Chapter 1

Introduction

I. HISTORICAL DEVELOPMENT

Before we go into details of the chemistry of polymers it is appropriate to briefly outline a few landmarks in the historical development of what we now know as polymers. Polymers have been with us from the beginning of time; they form the very basis (building blocks) of life. Animals, plants — all classes of living organisms — are composed of polymers. However, it was not until the middle of the 20th century that we began to understand the true nature of polymers. This understanding came with the development of plastics, which are true man-made materials that are the ultimate tribute to man's creativity and ingenuity. As we shall see in subsequent discussions, the use of polymeric materials has permeated every facet of our lives. It is hard to visualize today's world with all its luxury and comfort without man-made polymeric materials.

The plastics industry is recognized as having its beginnings in 1868 with the synthesis of cellulose nitrate. It all started with the shortage of ivory from which billiard balls were made. The manufacturer of these balls, seeking another production method, sponsored a competition. John Wesley Hyatt (in the U.S.) mixed pyroxin made from cotton (a natural polymer) and nitric acid with camphor. The result was cellulose nitrate, which he called celluloid. It is on record, however, that Alexander Parkes, seeking a better insulating material for the electrical industry, had in fact discovered that camphor was an efficient plasticizer for cellulose nitrate in 1862. Hyatt, whose independent discovery of celluloid came later, was the first to take out patents for this discovery.

Cellulose nitrate is derived from cellulose, a natural polymer. The first truly man-made plastic came 41 years later (in 1909) when Dr. Leo Hendrick Baekeland developed phenol–formaldehyde plastics (phenolics), the source of such diverse materials as electric iron and cookware handles, grinding wheels, and electrical plugs. Other polymers — cellulose acetate (toothbrushes, combs, cutlery handles, eyeglass frames); urea–formaldehyde (buttons, electrical accessories); poly(vinyl chloride) (flooring, upholstery, wire and cable insulation, shower curtains); and nylon (toothbrush bristles, stockings, surgical sutures) — followed in the 1920s.

Table 1.1 gives a list of some plastics, their year of introduction, and some of their applications. It is obvious that the pace of development of plastics, which was painfully slow up to the 1920s, picked up considerable momentum in the 1930s and the 1940s. The first generation of man-made polymers was the result of empirical activities; the main focus was on chemical composition with virtually no attention paid to structure. However, during the first half of the 20th century, extensive organic and physical developments led to the first understanding of the structural concept of polymers — long chains or a network of covalently bonded molecules. In this regard the classic work of the German chemist Hermann Staudinger on polyoxymethylene and rubber and of the American chemists W. T. Carothers on nylon stand out clearly. Staudinger first proposed the theory that polymers were composed of giant molecules, and he coined the word *macromolecule* to describe them. Carothers discovered nylon, and his fundamental research (through which nylon was actually discovered) contributed considerably to the elucidation of the nature of polymers. His classification of polymers as *condensation* or *addition* polymers persists today.

Following a better understanding of the nature of polymers, there was a phenomenal growth in the numbers of polymeric products that achieved commercial success in the period between 1925 and 1950. In the 1930s, acrylic resins (signs and glazing); polystyrene (toys, packaging and housewares industries); and melamine resins (dishware, kitchen countertops, paints) were introduced.

The search for materials to aid in the defense effort during World War II resulted in a profound impetus for research into new plastics. Polyethylene, now one of the most important plastics in the world, was developed because of the wartime need for better-quality insulating materials for such applications as radar cable. Thermosetting polyester resins (now used for boatbuilding) were developed for military use. The terpolymer acrylonitrile-butadiene-styrene (ABS), (telephone handsets, luggage,

