

PART I

BASIC CONCEPTS

1

INTRODUCTION TO POLYMERS AND POLYMER TYPES

ENRIQUE SALDÍVAR-GUERRA AND EDUARDO VIVALDO-LIMA

1.1 INTRODUCTION TO POLYMERS

1.1.1 Basic Concepts

Polymers are very large molecules, or macromolecules, formed by the union of many smaller molecules. These smaller units are termed *monomers* before they are converted into polymers. In fact, the word “polymer” has a Greek origin meaning “many members.” Natural polymers have been around since the early times in Planet Earth. Life itself is linked to polymers since deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and proteins, which are essential to all known forms of life, are macromolecules. Cellulose, lignin, starch, and natural rubber are just a few other examples of natural polymers. Some of these polymers were used by early human civilizations to produce simple artifacts; for example, the play balls from natural rubber for the ball game of several of the Mesoamerican civilizations (which contained ritual content and not only entertaining purposes). In the 1800s, natural polymers began to be chemically modified to produce many materials, such as vulcanized rubber, gun cotton, and celluloid. Although natural polymers are very important, this book is mainly concerned with synthetic polymers, especially organic synthetic polymers. The chemical reaction by which polymers are synthesized from monomers is termed *polymerization*; however, this is a generic term, since there are a number of chemical mechanisms involved in different polymerization reactions.

Synthetic polymers are relatively modern materials, since they entered into the technological and practical scene only in the first decades of the twentieth century. This makes them very different from some other materials that have been known to humanity for centuries or millennia.

Also, given the fact that synthetic polymers are created by chemical reactions, the possibilities of building different polymers are virtually endless, only restricted by chemical and thermodynamic laws and by the creativity of the synthetic polymer chemist. These endless possibilities have given rise to an enormous variety of synthetic polymers that find application in almost every conceivable field of human activity that deals with matter or physical objects. In addition, the enormous molecular structural versatility that is derived from the rich synthetic possibilities, translates into materials with extremely diverse properties, and therefore applications.

We can find polymers as components of many of the objects that surround us, as well as in a broad diversity of applications in daily life: clothing, shoes, personal care products, furniture, electrical and electronic appliances, packaging, utensils, automobile parts, coatings, paints, adhesives, tires, and so on. The list is endless, and these few examples should provide an idea of the importance of synthetic polymers to modern society, in terms of both their usefulness and the economic value that they represent.

1.1.2 History

Some synthetic polymers were inadvertently prepared since the mid-nineteenth century by chemists working in organic synthesis without necessarily knowing the chemical structure of these materials, although some of them may have had some intuition of the right character of these molecules as very large ones [1]. Only in 1920, Staudinger [2] proposed the concept of polymers as macromolecules, and this idea slowly gained acceptance among the scientific community during the next decade. Some of the supporting

evidence for the macromolecular concept came from measurements of high molecular weight molecules in rubber using physicochemical methods. Later, around 1929, Carothers [3] started an experimental program aimed at the synthesis of polymers of defined structures using well-known reactions of organic chemistry; this work, together with the confirmation of high molecular weight molecules by other experimental measurements (e.g., the viscosity of polymer solutions), helped to confirm the correctness of the macromolecular hypothesis of Staudinger. An interesting book on the history of polymer science is that by Morawetz [4].

1.1.3 Mechanical and Rheological Properties

1.1.3.1 Mechanical Properties Long chains with high molecular weights impart unique properties to polymers as materials. This can be illustrated by analyzing the change in the properties of the homologous series of the simplest hydrocarbon chains, the alkanes, which can be seen as constituted of ethylene repeating units (with methyl groups at the chain ends),¹ as the number of repeating units increase. At relatively low molecular weights (C_6 – C_{10}), compounds in these series are relatively volatile liquids (gasolines). As the number of ethylene units increases, the compounds in this series start to behave as waxes with low melting points. However, if the number of ethylene units exceeds some 200–300, such that the molecular weight of the chains is in the order of 5000–8000, the material starts to behave as a solid exhibiting the higher mechanical properties associated with a polymer (polyethylene in this case). In general, above some minimum molecular weight, polymers exhibit increased mechanical properties and they are considered “high polymers”, alluding to their high molecular weight.

The mechanical behavior of a polymer is characterized by stress–strain curves in which the stress (force per unit area) needed to stretch the material to a certain elongation is plotted. In order to experimentally generate these curves, a tension stress is applied on a polymer sample of known dimensions, which is elongated until it breaks. The elongation is expressed as a fractional or percentage increase of the original length of the sample, which is denominated strain, ε , and is defined as

$$\varepsilon = \frac{\Delta L}{L} \quad (1.1)$$

where L is the original length of the sample and ΔL is the increase in length under the applied tension. The nature of the stress–strain curve for a given polymer defines its

possible use as elastomer, fiber, or thermoplastic. Figure 1.1 shows the form of the stress–strain curves for these types of polymers, and Table 1.1 shows typical values of some of the mechanical properties that can be defined as a function of the stress–strain behavior.

The elastic or Young’s modulus is the initial slope of the stress–strain curve and gives a measure of the resistance to deformation of the material. The ultimate tensile strength is the stress required to rupture the sample, and the ultimate elongation is the extent of elongation at which the rupture of the sample occurs.

Mechanical properties are discussed here only in an introductory manner in order to understand the main applications of polymers. An extended discussion of the mechanical properties of polymers and their measurement can be found in Chapter 21.

