reasonable to assume that the reactivity of the active species at the chain end is independent of the degree of polymerization.

PROBLEMS

2.1 Polymerization of vinyl chloride produces poly(vinyl chloride) of high molar mass at low monomer conversions, whereas polymerization of ethylene glycol with terephthalic acid produces poly(ethylene terephthalate) of high molar mass only at very high conversions of the –OH and $–CO_2H$ groups. (See entries (6) and (9) in Table 1.1 for the chemical structures of the monomers and polymers.)

For each polymerization, explain what the observations indicate in terms of the type of polymerization taking place.

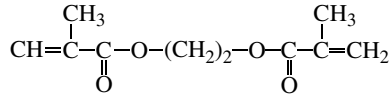
2.2 The following rate coefficient k_{ester} data were obtained from studies of the model esterification reactions shown below. (Data taken from Bhide, B.V. and Sudborough, J.J., *J. Indian Inst. Sci*., 8A, 89, 1925.)



x	1	2	3	4	5	8	9	11	13	15	17
k_{ester} / 10^{-4} dm^3 mol^{-1} s^{-1}	22.1	15.3	7.5	7.5	7.4	7.5	7.4	7.6	7.5	7.7	7.7

Discuss briefly the significance of these data for kinetics analysis of polyester formation.

2.3 Describe the effects on the *skeletal* structure of the polymer produced, if some ethylene glycol dimethacrylate were included in a polymerization of methyl methacrylate (see entry (5) of Table 1.1).



Ethylene glycol dimethacrylate

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3 Step Polymerization

3.1 INTRODUCTION

Step polymerizations are, in most cases, logical extensions of simple organic chemistry linking reactions to chain formation and were the first types of polymerizations to be understood from a fundamental perspective, the work of Carothers during the 1920s and 1930s being seminal in this respect. In this chapter, the most important types of step polymerization are introduced and exemplified. The mechanisms of the reactions are not shown because they are identical to the well-established mechanisms of the equivalent small molecule reactions which can be found in any university-level textbook on organic chemistry.

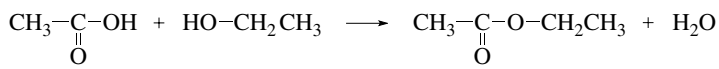
Most step polymerizations involve reactions which produce links that contain a heteroatom and so the polymers normally are grouped into generic classes according to the type of links created in the polymerization. Some of the most common classes of polymers named according to the linking group in the chain backbone are shown in Table 3.1.

The majority of step polymerizations are based on quite simple linking reactions and, for linear step polymerizations, the greatest challenge is the need to take the reactions to extremely high conversions in order to produce chains of sufficient length to realize useful properties. This is very demanding and, as a consequence, most polymers produced by linear step polymerization have molar masses in the range 10–100 kg mol^{-1}, but more often 15–30 kg mol^{-1}, which is much lower than for polymers prepared by chain polymerizations (typically 50–10,000 kg mol^{-1}).

Although this chapter is much shorter than the overall coverage of chain polymerization, this is because of the relative simplicity in the chemistry of step polymerizations and the diversity and relative complexity of the different types of chain polymerization (for which the mechanistic chemistry is presented in the following chapters because it is not covered in standard textbooks on organic chemistry). Thus, despite the shorter coverage in terms of the number of pages devoted to step polymerization, it is important to emphasize that step polymerizations are used extensively for commercial production of polymers, including many of those encountered in everyday life, such as polyesters, polyamides, polyurethanes, polycarbonate and epoxy resins, as well as many high-performance polymers (e.g. Kevlar, PEEK).

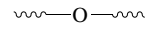
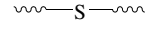
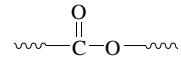
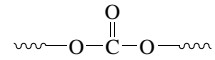
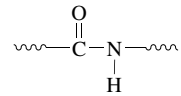
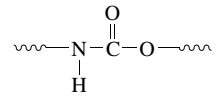
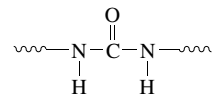
3.2 LINEAR STEP POLYMERIZATION

Step polymerizations involve successive reactions between pairs of mutually-reactive functional groups which initially are provided by the monomer(s). The number of functional groups present on a molecule of monomer is of crucial importance, as can be appreciated by considering the formation of ester linkages from the condensation reaction of carboxylic acid groups with hydroxyl groups. Acetic acid and ethyl alcohol are *monofunctional* compounds which upon reaction together yield ethyl acetate with the elimination of water

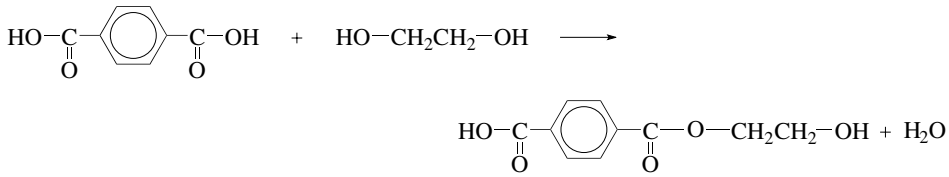


DOI: 10.1201/9781439894156-4

TABLE 3.1
Some Common Classes of Polymer Named according to the Heteroatom-Containing Linking Group in the Chain Backbone

Class of Polymer	Structure of Linking Group
Polyether	
Polysulphide	
Polyester	
Polycarbonate	
Polyamide	
Polyurethane	
Polyurea	

but because ethyl acetate is incapable of further reaction, a polymer chain cannot form. Now consider the reaction between terephthalic acid and ethylene glycol, both of which are *difunctional*



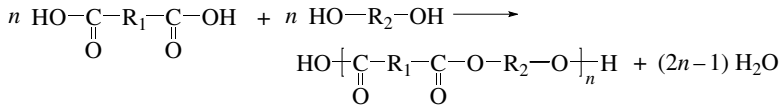
The product of their reaction is an ester which possesses one carboxylic acid end-group and one hydroxyl end-group (i.e. it also is difunctional). This *dimer*, therefore, can react with other molecules of terephthalic acid, ethylene glycol or dimer leading to the formation of *difunctional trimers* or *difunctional tetramer*. Growth of linear polymer chains then proceeds via further condensation reactions in the manner indicated for step polymerization in Table 2.1. Hence *linear step polymerizations* involve reactions of *difunctional monomers*. If a trifunctional monomer were included, reaction at each of the three functional groups would lead to the formation of a branched polymer and may ultimately result in the formation of a network. For example, if terephthalic acid were reacted with glycerol, $HOCH_2CH(OH)CH_2OH$, the product would be a non-linear polyester. It follows that polymerizations involving monomers of functionality greater than two will produce non-linear polymers, as was shown schematically in Figure 2.1 and is covered in detail in Section 3.3.

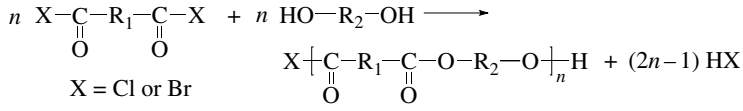
3.2.1 Polycondensation

Step polymerizations that involve reactions in which small molecules are eliminated are termed *polycondensations.*

3.2.1.1 Synthesis of Polyesters, Polyamides and Polyethers by Polycondensation

The formation of linear *polyesters* from reaction of carboxylic acid or acid halide groups with alcohol groups, as described in Section 3.2, is a classic example of polycondensation and may be represented more generally by

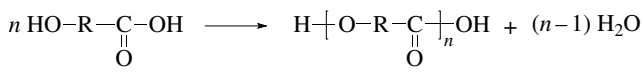




where R_1 and R_2 represent any divalent group (usually hydrocarbon). Reaction between carboxylic acid and alcohol groups is slow and the reactions have to be performed at moderate-to-high temperatures (80–300 °C), usually in the presence of an acid catalyst. The reaction between terephthalic acid and ethylene glycol shown in Section 3.2 produces poly(ethylene terephthalate), the most widely used polyester. Carboxylic acid halides are much more reactive and their reaction with alcohol groups to produce polyesters proceeds at room temperature, so they often are used in simple laboratory syntheses of polyesters.

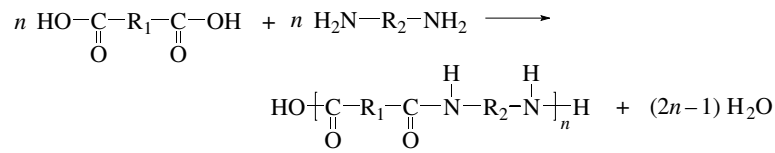
Reactions of the type shown above are referred to as *RA_2+RB_2 step polymerizations* where R is any divalent group and A and B represent the mutually-reactive functional groups.

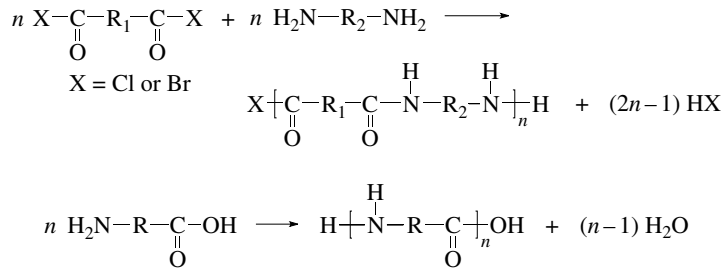
Polyesters also can be prepared from single monomers which contain both types of functional group, i.e. ω-hydroxy carboxylic acids (but not ω-hydroxy carboxylic acid halide monomers because they cannot be synthesized due to the high reactivity of carboxylic acid halide groups towards hydroxyl groups)



With each condensation reaction, the polymer chain grows but remains an ω-hydroxy carboxylic acid and so can react further. This is an example of an *ARB step polymerization*. The use of monomers of this type has the advantage that, provided they are pure, an exact stoichiometric equivalence of the two functional groups is guaranteed. As described quantitatively in Section 3.2.3.1, very slight excesses of one monomer in a RA_2+RB_2 polymerization reduce significantly the attainable degree of polymerization because the polymer chains become terminated with functional groups derived from the monomer present in excess (e.g. both end-groups are ultimately of type B if RB_2 is in excess). Since these functional groups are unreactive towards each other, further growth of the chains is not possible.