Table 1.1 *Introduction of Plastics Materials*

Date	Material	Typical Use
1868	Cellulose nitrate	Eyeglass frames
1909	Phenol–formaldehyde	Telephone handsets, knobs, handles
1919	Casein	Knitting needles
1926	Alkyds	Electrical insulators
1927	Cellulose acetate	Toothbrushes, packaging
1927	Poly(vinyl chloride)	Raincoats, flooring
1929	Urea–formaldehyde	Lighting fixtures, electrical switches
1935	Ethyl cellulose	Flashlight cases
1936	Polyacrylonitrile	Brush backs, displays
1936	Poly(vinyl acetate)	Flashbulb lining, adhesives
1938	Cellulose acetate butyrate	Irrigation pipe
1938	Polystyrene	Kitchenwares, toys
1938	Nylon (polyamide)	Gears, fibers, films
1938	Poly(vinyl acetal)	Safety glass interlayer
1939	Poly(vinylidene chloride)	Auto seat covers, films, paper, coatings
1939	Melamine–formaldehyde	Tableware
1942	Polyester (cross-linkable)	Boat hulls
1942	Polyethylene (low density)	Squeezable bottles
1943	Fluoropolymers	Industrial gaskets, slip coatings
1943	Silicone	Rubber goods
1945	Cellulose propionate	Automatic pens and pencils
1947	Epoxies	Tools and jigs
1948	Acrylonitrile-butadiene-styrene copolymer	Luggage, radio and television cabinets
1949	Allylic	Electrical connectors
1954	Polyurethane	Foam cushions
1956	Acetal resin	Automotive parts
1957	Polypropylene	Safety helmets, carpet fiber
1957	Polycarbonate	Appliance parts
1959	Chlorinated polyether	Valves and fittings
1962	Phenoxy resin	Adhesives, coatings
1962	Polyallomer	Typewriter cases
1964	Ionomer resins	Skin packages, moldings
1964	Polyphenylene oxide	Battery cases, high temperature moldings
1964	Polyimide	Bearings, high temperature films and wire coatings
1964	Ethylene–vinyl acetate	Heavy gauge flexible sheeting
1965	Polybutene	Films
1965	Polysulfone	Electrical/electronic parts
1970	Thermoplastic polyester	Electrical/electronic parts
1971	Hydroxy acrylates	Contact lenses
1973	Polybutylene	Piping
1974	Aromatic polyamides	High-strength tire cord
1975	Nitrile barrier resins	Containers

safety helmets, etc.) owes its origins to research work emanating from the wartime crash program on large-scale production of synthetic rubber.

The years following World War II (1950s) witnessed great strides in the growth of established plastics and the development of new ones. The Nobel-prize-winning development of stereo-specific catalysts by Professors Karl Ziegler of Germany and Giulio Natta of Italy led to the ability of polymer chemists to "order" the molecular structure of polymers. As a consequence, a measure of control over polymer properties now exists; polymers can be tailor-made for specific purposes.

The 1950s also saw the development of two families of plastics — acetal and polycarbonates. Together with nylon, phenoxy, polyimide, poly(phenylene oxide), and polysulfone they belong to the group of plastics known as the engineering thermoplastics. They have outstanding impact strength and thermal and dimensional stability — properties that place them in direct competition with more conventional materials like metals.

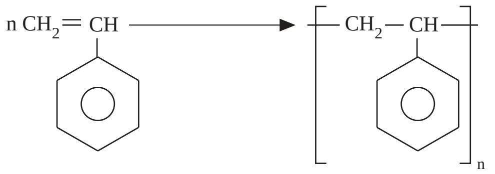
The 1960s and 1970s witnessed the introduction of new plastics: thermoplastic polyesters (exterior automotive parts, bottles); high-barrier nitrile resins; and the so-called high-temperature plastics, including such materials as polyphenylene sulfide, polyether sulfone, etc. The high-temperature plastics were initially developed to meet the demands of the aerospace and aircraft industries. Today, however, they have moved into commercial areas that require their ability to operate continuously at high temperatures.

In recent years, as a result of better understanding of polymer structure–property relationships, introduction of new polymerization techniques, and availability of new and low-cost monomers, the concept of a truly tailor-made polymer has become a reality. Today, it is possible to create polymers from different elements with almost any quality desired in an end product. Some polymers are similar to existing conventional materials but with greater economic values, some represent significant improvements over existing materials, and some can only be described as unique materials with characteristics unlike any previously known to man. Polymer materials can be produced in the form of solid plastics, fibers, elastomers, or foams. They may be hard or soft or may be films, coatings, or adhesives. They can be made porous or nonporous or can melt with heat or set with heat. The possibilities are almost endless and their applications fascinating. For example, *ablation* is the word customarily used by the astronomers and astrophysicists to describe the erosion and disintegration of meteors entering the atmosphere. In this sense, long-range missiles and space vehicles reentering the atmosphere may be considered man-made meteors. Although plastic materials are generally thermally unstable, ablation of some organic polymers occurs at extremely high temperatures. Consequently, selected plastics are used to shield reentry vehicles from the severe heat generated by air friction and to protect rocket motor parts from hot exhaust gases, based on the concept known as ablation plastics. Also, there is a “plastic armor” that can stop a bullet, even shell fragments. (These are known to be compulsory attire for top government and company officials in politically troubled countries.) In addition, there are flexible plastics films that are used to wrap your favorite bread, while others are sufficiently rigid and rugged to serve as supporting members in a building.

In the years ahead, polymers will continue to grow. The growth, from all indications, will be not only from the development of new polymers, but also from the chemical and physical modification of existing ones. Besides, improved fabrication techniques will result in low-cost products. Today the challenges of recycling posed by environmental problems have led to further developments involving alloying and blending of plastics to produce a diversity of usable materials from what have hitherto been considered wastes.

II. BASIC CONCEPTS AND DEFINITIONS

The word *polymer* is derived from classical Greek ***poly*** meaning “many” and ***meres*** meaning “parts.” Thus a polymer is a large molecule (macromolecule) built up by the repetition of small chemical units. To illustrate this, Equation 1.1 shows the formation of the polymer polystyrene.