1.1.3.2 Rheological Properties Thermoplastics are processed and shaped in the molten state. This can be loosely defined as a state in which a polymer flows under the action of heat and pressure. Molten polymers are non-Newtonian fluids, as opposed to the simpler Newtonian fluids. In the latter, the stress σ (force per unit area) is proportional to the shear rate $\dot{\gamma}$ (velocity per unit length) with a proportionality factor μ (viscosity) which is constant at a given temperature. Newtonian fluids follow the law

$$\sigma = \mu \dot{\gamma} \quad (1.2)$$

On the other hand, in a non-Newtonian fluid, the viscosity depends on the shear rate. Besides showing very high non-Newtonian viscosities, polymers exhibit a complex viscoelastic flow behavior, that is, their flow exhibits “memory”, as it includes an elastic component in addition to the purely viscous flow. Rheological properties are those that define the flow behavior, such as the viscosity and the melt elasticity, and they determine how easy or difficult is to process these materials, as well as the performance of the polymer in some applications. The rheology of the polymers and its effect on the processing of these materials are studied in Chapters 22 and 23.

1.1.4 Polymer States

There are several scales at which polymers can be observed. The repeating unit in a polymeric chain lies in the scale of a few angstroms, while a single polymer molecule or chain has characteristic lengths of a few to some tens of nanometers (considering the contour length of a chain). At the next scale, or mesoscale, clusters of chains can be observed. This scale is rather important since it defines the polymer morphology based on the order or disorder exhibited by the chains. Ordered regions are termed *crystalline* and disordered ones *amorphous*. In the crystalline regions, the polymer chains are packed in regular arrays termed

¹Strictly speaking, this is valid only for alkanes with a pair number of carbon atoms starting from butane, since ethylene has 2 C; however, this precision is irrelevant for this discussion (especially at high number of carbons).

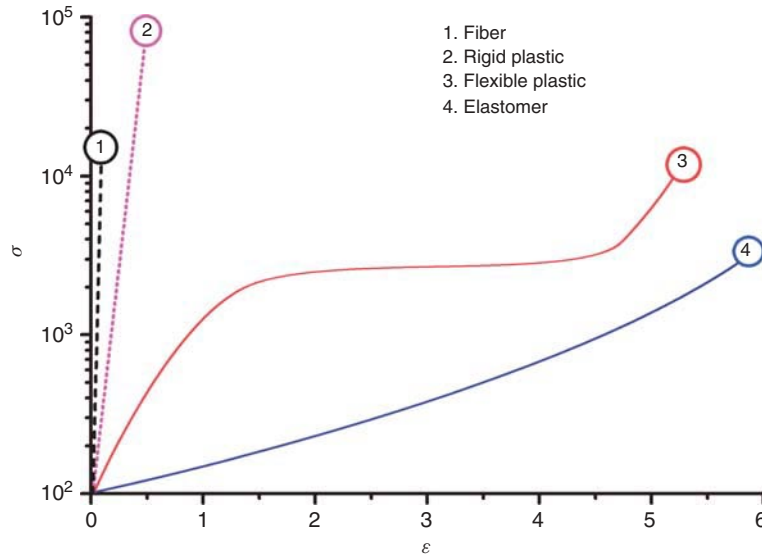


Figure 1.1 Schematic stress–strain curves for different types of polymers.

TABLE 1.1 Typical Values of Mechanical Properties for Different Polymer Types

| Type of Polymer (use) | Modulus (N/m ²) | Typical Elongations (Strain %) | Examples |
|-------------------------|--------------------------------|--------------------------------|-----------------------------------------------|
| Elastomers | $<2 \times 10^6$ | 400–1000 | Polybutadiene, polyisoprene, butyl rubber |
| Fibers | $>2 \times 10^9$ | 100–150 | Nylon (polyamide), polypropylene |
| Flexible thermoplastics | $0.15\text{--}3.5 \times 10^9$ | 20–800 | Polyethylene |
| Rigid thermoplastics | $0.7\text{--}3.5 \times 10^9$ | 0.5–10 | Polystyrene, PMMA, phenol-formaldehyde resins |

Abbreviation: PMMA, Poly(methyl methacrylate).

crystallites. Crystalline morphology is favored by structural regularity in the polymer chain and by strong intermolecular forces, as well as by some chain flexibility. Usually, in a crystalline polymer, both ordered and disordered regions are found; thus, the so-called crystalline polymers are actually semicrystalline. Examples of highly crystalline polymers are polyethylene and polyamides. On the other hand, completely amorphous polymers that owe their disordered morphology to bulky substituents and rigid chains are common, atactic polystyrene and poly methyl methacrylate being good examples of this category.

There are two important thermal properties that define the state of a polymer; these are the glass-transition temperature or T_g and the melting temperature, T_m . Below the glass-transition temperature, the amorphous regions of a polymer are in a glassy state showing practically no chain motions (at least in a practical time scale). Above the T_g , the polymer behaves as a viscous liquid reflecting motions of the polymer chains or chain segments. Also, at the T_g , many of the physicochemical properties of the polymer change in a relatively abrupt way (Fig. 1.2). The T_g can be defined in more precise thermodynamic terms, but this is further discussed in Chapter 2.

On the other hand, the T_m is a property exhibited by the crystalline regions of a polymer and is the temperature

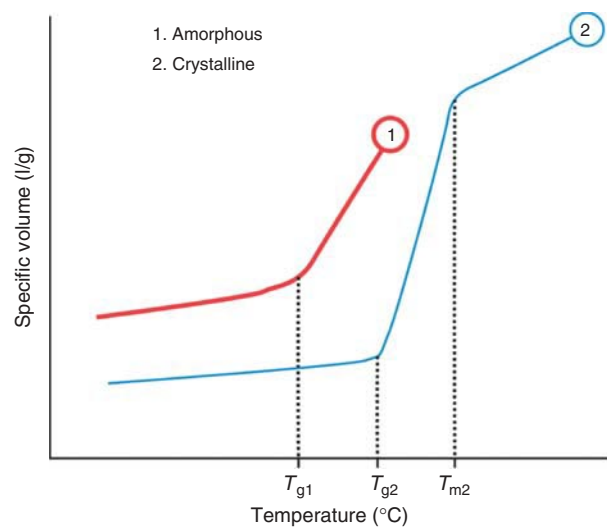


Figure 1.2 Schematic representation of the main thermal transitions in polymers in a plot of specific volume–temperature.

above which the crystalline regions melt and become disordered or amorphous. Since, for a given polymer $T_m > T_g$, above the melting point, the polymer will flow as a viscous liquid. Amorphous polymers exhibit only a T_g , while semicrystalline polymers exhibit both, a T_g and a T_m .