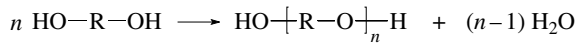
Polyamides can be prepared by polycondensations analogous to those used to prepare polyesters, the hydroxyl groups simply being replaced by amine groups, e.g.



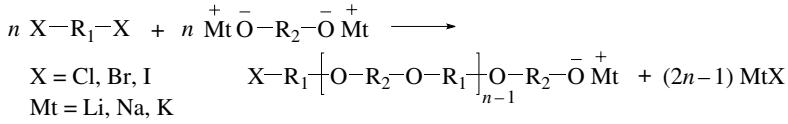


Aliphatic polyamides are called *nylons*, the most important of which are prepared by RA_2+RB_2 polymerization, e.g. nylon 6.6 ($R_1=(CH_2)_4$; $R_2=(CH_2)_6$) and nylon 6.10 ($R_1=(CH_2)_8$; $R_2=(CH_2)_6$), where the first number in the name is the number of carbon atoms in the diamine monomer and the second number is the number of carbon atoms in the diacid (or diacid halide) monomer. Control of the number of carbon atoms in each structural unit is important because this determines the extent to which the amide links in separate chains can align to form hydrogen bonds (see Section 17.8.3.1).

The formation of *polyethers* by dehydration of diols is one of relatively few examples of RA_2 polycondensation



but the polymerization is not very controlled. A much better method for synthesis of polyethers is the RA_2+RB_2 polycondensation of dihalides with dialkoxides



However, most polyethers are prepared by the ring-opening polymerization of epoxides, which is described in detail in Chapter 7.

3.2.1.2 Synthesis of Engineering and High-Performance Polymers by Polycondensation

Polymers with aromatic groups (e.g. 1,4-phenylene units) in the chain backbone tend to have improved mechanical properties and greater resistance to degradation on exposure to heat or radiation, effects which arise from the stiffening effect and high stability of aromatic groups. Such polymers are most easily prepared by step polymerization and find use in engineering and high-performance applications. Some specific examples of important aromatic polymers prepared by polycondensation are shown in Table 3.2.

3.2.1.3 Synthesis of Conducting Polymers by Polycondensation

Some important conducting polymers (Section 25.3.4) can be prepared by polycondensation. Several polycondensation routes to *trans*-poly(1,4-phenylene vinylene) have been developed, some of which are shown below.

(i) $RA_2 + RB_2$ polyaddition via Wittig coupling

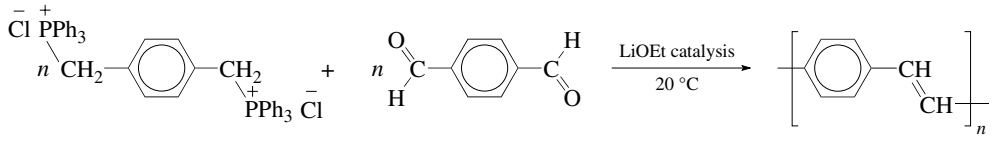
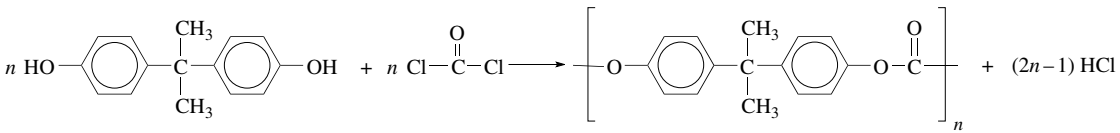
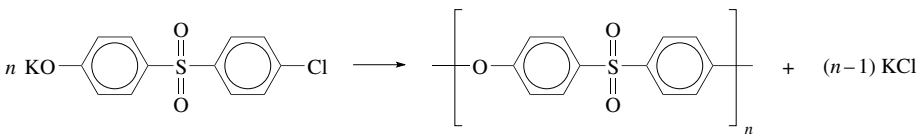
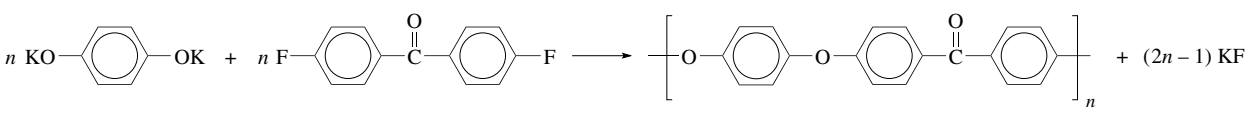
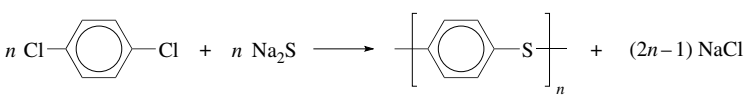
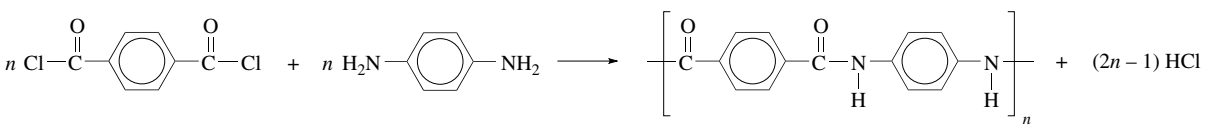
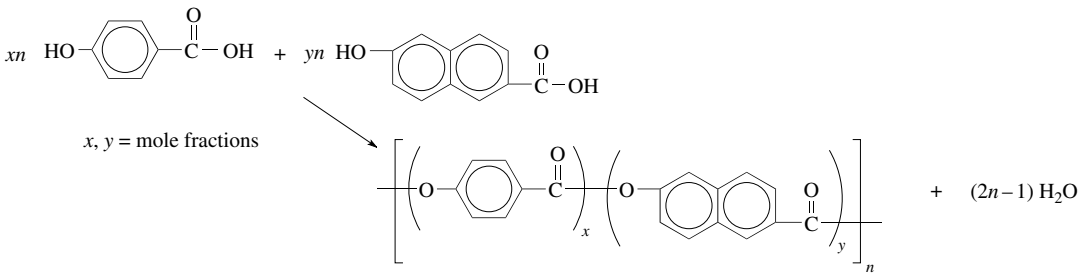
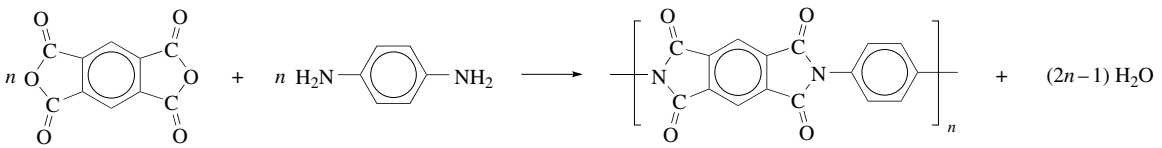
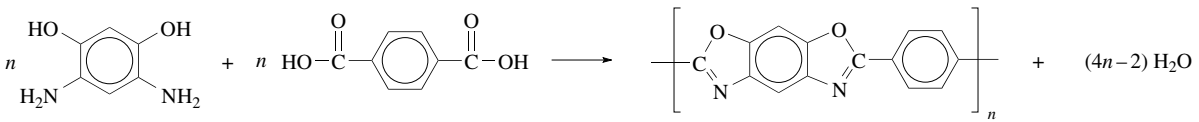


TABLE 3.2
Some Engineering and High-Performance Aromatic Polymers Prepared by Polycondensation

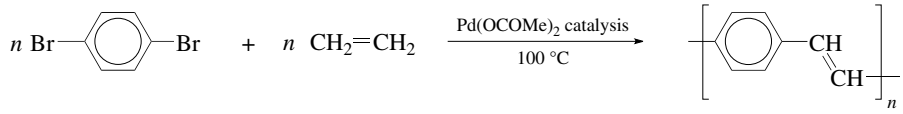
Polycondensation	Comments
 Polycarbonate (PC)	Mouldings and sheet; transparent and tough; used for safety glasses, screens and glazing, e.g. ‘Lexan’, ‘Merlon’
 Polyethersulphone (PES)	Mouldings, coatings, membranes, e.g. ‘Victrex PES’
 Polyetheretherketone (PEEK)	Mouldings, composites, bearings, coatings; very high continuous use temperature (260 °C), e.g. ‘Victrex PEEK’
 Poly(phenylene sulphide) (PPS)	Mouldings, composites, coatings, e.g. ‘Ryton’, ‘Tedur,’ ‘Fortron’
 Poly(*p*-phenylene terephthalamide) (PPTA)	High-modulus fibres, e.g. ‘Kevlar’, ‘Twaron’

(*continued*)

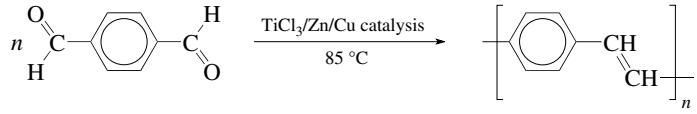
TABLE 3.2 (continued)
Some Engineering and High-Performance Aromatic Polymers Prepared by Polycondensation

Polycondensation	Comments
 Poly[(1,4-benzoate)-*co*-(2,6-naphthoate)]	Liquid crystalline polyester for mouldings and high-modulus fibres, e.g. 'Vectra', 'Vetran'
 A polyimide	Films, coatings, adhesives, laminates, e.g. 'Kapton', 'Vespel'
 Poly(*p*-phenylene benzoxazole) (PBO)	High-modulus fibres, e.g. 'Zylon'

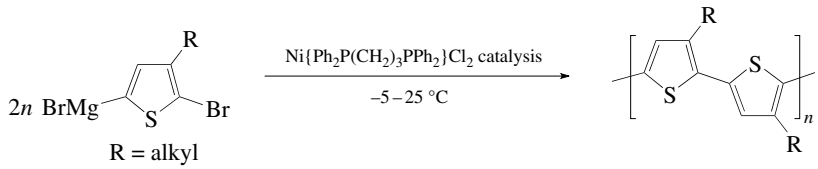
(ii) $RA_2 + RB_2$ polyaddition via Heck coupling



(iii) RA_2 polyaddition via McMurry coupling



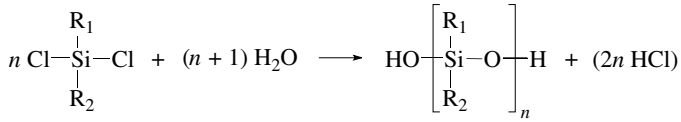
Regioregular poly(3-alkyl-2,5-thiophene)s can be synthesized by ARB polyaddition of semi-Grignard reagents of 2,5-dibromo-3-alkylthiophenes



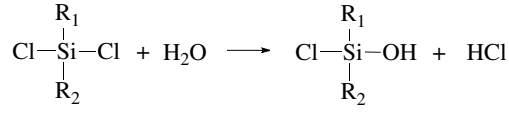
The mechanisms of the reactions described in this section are quite complex, so are not considered here, but they are described in reviews and in more advanced textbooks on organic chemistry.