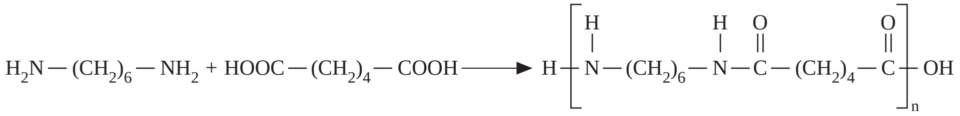


styrene (monomer) polystyrene (polymer)

(1) (2)

(1.1)

The styrene molecule (1) contains a double bond. Chemists have devised methods of opening this double bond so that literally thousands of styrene molecules become linked together. The resulting structure, enclosed in square brackets, is the polymer polystyrene (2). Styrene itself is referred to as a *monomer,* which is defined as any molecule that can be converted to a polymer by combining with other molecules of the same or different type. The unit in square brackets is called the *repeating unit.* Notice that the structure of the repeating unit is not exactly the same as that of the monomer even though both possess identical atoms occupying similar relative positions. The conversion of the monomer to the polymer involves a rearrangement of electrons. The residue from the monomer employed in the preparation of a polymer is referred to as the *structural unit.* In the case of polystyrene, the polymer is derived from a single monomer (styrene) and, consequently, the structural unit of the polystyrene chain is the same as its repeating unit. Other examples of polymers of this type are polyethylene, polyacrylonitrile, and polypropylene. However, some polymers are derived from the mutual reaction of two or more monomers that are chemically similar but not identical. For example, poly(hexamethylene adipamide) or nylon 6,6 (5) is made from the reaction of hexamethylenediamine (3) and adipic acid (4) (Equation 1.2).



$$H_2N-(CH_2)_6-NH_2 + HOOC-(CH_2)_4-COOH \longrightarrow H\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n OH \qquad (1.2)$$

hexamethylenediamine (3)

adipic acid (4)

poly(hexamethylene adipamide) (5)

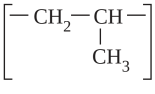
The repeating unit in this case consists of two structural units: $-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-$, the residue from hexamethylenediamine; and $-\overset{O}{\overset{\backslash}{C}}-(CH_2)_4-\overset{O}{\overset{\backslash}{C}}-$, the residue from adipic acid. Other polymers that have repeating units with more than one structural unit include poly(ethyleneterephthalate) and proteins. As we shall see later, the constitution of a polymer is usually described in terms of its structural units.

The subscript designation, n, in Equations 1.1 and 1.2 indicates the number of repeating units strung together in the polymer chain (molecule). This is known as the *degree of polymerization (DP).* It specifies the length of the polymer molecule. Polymerization occurs by the sequential reactions of monomers, which means that a successive series of reactions occurs as the repeating units are linked together. This can proceed by the reaction of monomers to form a *dimer,* which in turn reacts with another monomer to form a *trimer* and so on. Reaction may also be between dimers, trimers, or any molecular species within the reaction mixture to form a progressively larger molecule. In either case, a series of linkages is built between the repeating units, and the resulting polymer molecule is often called a *polymer chain,* a description which emphasizes its physical similarity to the links in a chain. Low-molecular-weight polymerization products such as dimers, trimers, tetramers, etc., are referred to as *oligomers.* They generally possess undesirable thermal and mechanical properties. A high degree of polymerization is normally required for a material to develop useful properties and before it can be appropriately described as a polymer. Polystyrene, with a degree of polymerization of 7, is a viscous liquid (not of much use), whereas commercial grade polystyrene is a solid and the DP is typically in excess of 1000. It must be emphasized, however, that no clear demarcation has been established between the sizes of oligomers and polymers.

The degree of polymerization represents one way of quantifying the molecular length or size of a polymer. This can also be done by use of the term *molecular weight (MW).* By definition, MW(Polymer) = DP × MW(Repeat Unit). To illustrate this let us go back to polystyrene (2). There are eight carbon atoms and eight hydrogen atoms in the repeating unit. Thus, the molecular weight of the repeating unit is 104 ($8 \times 12 + 1 \times 8$). If, as we stated above, we are considering commercial grade polystyrene, we will be dealing with a DP of 1000. Consequently, the molecular weight of this type of polystyrene is 104,000. As we shall see later, molecular weight has a profound effect on the properties of a polymer.

Example 1.1: What is the molecular weight of polypropylene (PP), with a degree of polymerization of 3×10^4?