1.1.5 Molecular Weight

Compounds made of small molecules exhibit a unique well-defined molecular weight; on the other hand, polymers exhibit a distribution of molecular weights since not all the polymer chains of a given sample will have the same molecular weight or chain length. Therefore, in order to characterize a given polymer sample, it is necessary to either describe the full molecular weight distribution (MWD) or some average quantities related to the distribution. Also, the MWD can be plotted in different ways using either length or weight for the abscissa and, for example, number average or weight average for the ordinate; the classical paper of Ray [5] shows different representations of the MWD. Two of the most common averages are the number average and weight average molecular weights, \bar{M}_n and \bar{M}_w , respectively, which are defined as

$$\bar{M}_n = \sum_x f_x^n M_x \quad (1.3)$$

$$\bar{M}_w = \sum_x f_x^w M_x \quad (1.4)$$

where f_x^n is the number fraction of chains having x monomer units and M_x is the molecular weight of a chain having x monomer units. Also,

$$M_x = xM_0 \quad (1.5)$$

with M_0 being the molecular weight of the monomer unit. f_x^w is the weight fraction of chains having x monomer units. In these definitions, and assuming long chains, the contribution of any initiator fragment at the end of a chain has been neglected. In mathematical terms, the number and weight fractions are defined as follows:

$$f_x^n = \frac{N_x}{\sum_x N_x} \quad (1.6)$$

$$f_x^w = \frac{xN_x}{\sum_x xN_x} \quad (1.7)$$

where N_x is the number of chains having x monomer units. Also note that

$$f_x^w = \frac{xN_x}{\sum_x xN_x} = \frac{xf_x^n}{\sum_x xf_x^n} \quad (1.8)$$

Other related quantities that are frequently used are the number average chain length (NACL) and the weight average chain length (WACL); also represented as \bar{r}_n and \bar{r}_w , respectively, in some texts. The NACL is also simply

termed the *degree of polymerization* or DP_n . They are simply related to \bar{M}_n and \bar{M}_w by the following equations:

$$\text{NACL} = \frac{\bar{M}_n}{M_0} \quad (1.9)$$

$$\text{WACL} = \frac{\bar{M}_w}{M_0} \quad (1.10)$$

Instead of giving average based on the weight of the repeating unit, these two quantities are based on the number of repeating units.

1.1.5.1 Moments of the Molecular Weight Distribution

Since the molecular weight is a distributed quantity, the concepts and properties of statistical distributions can be applied to the MWD. A statistical definition that is particularly useful is that of moment of a distribution. In statistics, the S th moment of the discrete distribution² f of a discrete random variable y_i is defined as

$$\mu_S = \sum_{i=1}^{\infty} y_i^S f(y_i), \quad S = 0, 1, 2, \dots \quad (1.11)$$

A graphical representation of the discrete distribution $f(y_i)$ is shown in Figure 1.3a. Figure 1.3b shows the analogous MWD represented as the (number) distribution f_x^n of the discrete variable M_x (notice the equivalence of the concept of distribution with those of fraction or frequency).

Equivalently, the S th moment of the MWD can be defined as

$$\mu_S = \sum_{x=1}^{\infty} M_x^S f_x^n, \quad S = 0, 1, 2, \dots \quad (1.12)$$

Now, the average molecular weights of the MWD can be more simply defined in terms of the moments (Eq. 1.12).

The number average molecular weight is simply

$$\bar{M}_n = \frac{\mu_1}{\mu_0} \quad (1.13)$$

since

$$\frac{\mu_1}{\mu_0} = \frac{\sum_{x=1}^{\infty} M_x f_x^n}{\sum_{x=1}^{\infty} f_x^n} = \frac{\bar{M}_n}{1} \quad (1.14)$$

²Notice that here we use the concept of distribution in a non-rigorous statistical sense. In rigorous statistical terms “distribution” usually alludes to the cumulative distribution function. Here, as in common language, by “distribution” we mean what in rigorous statistical terms is denoted as “density function” or “probability function”.