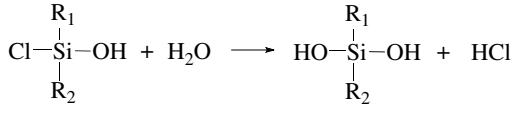
3.2.1.4 Synthesis of Polysiloxanes by Polycondensation

Polysiloxanes (also known simply as *siloxanes*) are unusual in that they have a completely inorganic backbone of –Si–O– bonds, which gives them high thermal stability. Synthesis of polysiloxanes by polycondensation is achieved through hydrolysis of highly-reactive dichlorodialkylsilanes

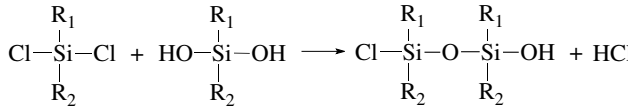


where R_1 and R_2 can be alkyl (e.g. methyl) or aryl (e.g. phenyl) groups and may be different or the same. The polycondensation is unusual in that after partial hydrolysis of the monomer via

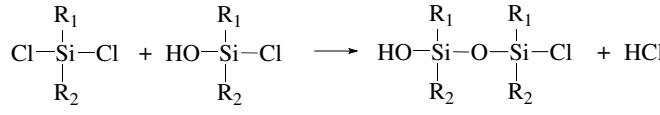


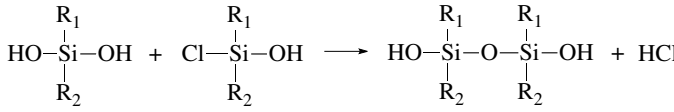


$RA_2 + RB_2$ polymerization

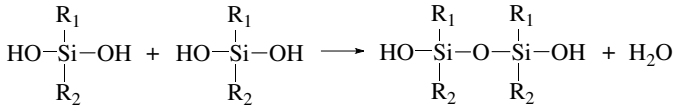


$RA_2 + ARB$ and $RB_2 + ARB$ polymerization

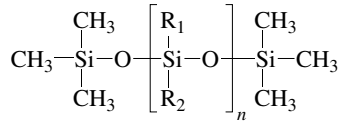




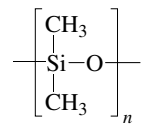
and RA_2 polymerization



can occur simultaneously. In order to control the degree of polymerization attained upon complete hydrolysis (as indicated in the general equation above), it is usual to include monofunctional chlorosilanes, e.g. chlorotrimethylsilane would lead to a polysiloxane with unreactive trimethylsilyl end groups



The most important monomer is dichlorodimethylsilane ($R_1 = R_2 = CH_3$) which produces poly(dimethyl siloxane) (PDMS)



PDMS

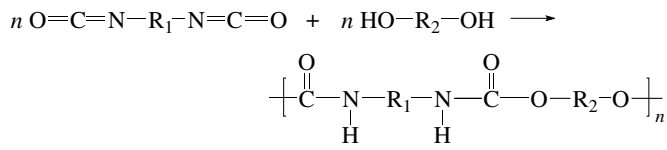
A massive range of commercial grades of PDMS are available, many of which are copolymers prepared by including low levels of other dichlorosilanes as comonomers, e.g. dichlorodiphenylsilane ($R_1 = R_2 = Ph$), which provides repeat units that further enhance thermal stability, and dichloromethylvinylsilane ($R_1 = CH_3$; $R_2 = CH{=}CH_2$), which provides C=C bonds for use in subsequent crosslinking. Polycondensation is used to prepare low-moderate molar mass grades of PDMS, which are liquids or soft solids. High molar mass grades for use as elastomers tend to be produced by ring-opening polymerization of cyclic siloxanes, as described in Chapter 7.

3.2.2 Polyaddition

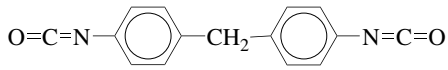
Step polymerizations in which the monomers react together without the elimination of other molecules are termed *polyadditions*. In contrast to polycondensation, there are relatively few important polymers prepared by polyaddition, the most important being polyurethanes and epoxy resins.

3.2.2.1 Synthesis of Linear Polyurethanes and Polyureas by Polyaddition

Linear *polyurethanes* are prepared by RA_2+RB_2 polyaddition of diisocyanates with diols

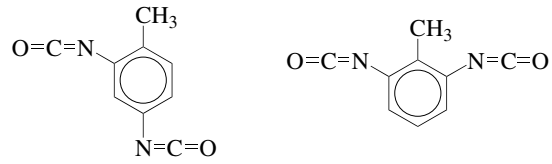


which proceeds quite rapidly at room temperature because isocyanate groups are highly reactive; nevertheless, catalysts often are used to increase the rate of polymerization. The most commonly used diisocyanates are



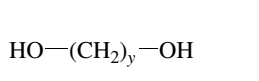
bis(4-isocyanatophenyl)methane,
methylene diphenylene diisocyanate (MDI)

1,6-diisocyanatohexane,
hexamethylene diisocyanate (HDI)

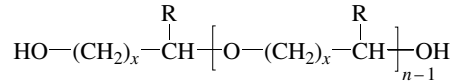


diisocyanatotoluene, toluene diisocyanate (TDI)
(mixed 2,4- and 2,6- isomers; 80% 2,4- in commercial TDI)

An extremely wide range of diols can be used, including simple diols and low molar mass α,ω-dihydroxy polyethers, e.g.



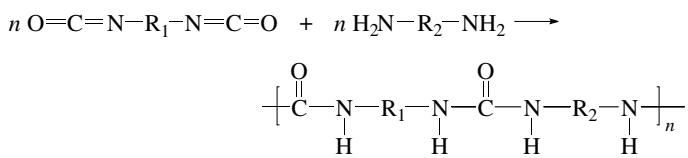
e.g. y = 2,3,4,6



e.g. x = 1, R = H or CH_3; x = 3, R = H

Historically, α,ω-dihydroxy polyesters also have been used, but polyether diols are now preferred. The choice of diisocyanate and diol determines the properties of the polyurethane, which can range from being a rigid solid (if low molar mass diols are used) to a rubbery material (e.g. if poly(propylene oxide) diols with molar masses of about 2–8 kg mol^{-1} are used). Many commercial linear polyurethanes are *segmented copolymers* prepared using a mixture of short- and long-chain diols (see Section 9.4.1).

The analogous reaction of diisocyanates with diamines yields *polyureas*

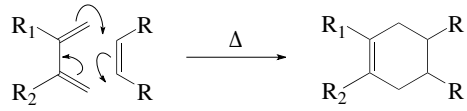


and proceeds at very high rates, such that intimate mixing of the monomers requires specialist high-speed mixing equipment. The diisocyanates used are the same as for preparation of polyurethanes. In addition to simple aliphatic amines and α,ω-diamino polyethers akin to the diols used in polyurethane synthesis, aromatic diamines also are used. By reacting diisocyanates with diols and diamines, poly(urethane-*co*-urea)s are produced.

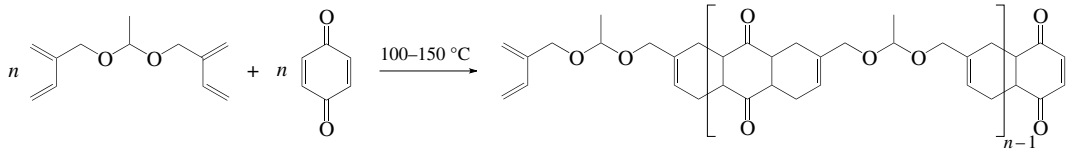
3.2.2.2 Other Polymers Prepared by Polyaddition

As stated above, besides polyurethanes and polyureas, relatively few polymers are prepared by polyaddition. Two further types of polyaddition will be considered here.