Solution: Structure of the repeating unit for PP



$$\left[-CH_2-\underset{\underset{CH_3}{|}}{CH}-\right] \qquad \text{(Str. 1)}$$

Molecular weight of repeat unit = $(3 \times 12 + 6 \times 1) = 42$
Molecular weight of polypropylene = $3 \times 10^4 \times 42 = 1.26 \times 10^6$

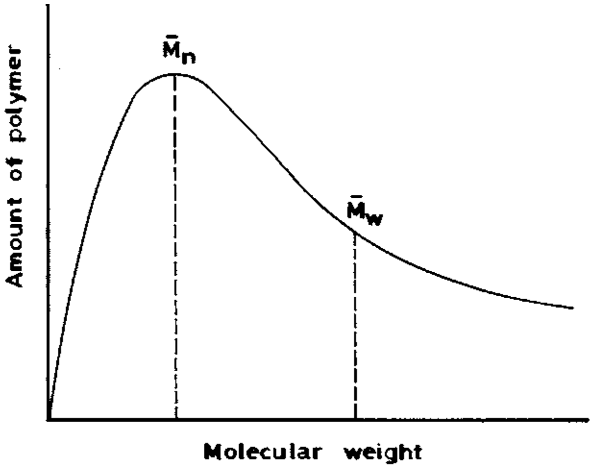


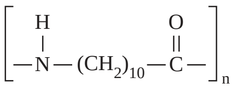
Figure 1.1 *Molecular weight distribution curve.*

So far, we have been discussing a single polymer molecule. However, a given polymer sample (like a piece of polystyrene from your kitchenware) is actually composed of millions of polymer molecules. For almost all synthetic polymers irrespective of the method of polymerization (formation), the length of a polymer chain is determined by purely random events. Consequently, any given polymeric sample contains a mixture of molecules having different chain lengths (except for some biological polymers like proteins, which have a single, well-defined molecular weight [monodisperse]). This means that a distribution of molecular weight exists for synthetic polymers. A typical molecular weight distribution curve for a polymer is shown in Figure 1.1.

The existence of a distribution of molecular weights in a polymer sample implies that any experimental measurement of molecular weight in the given sample gives only an average value. Two types of molecular weight averages are most commonly considered: the number-average molecular weight represented by $\overline{M}_n$, and the weight-average molecular weight $\overline{M}_w$. The number-average molecular weight is derived from measurements that, in effect, count the number of molecules in the given sample. On the other hand, the weight-average molecular weight is based on methods in which the contribution of each molecule to the observed effect depends on its size.

In addition to the information on the size of molecules given by the molecular weights $\overline{M}_w$ and $\overline{M}_n$, their ratio $\overline{M}_w/\overline{M}_n$ is an indication of just how broad the differences in the chain lengths of the constituent polymer molecules in a given sample are. That is, this ratio is a measure of polydispersity, and consequently it is often referred to as the heterogeneity index. In an ideal polymer such as a protein, all the polymer molecules are of the same size ($\overline{M}_w = \overline{M}_n$ or $\overline{M}_w/\overline{M}_n = 1$). This is not true for synthetic polymers – the numerical value of $\overline{M}_w$ is always greater than that of $\overline{M}_n$. Thus as the ratio $\overline{M}_w/\overline{M}_n$ increases, the molecular weight distribution is broader.

Example 1.2: Nylon 11 has the following structure



$$\left[-\overset{\displaystyle H}{\overset{|}{N}}-(CH_2)_{10}-\overset{\displaystyle O}{\overset{\|}{C}}-\right]_n$$

(Str. 2)

If the number-average degree of polymerization, $\overline{X}_n$, for nylon is 100 and $\overline{M}_w = 120{,}000$, what is its polydispersity?

Solution: We note that $\overline{X}_n$ and n(DP) define the same quantity for two slightly different entities. The degree of polymerization for a single molecule is n. But a polymer mass is composed of millions of molecules, each of which has a certain degree of polymerization. $\overline{X}_n$ is the average of these. Thus,

$$\overline{X}_n = \frac{\sum_{i=1}^{N} n_i\,M_r}{N}$$

where N = total number of molecules in the polymer mass
M_r = molecular weight of repeating unit
n_i = DP of molecule i.

Now $\overline{M}_n = \overline{X}_n M_r = 100\,(15 + 14 \times 10 + 28)$
$= 18{,}300$

$$\text{Polydispersity} = \frac{\overline{M}_w}{\overline{M}_n} = \frac{120{,}000}{18{,}300} = 6.56$$

III. CLASSIFICATION OF POLYMERS

Polymers can be classified in many different ways. The most obvious classification is based on the origin of the polymer, i.e., natural vs. synthetic. Other classifications are based on the polymer structure, polymerization mechanism, preparative techniques, or thermal behavior.