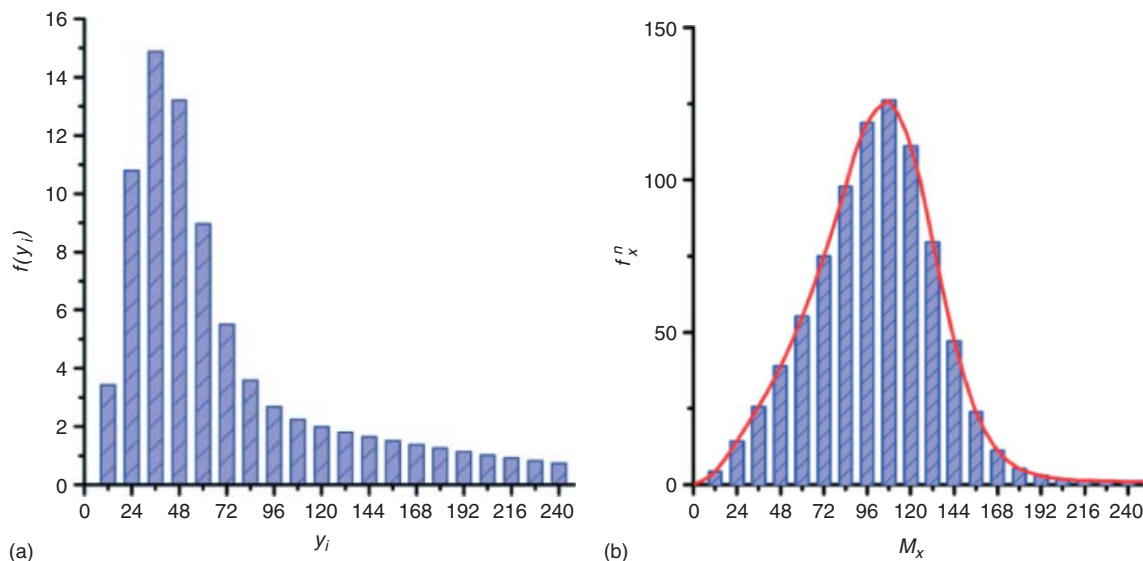


Figure 1.3 (a) A statistical discrete distribution (density) function f of the discrete random variable y_i . (b) Example of a discrete molecular weight distribution of a polymer represented as the number distribution f_x^n (or number fraction) of the discrete variable M_x .

Notice also that an equivalent physical definition of \overline{M}_n is

$$\overline{M}_n = \frac{\text{Polymer mass}}{\text{Polymer moles}} = \sum_x f_x^n M_x = \frac{\sum_x N_x M_x}{\sum_x N_x} \quad (1.15)$$

where the two right-most equalities come from application of Equations (1.3) and (1.6), respectively.

It is also possible to demonstrate (by application of equations (1.12), (1.5), (1.8), and (1.4) in that order) that

$$\overline{M}_w = \frac{\mu_2}{\mu_1} \quad (1.16)$$

Averages based on higher order moments are also used, for example,

$$\overline{M}_z = \frac{\mu_3}{\mu_2}; \quad \overline{M}_{z+1} = \frac{\mu_4}{\mu_3} \quad (1.17)$$

It should be emphasized that the discrete variable used here is M_x . In some textbooks and research papers, the moments of the MWD are defined in terms of the chain length distribution (CLD) (with chain length, x , being the discrete variable), which means that, in that case, the corresponding averages of the MWD defined in equations analogous to Equations (1.13), (1.16), and (1.17) need to be multiplied by M_0 .

A special average that can be estimated by measurements of the polymer solution intrinsic viscosity is the viscosimetric average molecular weight, which in terms of moments

is defined as

$$\overline{M}_v = \left(\frac{\mu_{\alpha+1}}{\mu_1} \right)^{1/\alpha} \quad (1.18)$$

where α is the exponent in the Mark-Houwink-Sakurada expression:

$$[\eta] = K \overline{M}_v^\alpha \quad (1.19)$$

in which $[\eta]$ is the intrinsic viscosity of a polymer solution and K and α are constants at a given temperature and for a given pair polymer–solvent [6].

Finally, the polydispersity index or molecular weight dispersity³ \mathcal{D} is defined as

$$\mathcal{D} = \frac{\overline{M}_w}{\overline{M}_n} \quad (1.20)$$

and it is a measure of the broadness of the MWD. It can be demonstrated that \mathcal{D} is related to the variance of the MWD by the following expression:

$$\sigma_{M_x}^2 = M_n^2 (\mathcal{D} - 1) \quad (1.21)$$

1.1.6 Main Types and Uses

In Section 1.2, we review in more detail the different criteria for the classification of polymers; however, at this point, it is convenient to describe some of the main types of polymers according to their use. On the basis of this, they

³The term “dispersity” instead of “polydispersity index” is now recommended by the IUPAC [7].

can be identified as plastics, thermosets, elastomers, fibers, paints, and coatings. These uses naturally derive from some of the thermodynamic and mechanical properties of the polymers, which were briefly described in Sections 1.1.3 and 1.1.4.

Plastics or *thermoplastics* are materials that can be shaped under heating. Once they are heated above certain temperature these materials flow as very viscous liquids and can adopt the shape of a mold; once they are cooled down again, they keep the new molded shape. In general terms, this process of heating and molding can be repeated a number of times; however, after some reprocessing of this sort, the polymeric chains can break or undergo reactions leading to reduced physical properties, a fact that sets practical limits to the recyclability of thermoplastics. Some of the most important thermoplastics by volume are polyethylene (low density polyethylene (LDPE) and high density polyethylene (HDPE)), polypropylene (PP), poly(vinyl chloride) (PVC) and polystyrene (PS or PSt), to name a few. Thermoplastics are synthesized in large amounts in polymerization plants and are then transformed by other users in processing equipment to form objects useful in packaging or as utensils, for example.

Thermosets, on the other hand, are polymers formed by the mixing and chemical reaction of fluid precursors into a mold; once the precursors react, a crosslinked network that cannot flow anymore under heating is created; therefore, reaction and molding into the final shape usually take place at the same time (by the RIM or reaction injection molding process). Examples of common thermosets are some polyesters, phenol-formaldehyde resins, epoxy resins, and polyurethanes, among others. Chapter 28 of this handbook elaborates on this topic.

Elastomers or *rubbers* are flexible materials that are mainly used in tires, hoses, and seals; as adhesives; or as impact modifiers of thermoplastics. They exhibit high resistance to impact, even at low temperatures at which materials increase their rigidity. For some of the applications (e.g., tires or hoses), these materials have to be slightly crosslinked once they are formed into the desired shape in order to impart them dimensional stability, since otherwise they tend to slowly flow. Elastomers are polymers that are used above their glass-transition temperature (T_g). Some examples of common elastomers are polybutadiene, which is used as an impact modifier of rigid plastics; SBR (copolymer of styrene and butadiene), mainly used in tires; EPDM (copolymer of ethylene, propylene, and a diene monomer, usually norbornene); NBR (copolymer of acrylonitrile and butadiene); and so on.