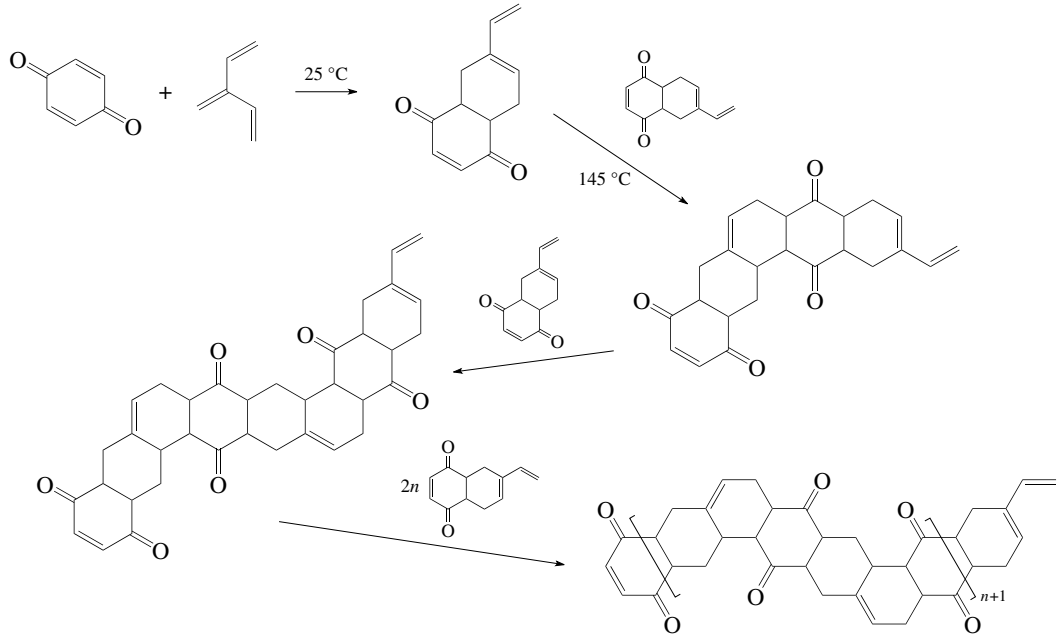
The Diels–Alder reaction of dienes with dienophiles is a 4+2 cycloaddition



where R_1, R_2 and R represent substituent groups, and carbon and hydrogen atoms are omitted for clarity. The reaction proceeds at temperatures of 25–150 °C and works best when R_1 and R_2 are electron donating and R is electron withdrawing (or vice versa), but it is reversible and the retro-reaction occurs at high temperatures. A wide variety of polymers have been prepared by Diels–Alder polyaddition, of which two examples will be given. Bis(2-buta-1,3-dienyl)methylacetal undergoes RA_2+RB_2 polyaddition with 1,4-benzoquinone to give a soluble amorphous Diels–Alder polymer

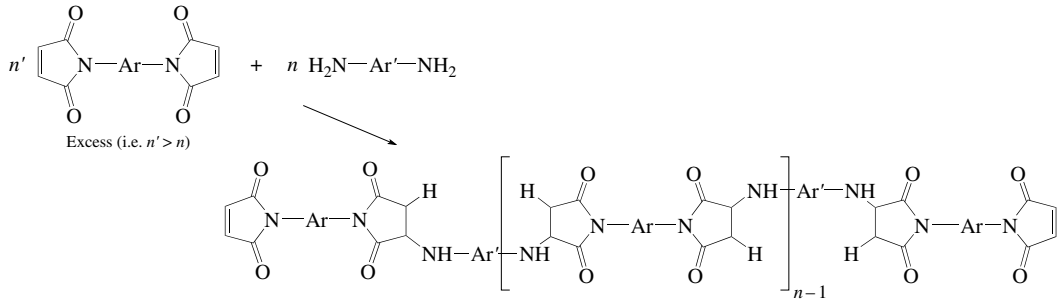


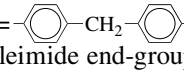
A more complex example involves the Diels–Alder reaction of 2-vinylbuta-1,3-diene with 1,4-benzoquinone, which first produces a monomeric adduct that then undergoes ARB polyaddition at higher temperature



The polymer is insoluble except at very low degrees of polymerization and the chain is completely rigid with a more crooked contour than indicated here because there are two possible orientations for the addition reaction; the structure shown arises from alternation of the orientation. Polymers of this type are called *ladder polymers*, based on the ladder-like nature of their backbone, and have improved thermal stability because two main-chain bonds must break for chain scission to occur.

Diels–Alder polymerizations largely have remained curiosities, but the RA_2+RB_2 polyaddition of diamines with bismaleimides has been commercialized. A generic example is shown below



where Ar and Ar′ are aromatic groups (e.g. Ar = Ar′ = ). As shown above, using an excess of bismaleimide produces oligomers with maleimide end-groups, which are known generically as *bismaleimide (BMI) resins*. This is only one of many methods for synthesis of BMI resins and a very wide range of structurally different BMI resins are available commercially for use as matrixes in composites and as high-performance adhesives. The BMI resins are converted to crosslinked materials *in situ* during processing by a second-stage reaction, e.g. free-radical polymerization of the C=C bonds in the maleimide end-groups or further reaction with polyfunctional amines.

3.2.3 Theoretical Treatment of Linear Step Polymerization

The principle of equal reactivity of functional groups (described in Section 2.4) is fundamental to simplification of the theoretical treatment of step polymerization and was shown to be valid for the most common polymerizations by the experimental studies of Flory. On this basis, step polymerization involves random reactions occurring between any two mutually-reactive molecular species. Intrinsically, each of the possible reactions is equally probable and their relative preponderances depend only upon the relative numbers of each type of molecular species (i.e. monomer, dimer, trimer, etc.). This assumption of equal reactivity is implicit in each of the theoretical treatments of step polymerization that follow.

3.2.3.1 Carothers Theory

Carothers developed a simple method of analysis for predicting the molar mass of polymers prepared by step polymerization. He recognized that the number-average degree of polymerization *with respect to monomer units* is given by the relation

$$\bar{x}_n = \frac{N_0}{N} \tag{3.1}$$

where

N_0 is the number of molecules present initially

N is the number of molecules remaining after a time t of polymerization

Assuming that there are equal numbers of mutually-reactive functional groups, $\bar{x}_n$ can be related to the *extent of reaction p* at time *t* which is given by

$$p = \frac{\text{Number of functional groups that have reacted}}{\text{Number of functional groups present initially}}$$

and is the probability that any functional group present initially has reacted. Since the total number of molecules decreases by one for each pair-wise reaction between functional groups

$$p = \frac{N_0 - N}{N_0} \quad \text{which rearranges to} \quad \frac{N_0}{N} = \frac{1}{1-p} \tag{3.2}$$

Combining Equations 3.1 and 3.2 gives the Carothers equation

$$\bar{x}_n = \frac{1}{1-p} \tag{3.3}$$

This equation is applicable to $RA_2 + RB_2$, ARB and RA_2 polymerizations in which there is an exact stoichiometric balance in the numbers of mutually-reactive functional groups. The equation highlights the need to attain very high extents of reaction of functional groups in order to produce polymers with useful physical properties. Normally, degrees of polymerization of the order of 100 or above are required, hence demanding values of $p \geq 0.99$. This clearly demonstrates the necessity for using monomers of high purity and chemical reactions that are either highly efficient or can be forced towards completion.

The number-average molar mass $\bar{M}_n$ is related to $\bar{x}_n$ by

$$\bar{M}_n = \bar{M}_0 \bar{x}_n$$

where $\bar{M}_0$ is the mean molar mass of a monomer unit and is given by

$$\bar{M}_0 = \frac{\text{Molar mass of the repeat unit}}{\text{Number of monomer units in the repeat unit}}$$

Slight stoichiometric imbalances significantly limit the attainable values of $\bar{x}_n$. Consider a $RA_2 + RB_2$ polymerization in which RB_2 is present in excess. The ratio of the numbers of the two different types of functional group (A and B) present initially is known as the *reactant ratio r*, and for linear step polymerization is always defined so that it is less than or equal to one. Thus for the reaction under consideration

$$r = \frac{N_A}{N_B} \tag{3.4}$$

where N_A and N_B are, respectively, the numbers of A and B functional groups present initially. Since there are two functional groups per molecule

$$N_0 = \frac{N_A + N_B}{2}$$

which upon substitution for N_A from Equation 3.4 gives

$$N_0 = \frac{N_B(1+r)}{2} \tag{3.5}$$

It is common practice to define the extent of reaction p in terms of the functional groups present in minority (i.e. A groups in this case). On this basis

$$\begin{aligned} \text{number of unreacted A groups} &= N_A - pN_A \\ &= rN_B(1-p) \\ \text{number of unreacted B groups} &= N_B - pN_A \\ &= N_B(1-rp) \end{aligned}$$

so that

$$N = \frac{rN_B(1-p) + N_B(1-rp)}{2}$$

i.e.

$$N = \frac{N_B(1+r-2rp)}{2} \tag{3.6}$$

Substitution of Equations 3.5 and 3.6 into Equation 3.1 yields the more *general Carothers equation*

$$\bar{x}_n = \frac{1+r}{1+r-2rp} \tag{3.7}$$

of which Equation 3.3 is the special case for $r=1$. Table 3.3 gives values of $\bar{x}_n$ calculated using Equation 3.7 and reveals the dramatic reduction in $\bar{x}_n$ when r is less than unity. Thus only very slight stoichiometric imbalances can be tolerated if useful polymers are to be formed, the corollary of which is that r must be controlled with great accuracy. It is now absolutely clear that, in order to control r with the necessary precision, the monomers used in linear step polymerizations must be of very high purity and that the linking reactions must be clean. Assuming these criteria are satisfied,

TABLE 3.3
Variation of $\bar{x}_n$ with p and r according to Equation 3.7

	$\bar{x}_n$ at				
r	$p=0.90$	$p=0.95$	$p=0.99$	$p=0.999$	$p=1.000$[a]
1.000	10.0	20.0	100.0	1000.0	∞
0.999	10.0	19.8	95.3	666.8	1999.0
0.990	9.6	18.3	66.8	166.1	199.0
0.950	8.1	13.4	28.3	37.6	39.0
0.900	6.8	10.0	16.1	18.7	19.0

[a] As $p \to 1, \bar{x}_n \to \frac{(1+r)}{(1-r)}$

Equation 3.7 can be used to exert control of molar mass by using slight imbalances in stoichiometry to place an upper limit on $\bar{x}_n$ for reactions taken to very high conversions of functional groups.

Equation 3.7 also is applicable to reactions in which a monofunctional compound is included to control $\bar{x}_n$, e.g. RA_2+RB_2+RB or $ARB+RB$. All that is required is to re-define the reactant ratio

$$r = \frac{N_A}{N_B + 2N_{RB}}$$

where

N_A and N_B are, respectively, the initial numbers of A and B functional groups from the difunctional monomer(s)

N_{RB} is the number of molecules of RB present initially.