A. NATURAL VS. SYNTHETIC

Polymers may either be naturally occurring or purely synthetic. All the conversion processes occurring in our body (e.g., generation of energy from our food intake) are due to the presence of enzymes. Life itself may cease if there is a deficiency of these enzymes. Enzymes, nucleic acids, and proteins are polymers of biological origin. Their structures, which are normally very complex, were not understood until very recently. Starch — a staple food in most cultures — cellulose, and natural rubber, on the other hand, are examples of polymers of plant origin and have relatively simpler structures than those of enzymes or proteins. There are a large number of synthetic (man-made) polymers consisting of various families: fibers, elastomers, plastics, adhesives, etc. Each family itself has subgroups.

B. POLYMER STRUCTURE

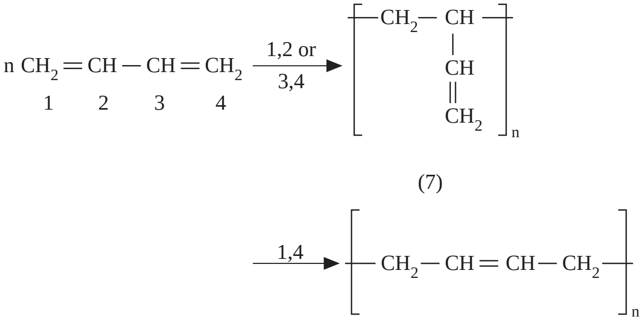
1. Linear, Branched or Cross-linked, Ladder vs. Functionality

As we stated earlier, a polymer is formed when a very large number of structural units (repeating units, monomers) are made to link up by covalent bonds under appropriate conditions. Certainly even if the conditions are “right” not all simple (small) organic molecules possess the ability to form polymers. In order to understand the type of molecules that can form a polymer, let us introduce the term *functionality.* The functionality of a molecule is simply its interlinking capacity, or the number of sites it has available for bonding with other molecules under the specific polymerization conditions. A molecule may be classified as monofunctional, bifunctional, or polyfunctional depending on whether it has one, two, or greater than two sites available for linking with other molecules. For example, the extra pair of electrons in the double bond in the styrene molecules endows it with the ability to enter into the formation of two bonds. Styrene is therefore bifunctional. The presence of two condensable groups in both hexamethylenediamine ($–NH_2$) and adipic acid (–COOH) makes each of these monomers bifunctional. However, functionality as defined here differs from the conventional terminology of organic chemistry where, for example, the double bond in styrene represents a single functional group. Besides, even though the interlinking capacity of a monomer is ordinarily apparent from its structure, functionality as used in polymerization reactions is specific for a given reaction. A few examples will illustrate this.

A diamine like hexamethylenediamine has a functionality of 2 in amide-forming reactions such as that shown in Equation 1.2. However, in esterification reactions a diamine has a functionality of zero. Butadiene has the following structure:

$$\begin{array}{cccc} CH_2{=} & CH{-} & CH{=} & CH_2 \\ 1 & 2 & 3 & 4 \end{array} \qquad \text{(Str. 3)}$$

From our discussion about the polymerization of styrene, the presence of two double bonds on the structure of butadiene would be expected to prescribe a functionality of 4 for this molecule. Butadiene may indeed be tetrafunctional, but it can also have a functionality of 2 depending on the reaction conditions (Equation 1.3).



(7)

(8)

(1.3)

Since there is no way of making a distinction between the 1,2 and 3,4 double bonds, the reaction of either double bond is the same. If either of these double bonds is involved in the polymerization reaction, the residual or unreacted double bond is on the structure attached to the main chain [i.e., part of the pendant group (7)]. In 1,4 polymerization, the residual double bond shifts to the 2,3 position along the main chain. In either case, the residual double bond is inert and is generally incapable of additional polymerization under the conditions leading to the formation of the polymer. In this case, butadiene has a functionality of 2. However, under appropriate reaction conditions such as high temperature or crosslinking reactions, the residual unsaturation either on the pendant group or on the backbone can undergo additional reaction. In that case, butadiene has a total functionality of 4 even though all the reactive sites may not be activated under the same conditions. Monomers containing functional groups that react under different conditions are said to possess *latent functionality.*

Now let us consider the reaction between two monofunctional monomers such as in an esterification reaction (Equation 1.4).

$$R\text{—COOH} + R'\text{—OH} \longrightarrow R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—O—}R' \tag{1.4}$$

acid (9)

alcohol (10)

ester (11)

You will observe that the reactive groups on the acid and alcohol are used up completely and that the product ester (11) is incapable of further esterification reaction. But what happens when two bifunctional molecules react? Let us use esterification once again to illustrate the principle (Equation 1.5).

$$\text{HOOC—}R\text{—COOH} + \text{HO—}R'\text{OH} \longrightarrow \text{HOOC—}R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—O—}R'\text{—OH} \tag{1.5}$$

bifunctional (12)

bifunctional (13)

bifunctional (14)

The ester (14) resulting from this reaction is itself bifunctional, being terminated on either side by groups that are capable of further reaction. In other words, this process can be repeated almost indefinitely. The same argument holds for polyfunctional molecules. It is thus obvious that the generation of a polymer through the repetition of one or a few elementary units requires that the molecule(s) must be at least bifunctional.