Fibers are polymers with very high moduli and very high resistance to deformation; therefore, they elongate very little. Some examples of polymers used as fibers are nylon (polyamide), polyesters, and polyacrylonitrile (acrylic fiber).

Paints and *coatings* are based on polymers that can form a film. The polymer is considered the binder or vehicle that carries the pigments and additives that are used to impart color or protect the surface of the substrates on which the paint or coating is applied. Some examples of polymers used as paint base are copolymers of styrene–butyl acrylate or of acrylic monomer–vinyl acetate. In the product, the polymer is either finely dispersed in water forming a latex or dissolved in a solvent (in oil-based paints). Latexes for paints are usually produced by emulsion polymerization (Chapter 14).

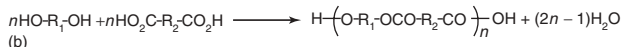
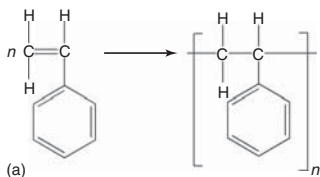
1.2 CLASSIFICATION OF POLYMERS

Given the versatility of polymers, they can be classified according to different criteria. In this section, we review some of these classifications.

1.2.1 Classification Based on Structure

This is one of the oldest and most important classification criteria originally proposed by Carothers [3] in 1929 and the one that splits polymers into two major types: addition and condensation polymers. The basis for the distinction is better understood by illustration with two examples belonging each one to one category: polystyrene as an addition polymer and a polyester as a condensation polymer. They are produced by the reactions shown in Scheme 1.1.

In both the cases, the structure shown in parenthesis or brackets in the main product of the reaction is called *repeating unit*. In an addition polymer, the repeating unit has the same composition as that of the monomer; the only difference is the change of chemical bonds with respect to those of the monomer. On the other hand, in a condensation polymer, according to the original idea of Carothers, some atoms of the monomer are lost as a condensation compound when the monomers react to form the repeating unit of the polymer. Some years after the original Carothers classification, it became clear that some polymers, for example, polyurethane, which is synthesized by the reaction between a diol and a diisocyanate, would not generate any condensation molecule, so they could not be classified as a condensation polymer; still their chemistry and structure had much more in common with those of condensation polymers than with those of addition polymers; therefore, the criterion for classification of a polymer as one of condensation type was changed to include this type of cases. The modern accepted criterion determines that a condensation polymer is that which satisfies any of the following conditions: (i) some atoms of the monomer are lost as a small molecule during their synthesis or (ii) they contain functional groups as part of the main polymer



Scheme 1.1 Examples of the synthesis reactions of (a) an addition polymer, polystyrene and (b) a condensation polymer, generic polyester with R_1 and R_2 being aliphatic or aromatic groups.

chain, such as ester, urethane, amide, or ether. If a polymer does not satisfy any of these criteria then it is an addition polymer.⁴ This issue is further discussed in Odian [8].

1.2.2 Classification Based on Mechanism

A second major classification of polymers was proposed by Flory [1] in 1953. This is based on the kinetic mechanism of the polymerization reaction. Flory classifies polymerizations into two categories:

1. Step-growth polymerization;
2. Chain polymerization.

1.2.2.1 Step-growth Polymerization The simplest scheme of this polymerization involves the reaction of a difunctional monomer AB, which contains both functional groups A and B in the molecule. For example, A can be an amine and B a carboxylic acid group. Another scheme involves the reaction between two difunctional monomers of the type AA and BB. In any case, each polymer linkage will have involved the reaction of the functional groups A and B coming from two molecules (monomers or chains). Some examples of polymers synthesized by this mechanism are polyurethane, polyamide, and polyester.

This mechanism shows the following features:

1. The chain growth occurs by steps; at each step, a reaction between the functional groups belonging to two monomers or chains occurs. If M_1 denotes monomer, M_2 dimer, M_3 trimer, and so on, the mechanism can be schematically represented as follows:



⁴IUPAC only defines the term polycondensation, but no condensation polymers; however this last classification is of widespread use.

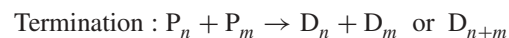
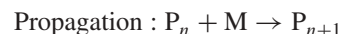


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2. The size of the chains increases gradually and relatively slowly.
3. Any two species in the system can react as long as they possess unreacted dissimilar functional groups.
4. Monomer disappears at low conversions.
5. Conversion is measured in terms of the functional groups reacted.

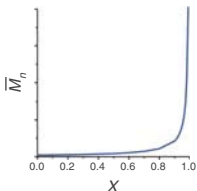
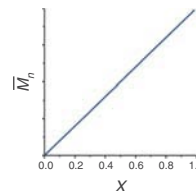
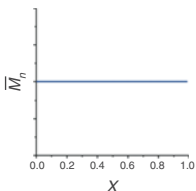
1.2.2.2 Chain Polymerization This is characterized by:

1. It requires a generator of active centers (usually an initiator for free radicals, anions, or cations).
2. Chain growth occurs by propagation of the active center (chain reaction of the active center with monomer).
3. The monomer only reacts with active centers (not with more monomer).
4. Monomer is present throughout all the reaction.
5. There is high molecular weight polymer present at any time during the polymerization, so the contents of the reaction at any time are unreacted monomer, unreacted initiator, and high molecular weight polymer. There are no significant amounts of intermediate size species (dimer, trimers, etc.).
6. Since there is a clear distinction between monomer and polymer, the conversion is measured in terms of the monomer already incorporated in a polymer chain.
7. The reaction mechanism for free radical polymerization as an example can be represented as follows:



In the initiation steps, the initiator I decomposes generating two active centers (primary radicals) R, which react with a monomer M to produce an active polymer of length 1, P_1 , having an active center. The active polymer grows by propagation of the active center adding a monomer unit in each propagation reaction. Finally, two active centers react, forming dead polymer of length n , D_n .