The factor of 2 is required because one RB molecule has the same quantitative effect in limiting $\bar{x}_n$ as one excess RB_2 molecule.

3.2.3.2 Statistical Theory

The theory of Carothers is restricted to prediction of number-average quantities. In contrast, simple statistical analyses based upon the random nature of step polymerization allow prediction of degree of polymerization distributions. Such analyses were first described by Flory.

For simplicity RA_2+RB_2 and ARB polymerizations in which there is exactly equivalent stoichiometry will be considered here. The first stage in the analysis is to calculate the probability $P(x)$ of existence of a molecule consisting of exactly x monomer units at time t when the extent of reaction is p. A molecule containing x monomer units is created by the formation of a sequence of $(x-1)$ linkages. The probability that a particular sequence of linkages has formed is the product of the probabilities of forming the individual linkages. Since p is the probability that a functional group has reacted, the probability of finding a sequence of two linkages is p^2, the probability of finding a sequence of three linkages is p^3 and the probability of finding a sequence of $(x-1)$ linkages is $p^{(x-1)}$. For a molecule to contain exactly x monomer units, the xth (i.e. last) unit must possess a terminal unreacted functional group. The probability that a functional group has not reacted is $(1-p)$ and so

$$P(x) = (1-p)p^{(x-1)} \tag{3.8}$$

Since $P(x)$ is the probability that a molecule chosen at random contains exactly x monomer units, it must also be the *mole fraction* of x-mers. If the total number of molecules present at time t is N, then the total number N_x of x-mers is given by

$$N_x = N(1-p)p^{(x-1)} \tag{3.9}$$

Often N cannot be measured and so is eliminated by substitution of the rearranged form of Equation 3.2, $N = N_0(1-p)$, to give

$$N_x = N_0(1-p)^2 p^{(x-1)} \tag{3.10}$$

which is an expression for the number of molecules of degree of polymerization x in terms of the initial number of molecules N_0 and the extent of reaction p.

The weight fraction w_x of x-mers is given by

$$w_x = \frac{\text{Total mass of molecules with degree of polymerization } x}{\text{Total mass of all the molecules}}$$

Thus, neglecting end groups

$$w_x = \frac{N_x(x\bar{M}_0)}{N_0\bar{M}_0} = \frac{xN_x}{N_0} \tag{3.11}$$

Combining Equations 3.10 and 3.11 gives

$$w_x = x(1-p)^2 p^{(x-1)} \tag{3.12}$$

Equations 3.8 and 3.12 define what is known as the *most probable* (or *Flory* or *Flory–Schulz*) *distribution*, the most important features of which are illustrated by the plots shown in Figure 3.1. Thus the mole fraction $P(x)$ decreases continuously as the number of monomer units in the polymer chain increases, i.e. at all extents of reaction, the mole fraction of monomer is greater than that of any other species. In contrast, the weight fraction distribution shows a maximum at a value of x that is very close to $\bar{x}_n$. As the extent of reaction increases, the maximum moves to higher values of x and the weight fraction of monomer becomes very small.

Knowledge of the distribution functions (i.e. $P(x)$ and w_x) enables molar mass averages to be evaluated. From Equation 1.3 the number-average molar mass may be written as

$$\bar{M}_n = \sum P(x)M_x$$

Recognizing that $M_x = x\bar{M}_0$ and substituting for $P(x)$ using Equation 3.8 gives

$$\bar{M}_n = \sum x\bar{M}_0(1-p)p^{(x-1)}$$

$$\text{i.e. } \bar{M}_n = \bar{M}_0(1-p)\sum xp^{(x-1)}$$

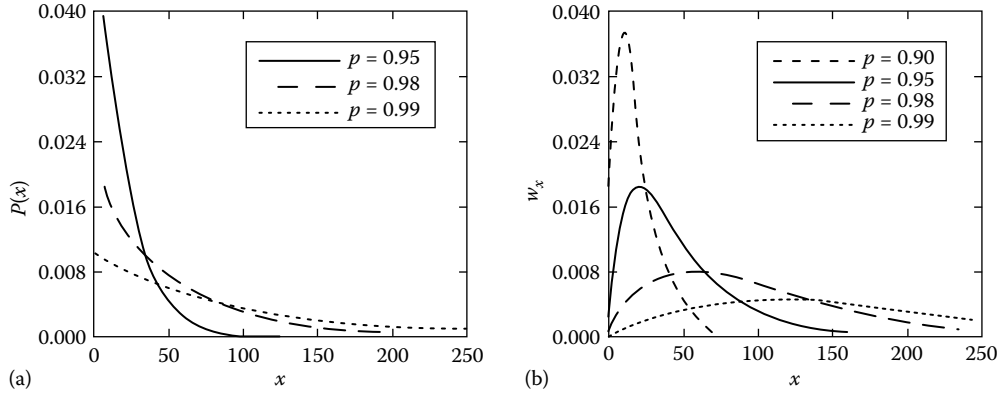


FIGURE 3.1 (a) Mole-fraction distribution $P(x)$ and (b) weight-fraction distribution w_x of degree of polymerisation x with respect to monomer units for various extents of reaction p in a linear step polymerisation with a reactant ratio $r = 1$. Note that the values of number-average degree of polymerisation $\bar{x}_n$ with respect to monomer units corresponding to $p = 0.90$, 0.95, 0.98 and 0.99 are, respectively: 10, 20, 50 and 100. (Data taken from Flory, *J. Am. Chem. Soc.*, 58, 1877, 1936.)

Using the mathematical relation

$$\sum_{x=1}^{\infty} xp^{(x-1)} = (1-p)^{-2} \quad \text{for } p < 1$$

the equation for $\bar{M}_n$ reduces to

$$\bar{M}_n = \frac{\bar{M}_0}{(1-p)} \tag{3.13}$$

Since $\bar{x}_n = \bar{M}_n/\bar{M}_0 = 1/(1-p)$ this equation is equivalent to the Carothers Equation 3.3, but this time it has been derived from purely statistical considerations.

The application of Equation 1.8 enables the weight-average molar mass to be written as

$$\bar{M}_w = \sum w_x M_x$$

Using Equation 3.12 it follows that

$$\bar{M}_w = \bar{M}_0(1-p)^2 \sum x^2 p^{(x-1)}$$

and another mathematical relation

$$\sum_{x=1}^{\infty} x^2 p^{(x-1)} = (1+p)(1-p)^{-3} \quad \text{for } p < 1$$

leads to

$$\bar{M}_w = \bar{M}_0 \frac{(1+p)}{(1-p)} \tag{3.14}$$

and hence to the weight-average degree of polymerization

$$\bar{x}_w = \frac{(1+p)}{(1-p)} \tag{3.15}$$

Combining Equations 3.13 and 3.14 gives an equation for the molar mass dispersity $\bar{M}_w/\bar{M}_n$

$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + p \tag{3.16}$$

which for most linear polymers prepared by step polymerization is close to 2 (since high values of p are required to form useful polymers).

The mole fraction and weight fraction distributions for step polymerizations in which there is a stoichiometric imbalance are similar to those just derived for the case of exactly equivalent stoichiometry. Thus all linear step polymerizations lead to essentially the same form of molar mass distribution.

Before closing this section, it must again be emphasized that the degrees of polymerization given are with respect to monomer units *and not* repeat units.

3.2.3.3 Kinetics of Step Polymerization

The assumption of equal reactivity of functional groups also greatly simplifies the kinetics of step polymerization since a single rate coefficient applies to each of the step-wise reactions. It is usual to define the overall rate of reaction as the rate of decrease in the concentration of one or other of the functional groups, i.e. in general terms for equimolar stoichiometry

$$\text{Rate of reaction} = -\frac{\mathrm{d[A]}}{\mathrm{d}t} = -\frac{\mathrm{d[B]}}{\mathrm{d}t}$$

Most step polymerizations involve bimolecular reactions, which often are catalysed. Thus, neglecting elimination products in polycondensations, the general elementary reaction is

$$\sim\!\!\sim\!\mathrm{A} + \mathrm{B}\!\sim\!\!\sim + \text{catalyst} \longrightarrow \sim\!\!\sim\!\mathrm{AB}\!\sim\!\!\sim + \text{catalyst}$$

and so the rate of reaction is given by

$$-\frac{\mathrm{d[A]}}{\mathrm{d}t} = k'[\mathrm{A}][\mathrm{B}][\text{Catalyst}] \tag{3.17}$$

where k' is the rate coefficient for the reaction. Since the concentration of a true catalyst does not change as the reaction proceeds, it is usual to simplify the expression by letting $k = k'[\text{Catalyst}]$ giving

$$-\frac{\mathrm{d[A]}}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}] \tag{3.18}$$

For equimolar stoichiometry $[\mathrm{A}] = [\mathrm{B}] = c$ and Equation 3.18 becomes

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = kc^2$$

This equation may be integrated by letting $c = c_0$ at $t = 0$

$$\int_{c_0}^{c} -\frac{\mathrm{d}c}{c^2} = \int_0^t k\mathrm{d}t$$

and gives

$$\frac{1}{c} - \frac{1}{c_0} = kt$$

which may be rewritten in terms of the extent of reaction by recognizing that $c_0/c = N_0/N$ and applying Equation 3.2

$$\frac{1}{(1-p)} - 1 = c_0 kt \tag{3.19}$$

This equation also applies to reactions which proceed in the absence of catalyst, though the rate coefficient is different and obviously does not include a term in catalyst concentration.