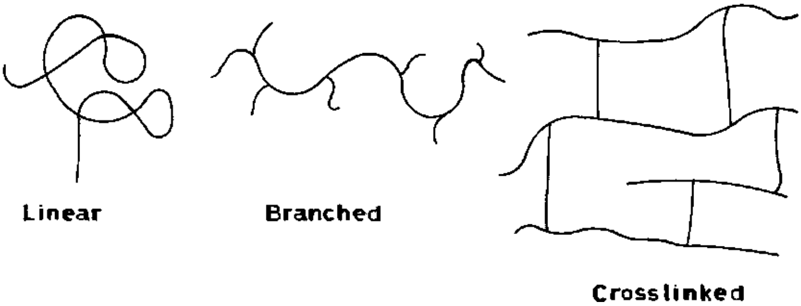
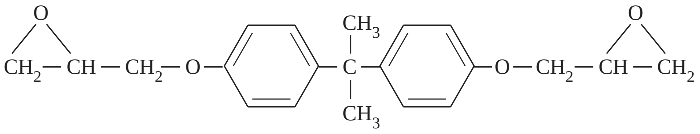


Figure 1.2 *Linear, branched, and cross-linked polymers.*

The structural units resulting from the reaction of monomers may in principle be linked together in any conceivable pattern. Bifunctional structural units can enter into two and only two linkages with other structural units. This means that the sequence of linkages between bifunctional units is necessarily linear. The resulting polymer is said to be *linear.* However, the reaction between polyfunctional molecules results in structural units that may be linked so as to form nonlinear structures. In some cases the side growth of each polymer chain may be terminated before the chain has a chance to link up with another chain. The resulting polymer molecules are said to be *branched.* In other cases, growing polymer chains become chemically linked to each other, resulting in a *cross-linked* system (Figure 1.2).

The formation of a cross-linked polymer is exemplified by the reaction of epoxy polymers, which have been used traditionally as adhesives and coatings and, more recently, as the most common matrix in aerospace composite materials. Epoxies exist at ordinary temperatures as low-molecular-weight viscous liquids or prepolymers. The most widely used prepolymer is diglycidyl ether of bisphenol A (DGEBA), as shown below (15):



(Str. 4)

diglycidyl ether of bisphenol A (DGEBA)
(15)

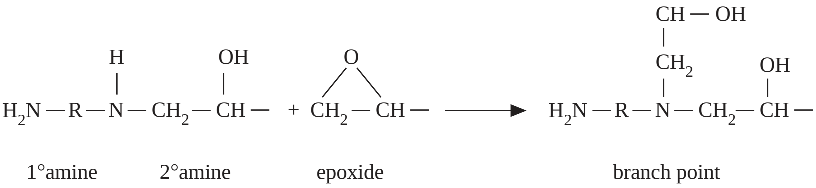
The transformation of this viscous liquid into a hard, cross-linked three-dimensional molecular network involves the reaction of the prepolymer with reagents such as amines or Lewis acids. This reaction is referred to as *curing.* The curing of epoxies with a primary amine such as hexamethylenediamine involves the reaction of the amine with the epoxide. It proceeds essentially in two steps:

1. The attack of an epoxide group by the primary amine

(1.6)

1°amine 1°amine epoxide 1°amine 2°amine
(16) (17) (18)

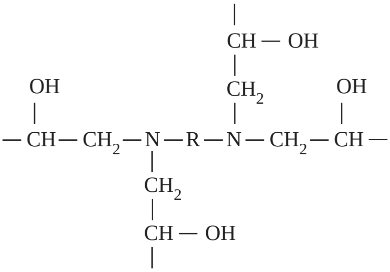
2. The combination of the resulting secondary amine with a second epoxy group to form a branch point (19).



(19)

(1.7)

The presence of these branch points ultimately leads to a cross-linked infusible and insoluble polymer with structures such as (20).

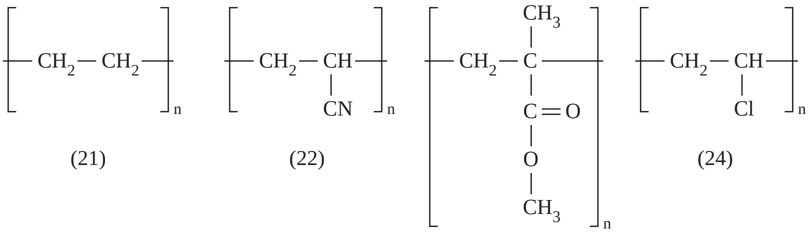


(20)

(Str. 5)

In this reaction, the stoichiometric ratio requires one epoxy group per amine hydrogen. Consequently, an amine such as hexamethylenediamine has a functionality of 4. Recall, however, that in the reaction of hexamethylenediamine with adipic acid, the amine has a functionality of 2. In this reaction DGEBA is bifunctional since the hydroxyl groups generated in the reaction do not participate in the reaction. But when the curing of epoxies involves the use of a Lewis acid such as BF_3, the functionality of each epoxy group is 2; that is, the functionality of DGEBA is 4. Thus the curing reactions of epoxies further illustrate the point made earlier that the functionality of a given molecule is defined for a specific reaction. By employing different reactants or varying the stoichiometry of reactants, different structures can be produced and, consequently, the properties of the final polymer can also be varied.