TABLE 1.2 Differences Between the Step-Growth and the Chain Polymerization Mechanisms

| Feature | Step-Growth Mechanism | Chain (Living) | Chain (with Termination) |
|--------------------------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| Number and class of reactions | Only one between dissimilar groups (A and B) | Two reactions: initiation and propagation | Three reactions: initiation, propagation, and termination |
| Reactive species | Two species of any size having dissimilar groups | Active species of any size with monomer | Active species of any size with monomer or among them (termination) |
| Monomer consumption | Monomer disappears early in the reaction | Monomer is present up to high conversion | Monomer is present up to high conversion |
| Conversion | On the basis of reacted functional groups | On the basis of polymerized monomer | On the basis of polymerized monomer |
| Average molecular weight versus conversion |  |  |  |

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The differences between the step-growth and the chain polymerization mechanisms are summarized in Table 1.2. Notice that chain polymerizations may include bimolecular termination reactions (as in the free radical mechanism) or may not (as in living anionic or cationic polymerizations).

Although sometimes the classifications of condensation and step-growth polymers are considered to be interchangeable, as well as those of addition and chain-growth polymers, one must be aware that the classification of a polymer only by structure or only by mechanism may lead to ambiguities. Odian [8] recommends to classify a polymer attending both, structure and mechanism, in order to avoid this problem. Tables 1.3 and 1.4 contain examples of common addition and condensation polymers, respectively.

1.2.3 Classification by Chain Topology

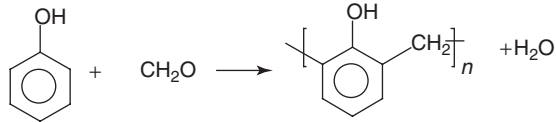
Two polymers having the same chemical composition but different chain topology can exhibit profound differences in crystallinity, physical properties, rheological behavior, and so on. For example, the differences in density, crystallinity, as well as mechanical and rheological properties of LDPE and HDPE derive from the presence or not of long and short branches along the polymer chain. Linear chains are those with no branches; these are shown schematically in Figure 1.4a. Branched chains have at least one branch along the main chain. These branches are classified as short (usually less than 10 repeating units) or long, and they are schematically illustrated in Figure 1.4b. Branches can also be classified, according to Flory, as trifunctional or tetrafunctional, depending on the number of paths departing from the branching point. If the branches are formed by repeating units (monomer) different from those forming

TABLE 1.3 Examples of Common Addition Polymers

| Addition Polymers | Repeating Unit |
|---------------------------|------------------------------------------------------------------------------------------------|
| Polyacrylonitrile | $\text{---CH}_2\text{---CH---}$ CN |
| Polybutadiene | $\text{---CH}_2\text{---CH=CH---CH}_2\text{---}$ |
| Polyethylene | $\text{---CH}_2\text{---CH}_2\text{---}$ |
| Poly(methyl methacrylate) | $\text{---CH}_2\text{---C---}$ CH ₃ CO ₂ CH ₃ |
| Polypropylene | $\text{---CH}_2\text{---CH---}$ CH ₃ |
| Polystyrene | $\text{---CH}_2\text{---CH---}$ φ |
| Poly(vinyl chloride) | $\text{---CH}_2\text{---CH---}$ Cl |

the main chain, the branched polymer is a graft copolymer (Figure 1.4c, see also Chapter 6). Crosslinked polymers are those forming a three-dimensional network and are shown in Figure 1.4d; they are insoluble and have very restricted chain-segment mobility; therefore, they do not flow (a discussion on the processes leading to crosslinked polymers can be found in Chapter 9).

TABLE 1.4 Examples of Common Condensation Polymers

| Polymer | Synthesis Reaction → Repeating Unit |
|---------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Polyamide | $\text{H}_2\text{N}-\text{R}_1-\text{NH}_2 + \text{HO}_2\text{C}-\text{R}_2-\text{CO}_2\text{H} \longrightarrow \text{H}-\left[\text{NH}-\text{R}_1-\text{NHCO}-\text{R}_2-\text{CO} \right]_n-\text{OH} + \text{H}_2\text{O}$ |
| Polyester | $\text{HO}-\text{R}_1-\text{OH} + \text{HO}_2\text{C}-\text{R}_2-\text{CO}_2\text{H} \longrightarrow \text{H}-\left[\text{O}-\text{R}_1-\text{OCO}-\text{R}_2-\text{CO} \right]_n-\text{OH} + \text{H}_2\text{O}$ |
| Phenol-formaldehyde |  |
| Urea-formaldehyde | $\text{H}_2\text{N}-\text{CO}-\text{NH}_2 + \text{CH}_2\text{O} \longrightarrow \left[\text{HN}-\text{CO}-\text{NH}-\text{CH}_2 \right]_n + \text{H}_2\text{O}$ |
| Polyurethane | $\text{HO}-\text{R}_1-\text{OH} + \text{OCN}-\text{R}_2-\text{NCO} \longrightarrow \left[\text{O}-\text{R}_1-\text{OCO}-\text{NH}-\text{R}_2-\text{NH}-\text{CO} \right]_n$ |