Certain step polymerizations are self-catalysed, that is, one of the types of functional group also acts as a catalyst (e.g. carboxylic acid groups in a polyesterification). In the absence of an added catalyst the rate of reaction for such polymerizations is given by

$$-\frac{\mathrm{d[A]}}{\mathrm{d}t} = k''[\mathrm{A}][\mathrm{B}][\mathrm{A}] \tag{3.20}$$

assuming that the A groups catalyse the reaction. Again letting [A] = [B] = c, Equation 3.20 becomes

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = k''c^3$$

which upon integration over the same limits as before gives

$$\frac{1}{c^2} - \frac{1}{c_0^2} = 2k''t$$

or in terms of the extent of reaction

$$\frac{1}{(1-p)^2} - 1 = 2c_0^2 k''t \tag{3.21}$$

Equations 3.19 and 3.21 have been derived assuming that the reverse reaction (i.e. depolymerisation) is negligible. This is satisfactory for many polyadditions, but for reversible polycondensations, it requires the elimination product to be removed continuously as it is formed. The equations have been verified experimentally using step polymerizations that satisfy this requirement, as is shown by the polyesterification data plotted in Figure 3.2. These results further substantiate the validity of the principle of equal reactivity of functional groups.

3.2.4 Ring Formation

A complication not yet considered is the *intramolecular* reaction of terminal functional groups on the same molecule. This results in the formation of cyclic molecules (i.e. rings), e.g. in the preparation of a polyester

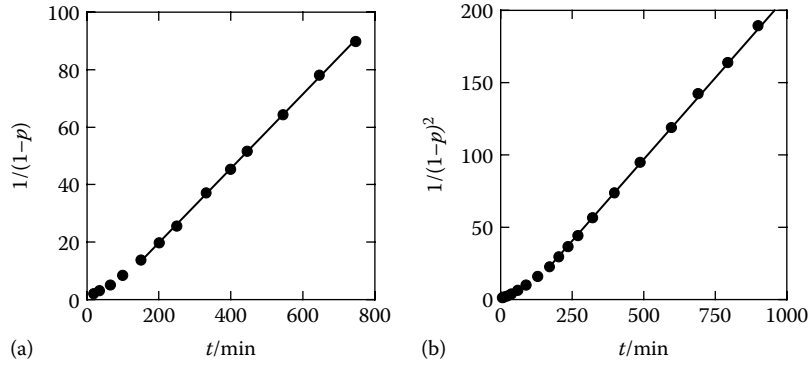
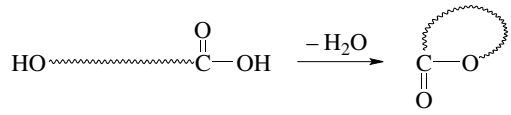
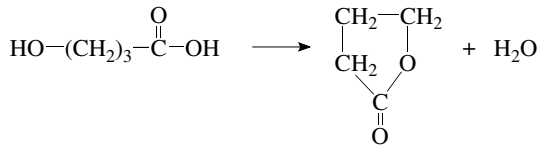


FIGURE 3.2 (a) Plot of $1/(1-p)$ as a function of time for the polymerization of diethylene glycol with adipic acid using *p*-toluene sulphonic acid as a catalyst at 109 °C and (b) plot of $1/(1-p)^2$ as a function of time for the polymerization of diethylene glycol with adipic acid at 166 °C. (Data taken from Flory, *J. Am. Chem. Soc.*, 61, 3334, 1939.)



The ease of ring formation depends strongly upon the number of atoms linked together in the ring. For example, 5-, 6- and, to a lesser extent, 7-membered rings are stable and often form in preference to linear polymer. For the self-condensation of ω-hydroxy carboxylic acids HO—$(CH_2)_i$—CO_2H when $i=3$ only the monomeric lactone is produced.



When $i=4$, some polymer is produced in addition to the corresponding monomeric lactone, and when $i=5$, the product is a mixture of polymer with some of the monomeric lactone.

Normally, 3- and 4-membered rings and 8- to 11-membered rings are unstable due to bond-angle strain and steric repulsions between atoms crowded into the centre of the ring, respectively, and usually are not formed. Whilst 12-membered and larger rings are more stable and can form, their probability of formation decreases as the ring size increases. This is because the probability of the two ends of a single chain meeting decreases as their separation (i.e. the chain length) increases. Thus large rings rarely form.

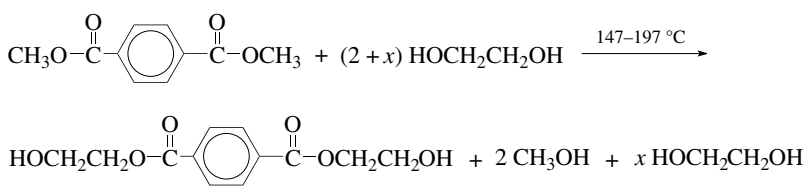
Ring formation disturbs the form of the molar mass distribution and reduces the ultimate molar mass. However, since linear polymerization is a bimolecular process and ring formation is a unimolecular process, it is possible to greatly promote the former process relative to the latter by using high monomer concentrations. This is why many step polymerizations are performed in bulk (i.e. using only monomer(s) plus catalysts in the absence of a solvent).

3.2.5 Linear Step Polymerization Processes

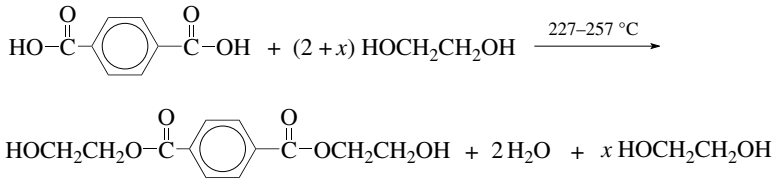
Although step polymerizations can be carried out in a solvent that dissolves the monomers and the polymer to be produced, finding suitable solvents can be difficult because the polymers often are semi-crystalline and of low solubility. The isolation of the polymer from the solvent also can prove difficult. Hence, most step polymerizations are performed by reacting liquid monomers together in the absence of a solvent.

The preceding sections highlight the many constraints upon the formation of high molar mass polymers by linear step polymerization. Special polymerization systems often have to be developed to overcome these constraints and are exemplified here by systems developed for the preparation of polyesters and polyamides.

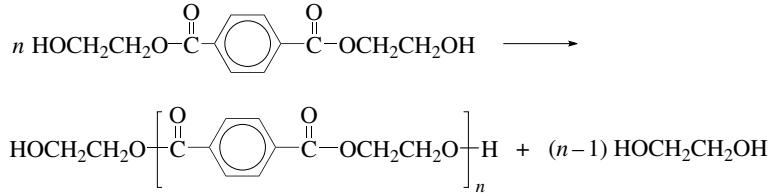
Ester interchange (or *transesterification*) reactions commonly are employed in the production of polyesters, the most important example being the preparation of poly(ethylene terephthalate). The direct polyesterification reaction of terephthalic acid with ethylene glycol indicated in Table 1.1 is complicated by the high melting point of terephthalic acid (in fact it sublimes at 300 °C before melting) and its low solubility. Thus poly(ethylene terephthalate) is prepared in a two-stage process. The first stage involves formation of bis(2-hydroxyethyl)terephthalate either by reaction of dimethylterephthalate with an excess of ethylene glycol (i.e. via ester interchange)



or more commonly nowadays by direct esterification of terephthalic acid with an excess of ethylene glycol

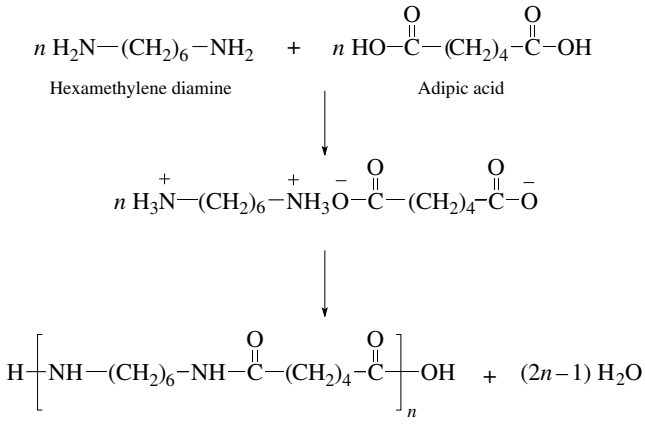


The methanol or water produced during these first-stage reactions is removed as it is formed. On completion of the first stage, the reaction temperature is raised to about 277 °C so that the excess ethylene glycol and the ethylene glycol produced by further ester interchange reactions can be removed, and so that the polymer is formed above its melting temperature (265 °C)



Thus by using ester interchange reactions and removing the ethylene glycol produced, the need for strict stoichiometric control is eliminated.

The preferred method for preparing aliphatic polyamides from diamines and diacids is *melt polymerization* of the corresponding nylon salt. For example, in the preparation of nylon 6.6, hexamethylene diamine and adipic acid are first reacted together at low temperature to form hexamethylene diammonium adipate (nylon 6.6 salt) which then is purified by recrystallisation. The salt is heated gradually up to about 277 °C to effect melt polymerization and maintained at this temperature whilst removing the water produced as steam



A major advantage of melt polymerization by *salt dehydration* is that the use of a pure salt guarantees exact 1:1 stoichiometry.

A convenient method for preparation of polyesters and polyamides in the laboratory is the reaction of diacid chlorides with diols and diamines, respectively (i.e. Schotten–Baumann reactions).