Polystyrene (2), polyethylene (21), polyacrylonitrile (22), poly(methyl methacrylate) (23), and poly(vinyl chloride) (24) are typical examples of linear polymers.

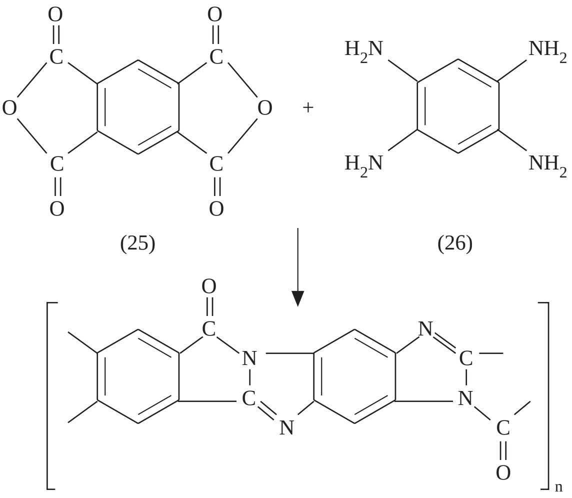


$$\left[-CH_2-CH_2-\right]_n \quad \left[-CH_2-\underset{CN}{\underset{|}{CH}}-\right]_n \quad \left[-CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{\underset{CH_3}{|}}{\underset{O}{|}}}{\underset{C=O}{\underset{|}{C}}}}}-\right]_n \quad \left[-CH_2-\underset{Cl}{\underset{|}{CH}}-\right]_n$$

(21) (22) (23) (24)

(Str. 6)

Substituent groups such as $-CH_3$, $-O-\overset{O}{\overset{\backslash}{C}}-CH_3$, $-Cl$, and $-CN$ that are attached to the main chain of skeletal atoms are known as *pendant groups*. Their structure and chemical nature can confer unique properties on a polymer. For example, linear and branched polymers are usually soluble in some solvent at normal temperatures. But the presence of polar pendant groups can considerably reduce room temperature solubility. Since cross-linked polymers are chemically tied together and solubility essentially involves the separation of solute molecules by solvent molecules, cross-linked polymers do not dissolve, but can only be swelled by liquids. The presence of cross-linking confers stability on polymers. Highly cross-linked polymers are generally rigid and high-melting. Cross-links occur randomly in a cross-linked polymer. Consequently, it can be broken down into smaller molecules by random chain scission. *Ladder polymers* constitute a group of polymers with a regular sequence of cross-links. A ladder polymer, as the name implies, consists of two parallel linear strands of molecules with a regular sequence of cross-links. Ladder polymers have only condensed cyclic units in the chain; they are also commonly referred to as double-chain or double-strand polymers. A typical example is poly(imidazopyrrolone) (27), which is obtained by the polymerization of aromatic dianhydrides such as pyromellitic dianhydride (25) or aromatic tetracarboxylic acids with *ortho*-aromatic tetramines like 1,2,4,5-tetraaminobenzene (26):



(25) (26)

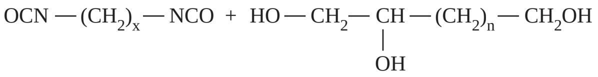
(27)

(Str. 7)

The molecular structure of ladder polymers is more rigid than that of conventional linear polymers. Numerous members of this family of polymers display exceptional thermal, mechanical, and electrical behavior. Their thermal stability is due to the molecular structure, which in essence requires that two bonds must be broken at a cleavage site in order to disrupt the overall integrity of the molecule; when only one bond is broken, the second holds the entire molecule together.

Example 1.3: Show the polymer formed by the reaction of the following monomers. Is the resulting polymer linear or branched/cross-linked?

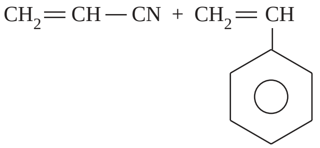
i.



$$OCN-(CH_2)_x-NCO + HO-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-(CH_2)_n-CH_2OH$$

(Str. 8)

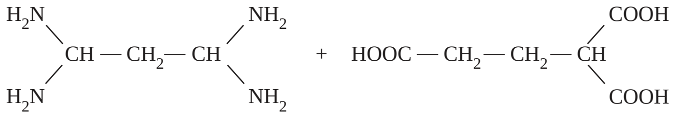
ii.