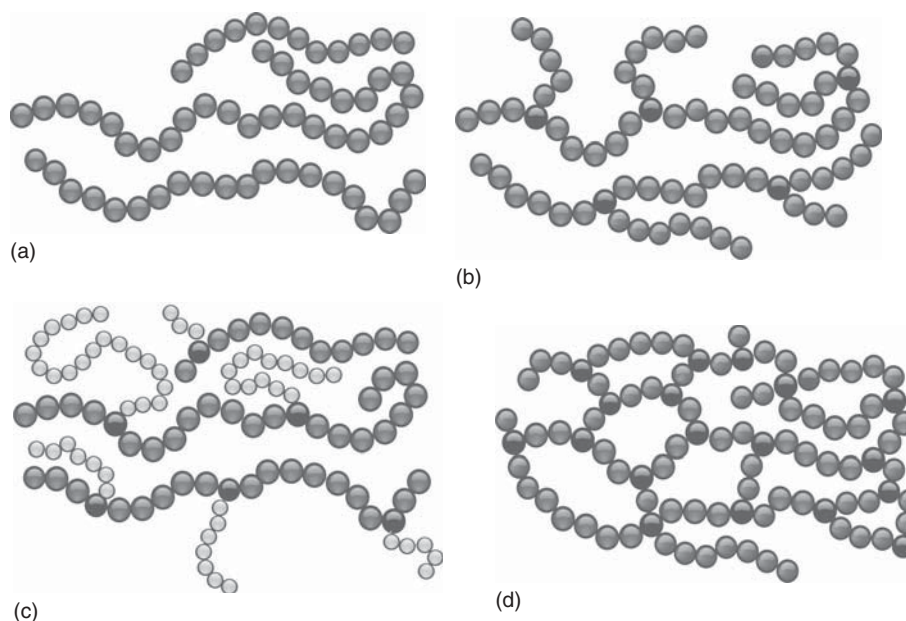


Figure 1.4 Different polymer chain topologies: (a) linear polymer; (b) branched polymer; (c) graft copolymer; and (d) crosslinked polymer. Dotson NE, Galván R, Laurence RL, Tirrell M. *Polymerization Process Modeling*. VCH Publishers; 1995. p 35 [8]. Copyright 1995 Wiley-VCH Verlag GmbH & Co. KGaA.

1.2.4 Other Classification Criteria

1.2.4.1 Homopolymer and Copolymer If only one type of monomer or repeating unit constitutes the macromolecule (without considering the chain ends) then the polymeric substance is termed a *homopolymer*. If, on the other hand, more than one type of repeating unit is present in the macromolecule, the polymeric substance is a *copolymer*. The macromolecule produced in the specific case of a reacting mixture containing three different monomers or monomer units is termed *terpolymer*. Depending on the randomness or order in which two or more types of repeating units are present in the macromolecule, there are

different types of copolymers: random, block, alternate, and so on. These are described in Chapter 6.

1.2.4.2 Origin Another possible classification of polymeric substances can be based on the origin of the material or the repeating units. In this sense, one can have *natural* and *synthetic* polymers, if they occur in nature or if they are synthesized in a chemical laboratory, respectively. Of course, natural polymers are of great importance, but they fall out of the scope of this handbook, which is mainly concerned with synthetic polymers.

Also, among the synthetic polymers, one can distinguish between organic and inorganic polymers, depending on

the presence or absence of carbon atoms in the polymer chain backbone. Synthetic organic polymers are by far the most studied and utilized polymeric substances of the two categories, mainly because of the availability of organic monomers coming from the petrochemical industry, and this handbook is mainly concerned with this type of polymers.

On the other hand, inorganic polymers have long been known, and recently, increasing research is being done in this field. Typical inorganic polymers contain oxygen, silicon, nitrogen, or phosphorus in their backbones [10]. Inorganic polymers can overcome some of the disadvantages of organic polymers, such as degradability at relatively low temperatures, or in the presence of oxygen or radiation, and they are expected to become more important in the future. The reader can find more details on this subject elsewhere [10].

1.2.4.3 Biodegradability *Biodegradable polymers* are those that degrade by the action of biological agents (e.g., microorganisms, bacteria or fungi) in ambient or mild conditions, and in relatively short times. In order to be more specific, it is necessary to set a time frame for degradability, to define the environmental conditions under which degradation is supposed to occur, and also to what extent the polymer must degrade in order to be considered biodegradable [11]. Most of the commodity polymers are not biodegradable: polyethylenes, poly(ethylene terephthalate) (PET), PVC, polystyrene, and so on. The development and commercialization of biodegradable polymers in significant amounts is relatively recent (since around the year 2001), but an accelerated growth of this industry is expected because of worldwide growing environmental concerns. Some examples of biodegradable polymers are poly(lactic acid) (PLA), poly(hydroxyalkanoates) (PHA) [12], and polycaprolactones.

1.2.4.4 Production Volume Finally, polymers can be classified by production volume. Large production volume polymers are *commodities*, and they are usually produced by continuous processes with very low profit margins per weight unit. Mostly, mature technologies are used to produce them, and the investment in R&D that is used to improve the production processes or products tends to be relatively low. Main examples of commodities are polyethylene (LDPE and HDPE), polypropylene, PVC, PET, polystyrene, and derivatives. These five families of polymers constitute those produced in largest volume. Estimated worldwide production of polymers in 2003 was around 200 million Tons, with an annual estimated global growth rate of 3.4% [13]. About 80% of the total polymer production is composed of the five families of commodities mentioned above.

On the other hand, *specialty polymers* are produced in smaller quantities, in batch or semibatch processes, and have high profit margins per weight unit. They require high investment in R&D in order to offer significant advantages over existing products for specific applications.

1.3 NOMENCLATURE

Unfortunately, at present, the naming of polymers is not uniform. The International Union for Pure and Applied Chemistry (IUPAC) has established some systematic rules for the naming of polymers, but they are not used by everyone. For some polymers, there are common or trade names that are used almost exclusively, instead of the more systematic IUPAC names. The lack of rigor and uniformity in naming polymers may occasionally give rise to confusions; in this book, different types of names are used as long as there is no ambiguity in the identification of the polymer.