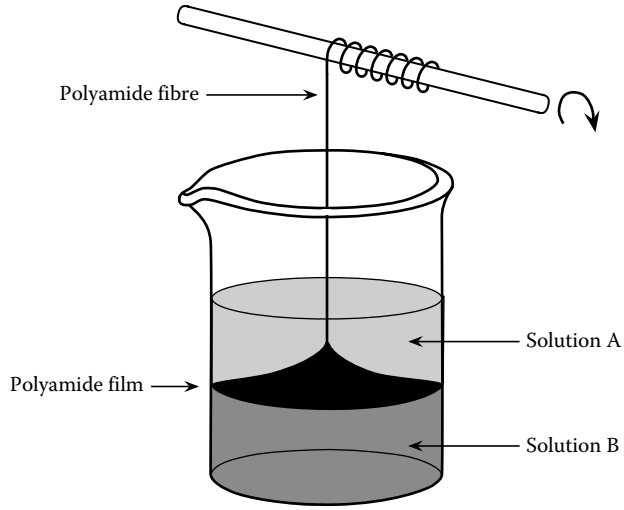
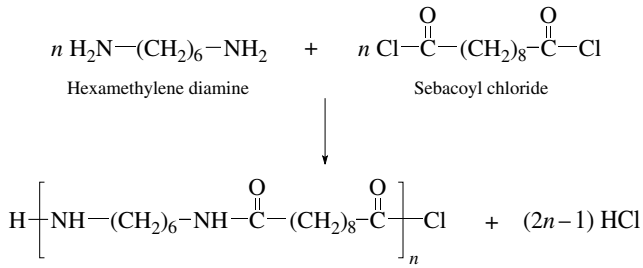


FIGURE 3.3 Schematic illustration of interfacial polymerization to produce a polyamide. A is an aqueous solution of the diamine and B is a solution of the diacid chloride in carbon tetrachloride. The polyamide is produced as a film at the interface between the two solutions and can be drawn off in the form of a fibre. It is usual to include a base (e.g. NaOH) in solution A in order to neutralize the HCl formed by the reaction.

These reactions proceed rapidly at low temperatures and often are performed as *interfacial polymerizations* in which the two reactants are dissolved separately in immiscible solvents which are then brought into contact. The best known example of this is the 'nylon rope trick' where a continuous film of nylon is drawn from the interface as illustrated in Figure 3.3. For example, the preparation of nylon 6.10 would proceed by the following reaction

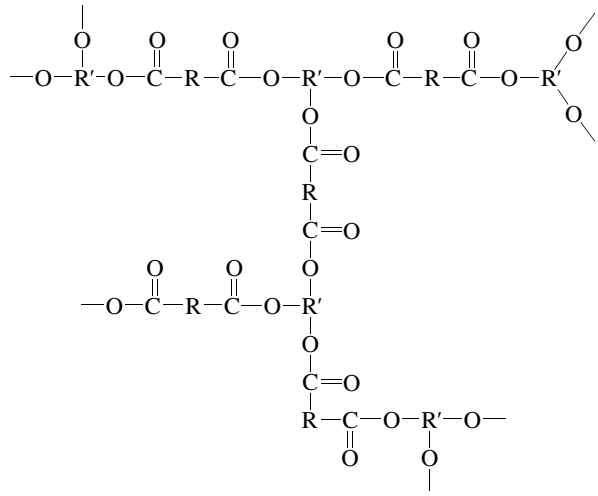


The reaction takes place at the organic solvent side of the interface and, because it usually is diffusion-controlled, there is no need for strict control of stoichiometry.

3.3 NON-LINEAR STEP POLYMERIZATION

The inclusion of a monomer with a functionality greater than two has a dramatic effect upon the structure and molar mass of the polymer formed. In the early stages of such reactions, the polymer has a branched structure and, consequently, increases in molar mass much more rapidly with extent of reaction than for a linear step polymerization. As the reaction proceeds, further branching reactions lead ultimately to the formation of complex network structures which have properties

that are quite different from those of the corresponding linear polymer. For example, reaction of a dicarboxylic acid $R(COOH)_2$ with a triol $R'(OH)_3$ would lead to structures of the type



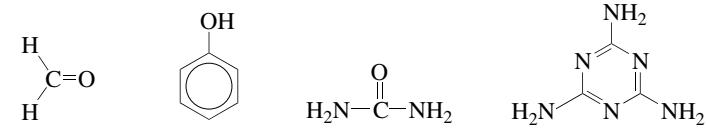
The point at which the first network molecule is formed is known as the *gel point* because it is manifested by *gelation*, that is, an abrupt change of the reacting mixture from a viscous liquid to a solid gel which shows no tendency to flow. Before dealing with theoretical predictions of the gel point, the chemistry of some important network-forming step polymerizations will be described.

3.3.1 Network Polymers

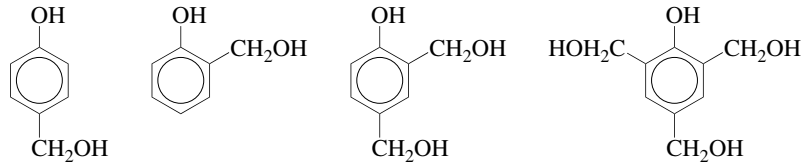
Network polymers produced by step polymerizations were amongst the first types of synthetic polymers to be commercialized and often are termed *resins*. The polymers are completely intractable and so at the stage when the network chains are generated, the polymerizations must be carried out within a mould to produce the required artefact.

3.3.1.1 Formaldehyde-Based Resins

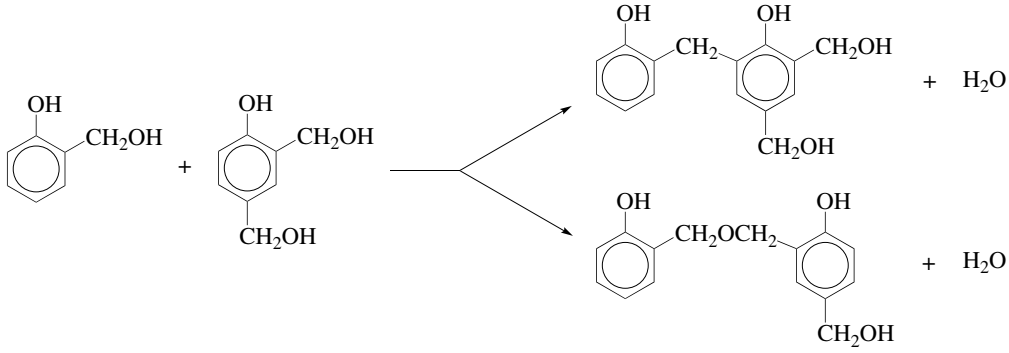
Formaldehyde-based resins were the first network polymers prepared by step polymerization to be commercialized. They are prepared in two stages. The first involves the formation of a prepolymer of low molar mass which may either be a liquid or a solid. In the second stage, the prepolymer is forced to flow under pressure to fill a heated mould in which further reaction takes place to yield a highly crosslinked, rigid polymer in the shape of the mould. Since formaldehyde is difunctional, in order to form a network polymer the co-reactants must have a functionality f greater than two; those most commonly employed are phenol ($f=3$), urea ($f=4$) and melamine ($f=6$)



The hydroxyl group in phenol activates the benzene ring towards substitution in the 2-, 4- and 6-positions. Upon reaction of phenol with formaldehyde, methylol substituent groups are formed, e.g.

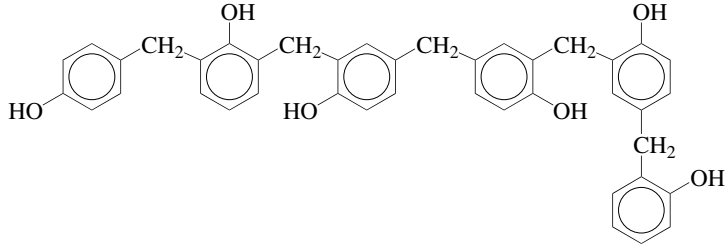


Further reaction leads principally to the formation of methylene bridges but also to dimethylene ether links



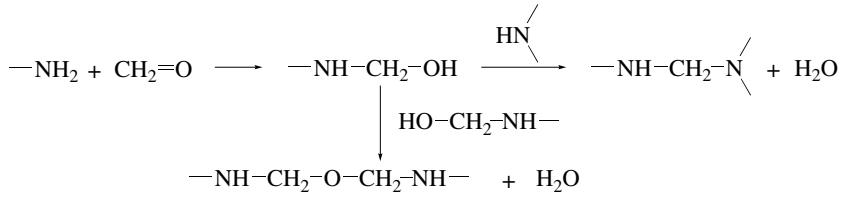
There are two types of *phenol–formaldehyde resin*. Those prepared using an excess of formaldehyde with base catalysis are known as *resoles*. The resole prepolymers possess many unreacted methylol groups that upon further heating react to produce the network structure.

Novolaks are prepared using an excess of phenol and acid catalysis, which promotes condensation reactions of the methylol groups. Thus the prepolymers produced contain no methylol groups and are unable to crosslink, e.g.



Normally, they are dried and ground to a powder, then compounded (i.e. mixed) with fillers (e.g. mica, glass fibres, sawdust), colourants and hardeners. Hexamethylenetetramine, with magnesium or calcium oxide as a catalyst, usually is employed as the hardener to activate curing (i.e. crosslinking) when the compound is converted into an artefact by heating in a mould. Most of the crosslinks formed are methylene bridges, though some dimethylene amine ($–CH_2–NH–CH_2–$) links are formed. The fillers are added to reduce the cost and to improve the electrical or mechanical properties of the resin.

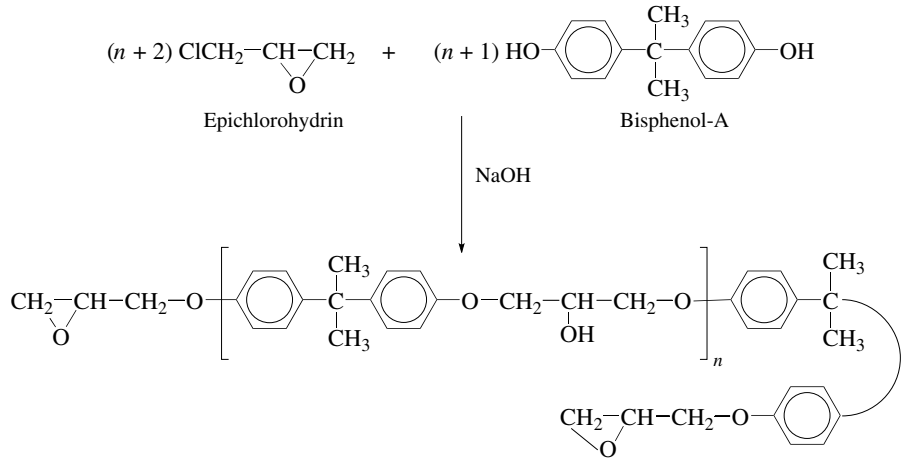
The chemistry of *urea–formaldehyde* and *melamine–formaldehyde* resins involves the formation and condensation reactions of *N*-methylol groups, e.g. in general terms



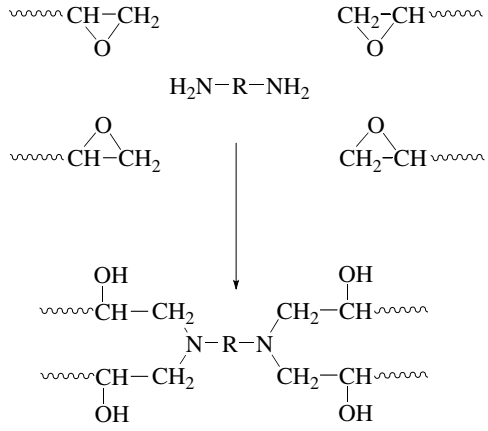
The reactions usually are arrested at the prepolymer stage by adjusting the pH of the reacting mixture to slightly alkaline. After blending (e.g. with fillers, pigments, hardeners, etc.) the prepolymers are cured by heating in a mould. The hardeners are compounds (e.g. ammonium sulphamate) which decompose at mould temperatures to give acids that catalyse further condensation reactions.

3.3.1.2 Epoxy Resins

Epoxy resins are low molar mass prepolymers containing epoxide end-groups. The most important are the diglycidyl ether prepolymers prepared by the reaction of excess epichlorohydrin with bisphenol-A in the presence of a base

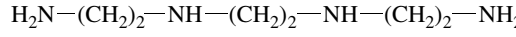


These prepolymers are either viscous liquids or solids depending upon the value of n. Usually, they are cured by the use of multifunctional amines which undergo a polyaddition reaction with the terminal epoxide groups in the manner indicated below (for a diamine, $f=4$)

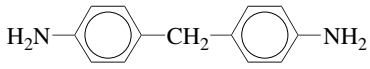


Together, the amine R group and epoxy resin chain length control the mechanical properties of the fully-cured resin. Some examples of polyfunctional amines used to cure epoxy resins are shown below together with their functionalities and common names

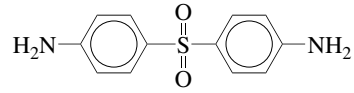
Diethylenetriamine (DETA), $f = 5$



Triethylenetetramine (TETA), $f = 6$



4,4′-Diaminodiphenylmethane (DDM), $f = 4$

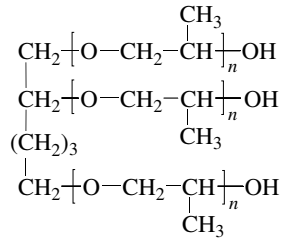


4,4′-Diaminodiphenylsulphone (DDS), $f = 4$

Epoxy resins are characterized by low shrinkage on curing and find use as adhesives, electrical insulators, surface coatings and matrix materials for fibre-reinforced composites.

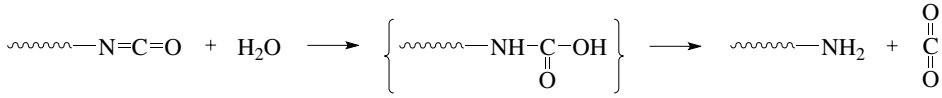
3.3.1.3 Network Polyurethanes

Polyurethane networks find a wide variety of uses (e.g. elastomers, flexible foams and rigid foams) and usually are prepared by the reaction of diisocyanates with *polyols*, which are branched polyether (or, less commonly, polyester) prepolymers that have hydroxyl end-groups, e.g. reaction of MDI (Section 3.2.2.1) with a poly(propylene oxide) triol



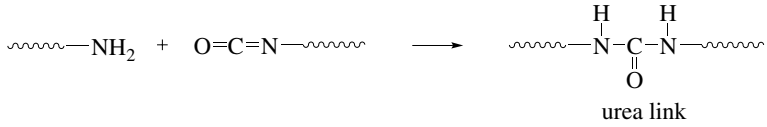
via the chemistry described in Section 3.2.2.1. Commercial poly(propylene oxide) polylols often have terminal ethylene oxide units (i.e. $–O–CH_2–CH_2–OH$) (see Section 7.3.1) to increase reactivity (i.e. primary $–CH_2OH$ groups are more reactive than the secondary $–CH(CH_3)OH$ groups). The molar mass and functionality of the prepolymer determine the crosslink density and hence the flexibility of the network formed. Typically, polyether polyols have a functionality of 3–6 and those with $\bar{M}_n$ of up to about 1 kg mol^{-1} are used to prepare rigid polyurethanes, whereas flexible polyurethanes are prepared from those with $\bar{M}_n$ of about 2–8 kg mol^{-1}.

Polyurethane foams can be formed by inclusion of a small amount of water, which reacts rapidly with the isocyanate groups to give an unstable carbamic acid that instantly decomposes to produce an amine end-group and carbon dioxide gas, which causes foaming of the polyurethane as it is formed



a carbamic acid gas

The amine end-group is extremely reactive towards isocyanate groups, so reacts immediately to form a *urea* link



Polyurethane foams can also be produced by inclusion of compounds that vaporize due to the heat released by the exothermic reaction of isocyanates groups with hydroxyl groups.

3.3.2 Gelation Theory

Three-dimensionally crosslinked polymers are incapable of macroscopic viscous flow because, at the molecular level, the crosslinks prevent the network chains from flowing past one another. When the first *network molecule* forms in a non-linear polymerization, it encompasses the whole reactant mixture which instantly becomes immobilized; this corresponds to the *gel point*, which clearly is a very important stage in a network-forming polymerization. Much effort has been devoted to prediction of the extent of reaction at the gel point. Here, simple theories for the gel point in non-linear step polymerizations are introduced.

3.3.2.1 Carothers Theory of Gelation

A simple theory for prediction of gel points can be derived using the principles employed in the linear step polymerization theory of Carothers (Section 3.2.3.1). When there is a stoichiometric balance in the numbers of mutually-reactive functional groups, the number-average functionality f_{av} is used and is defined by

$$f_{av} = \frac{\sum N_i f_i}{\sum N_i}$$

where N_i is the initial number of molecules of monomer i which has functionality f_i. Thus, if there are N_0 molecules present initially, the total number of functional groups present is $N_0 f_{av}$. If at time t there are N molecules present, then the number of functional groups that have reacted is $2(N_0 - N)$ since the number of molecules decreases by one for each link produced by the reaction together of *two* functional groups. Therefore the extent of reaction p, which is the probability that a functional group present initially has reacted, is given by

$$p = \frac{2(N_0 - N)}{N_0 f_{av}}$$

Simplifying and substituting for N/N_0 using Equation 3.1 gives

$$p = \frac{2}{f_{av}}\left(1 - \frac{1}{\bar{x}_n}\right) \tag{3.22}$$

which can be rearranged to

$$\bar{x}_n = \frac{2}{2 - pf_{av}} \tag{3.23}$$

This equation reduces to the simple Carothers Equation 3.3 when $f_{av} = 2.0$. Slight increases in f_{av} above 2.0 give rise to substantial increases in the value of $\bar{x}_n$ attained at specific extents of reaction, as is demonstrated in Table 3.4.

TABLE 3.4
Values of $\bar{x}_n$ for Different Values of p and f_{av} Calculated using Equation 3.23

	$\bar{x}_n$ at				
f_{av}	$p=0.50$	$p=0.70$	$p=0.90$	$p=0.95$	$p=0.99$
2.0	2	3.33	10	20	100
2.1	2.10	3.77	18.18	400	Gelled
2.2	2.22	4.35	100	Gelled	Gelled
2.3	2.35	5.13	Gelled	Gelled	Gelled

If it is postulated that gelation occurs when $\bar{x}_n$ goes to infinity, then it follows from Equation 3.22 that the critical extent of reaction p_c for gelation is given by

$$p_c = \frac{2}{f_{av}} \tag{3.24}$$

It is possible to extend the theory to prediction of p_c when there is an imbalance of stoichiometry. However, this simple method of analysis will not be pursued further here because it is rather inelegant and always yields overestimates of p_c. The approach is fundamentally flawed because it is based upon $\bar{x}_n$, an average quantity, tending to infinity. Molecules with degrees of polymerization both larger and smaller than $\bar{x}_n$ are present, and it is the largest molecules that undergo gelation first.

3.3.2.2 Statistical Theory of Gelation

The basic statistical theory of gelation was first derived by Flory who considered the reaction of an f-functional monomer RA_f ($f>2$) with the difunctional monomers RA_2 and RB_2. It is necessary to define a parameter called the *branching coefficient*, α, which is the probability that an f-functional unit is connected via a chain of difunctional units to another f-functional unit. In other words α is the probability that the general sequence of linkages shown below exists

$$_{(f-1)}\text{AR—AB—R—B}\left[\text{A—R—AB—R—B}\right]_i\text{A—R—A}_{(f-1)}$$

In order to derive an expression for α from statistical considerations it is necessary to introduce another term, γ, which is defined as the initial ratio of A groups from RA_f molecules to the total number of A groups. Using γ, it is possible to calculate the probabilities for the existence of each of the linkages in the general sequence given above. If the extent of reaction of the A groups is p_A and of the B groups is p_B then

$$\text{probability of } {}_{(f-1)}\text{AR—}\overrightarrow{\text{AB}}\text{—R—B} = p_A$$

$$\text{probability of B—R—}\overrightarrow{\text{BA}}\text{—R—A} = p_B(1-\gamma)$$

$$\text{probability of A—R—}\overrightarrow{\text{AB}}\text{—R—B} = p_A$$

$$\text{probability of B—R—}\overrightarrow{\text{BA}}\text{—RA}_{(f-1)} = p_B\gamma$$

where the arrows indicate the linkages under consideration and the direction in which the chain is extending. Thus the probability that the general sequence of linkages has formed is

$$p_A[p_B(1-\gamma)p_A]^i p_B\gamma$$