Three naming systems are briefly discussed here: (i) conventional nomenclature based on source or structure, (ii) IUPAC structure-based nomenclature, and (iii) trade and common names and abbreviations. A deeper discussion can be found in the text by Odian [8].

1.3.1 Conventional Nomenclature.

The most common nonofficial (non-IUPAC) convention used to name polymers is based on the source from which the polymer is formed. This is particularly useful for polymers formed of a single monomer (homopolymers) synthesized by addition, ring-opening, or condensation polymerizations (Section 1.2). This rule consists in using the prefix “poly” followed by the name of the monomer (repeating unit), frequently enclosed in parenthesis, although, in many cases, the name of the monomer is simply written after the prefix without separation. Examples of this convention are poly(methyl methacrylate), polystyrene, polypropylene, PVC, poly(ethylene oxide), and PLA. The parentheses are used in cases in which otherwise ambiguity would arise.

For condensation polymers formed by two bifunctional monomers (of the type AA and BB, where A and B are different functional groups, see Section 1.2) the rule varies to reflect the structure of the repeating unit. In this case, instead of the monomer(s) name, the name of the structural group formed by the reaction of the two functional groups (A and B) is used as the base for the nomenclature and is enclosed in parentheses following the prefix “poly.” Consider, for example, the polymer formed by the reaction of ethylene glycol HO—CH₂—CH₂—OH (a monomer containing two OH or “A” groups) and terephthalic acid HO₂C—C₆H₄—CO₂H (monomer containing two COOH or “B” groups). The reaction between the carboxyl and

TABLE 1.5 Widespread Abbreviations for Some Common Polymers

| Abbreviation | Polymer | Abbreviation | Polymer |
|--------------|--------------------------------------------|--------------|--------------------------------------------|
| ABS | Acrylonitrile-butadiene-styrene terpolymer | PET | Poly(ethylene terephthalate) |
| BR | Butyl rubber or poly(isobutylene) | PLA | Poly(lactic acid) |
| EPDM | Ethylene-propylene-diene monomer rubber | PMMA | Poly(methyl methacrylate) |
| EPR | Ethylene-propylene rubber | PS (or GPPS) | Polystyrene or general purpose polystyrene |
| EPS | Expandable polystyrene | PP | Polypropylene |
| HDPE | High density polyethylene | PTFE | Poly(tetrafluoroethylene) |
| HIPS | High impact polystyrene | PU | Polyurethane |
| LDPE | Low density polyethylene | PVA | Poly(vinyl alcohol) |
| LLDPE | Linear low density polyethylene | PVC | Poly(vinyl chloride) |
| MBS | Methyl methacrylate-butadiene-styrene | PVDC | Poly(vinylidene chloride) |
| NBR | Acrylonitrile-butadiene rubber | PVDF | Poly(vinylidene fluoride) |
| PA | Polyamide | SAN | Styrene acrylonitrile copolymer |
| PAN | Polyacrylonitrile | SBR | Styrene-butadiene rubber |
| PBT | Poly(butylene terephthalate) | SBS | Styrene-butadiene-styrene block copolymer |
| PC | Polycarbonate | SIS | Styrene-isoprene-styrene block copolymer |
| PEO | Poly(ethylene oxide) | SMA | Styrene-maleic anhydride copolymer |

the hydroxyl groups can be considered to yield the ester group or repeating structural unit “ethylene terephthalate.” Therefore, the resulting polymer is denoted poly(ethylene terephthalate).

1.3.2 IUPAC Structure-based Nomenclature

The IUPAC nomenclature is not discussed here in detail, only the main idea behind it. Complete details can be found in the text by Odian [8] or in the original source [14].

The IUPAC rules for naming polymers are applicable to *single-strand* polymers, which are those comprising constitutional units connected in such a way that adjacent constitutional units are linked one to another by two atoms, one on each constitutional unit. The large majority of common polymers are single-strand ones. The IUPAC nomenclature is based on the selection of a preferred constitutional repeating unit or CRU, where the CRU is the smallest possible repeating unit of the polymer. This is named by the prefix poly followed by the name of the CRU in parentheses or brackets. This rule coincides with the simpler non-IUPAC rule given before, except for polymers in which the repeating unit (monomer) is formed by two identical halves (such as ethylene). The IUPAC naming system is more powerful and general than other conventional systems since the CRU is named following the rules for small organic compounds.

1.3.3 Trade Names, Common Names, and Abbreviations

Trade names have become well established for certain polymers. A good example is nylon, which is the trade name of the generic family of polyamides. When the polyamide is

based on the condensation of a diamine and a dicarboxylic acid, the word nylon is followed by two numbers, for example, nylon 6,6, which correspond to the number of carbon atoms in the diamine and the dicarboxylic acid parts of the repeating unit, respectively. On the other hand, if the polyamide is based on a single monomer, a single number reflecting the number of carbon atoms in the repeating unit follows the word nylon, as in nylon 6.

Other examples of well-established trade names are Kevlar (poly(paraphenylene terephthalamide)), Plexy-glass (sheets of poly(methyl methacrylate)), Teflon (poly(tetrafluoroethylene)), and Dacron (PET fiber).

Abbreviations and common names are also widely used, especially in industry and also to some extent in technical journals and academic environments. Table 1.5 contains a nonexhaustive list of some of the more common abbreviations in use; many of them refer to copolymers (for more information on copolymer naming rules, see Chapter 6). The reader must be aware of some details regarding the brief polymer description in Table 1.5 (columns 2 and 4); some of these materials are not pure polymers, but rather a complex mixture of two or three different polymers forming a two-phase material, such as in the case of high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS), and methyl methacrylate-butadiene-styrene (MBS); see Chapter 10 for more details on the structure of these materials.

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