$CH_2=CH-CN + CH_2=CH$

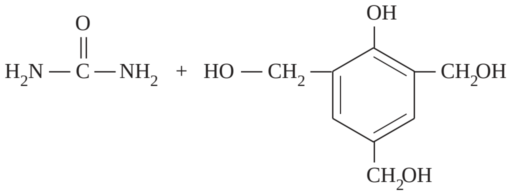
(Str. 9)

iii.



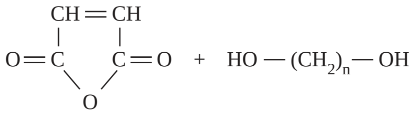
(Str. 10)

iv.



(Str. 11)

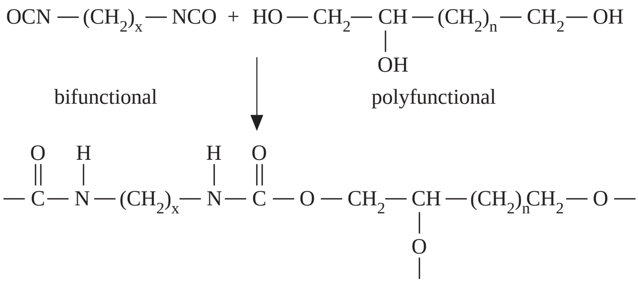
v.



(Str. 12)

Solution:

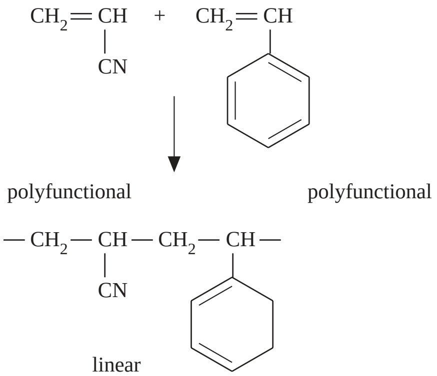
i.



branched/cross-linked

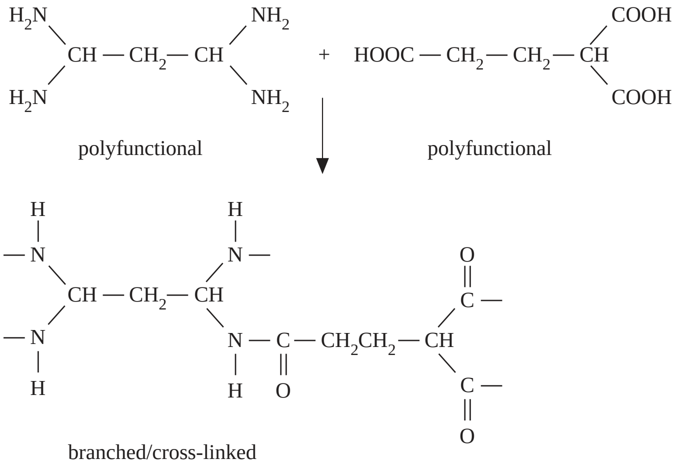
(Str. 13)

ii.



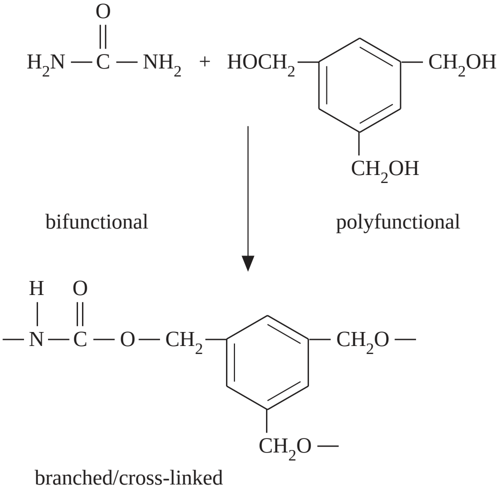
(Str. 14)

iii.



(Str. 15)

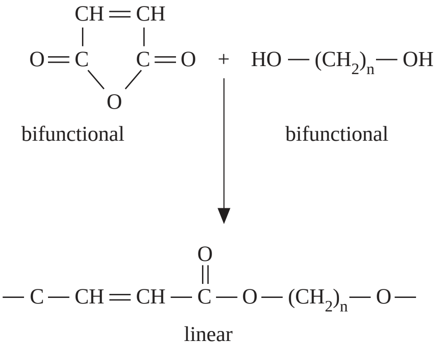
iv.



(Str. 16)

The resulting secondary hydrogens in the urea linkages are capable of additional reaction depending on the stoichiometric proportions of reactants. This means that, in principle, the urea molecule may be polyfunctional (tetrafunctional).

v.

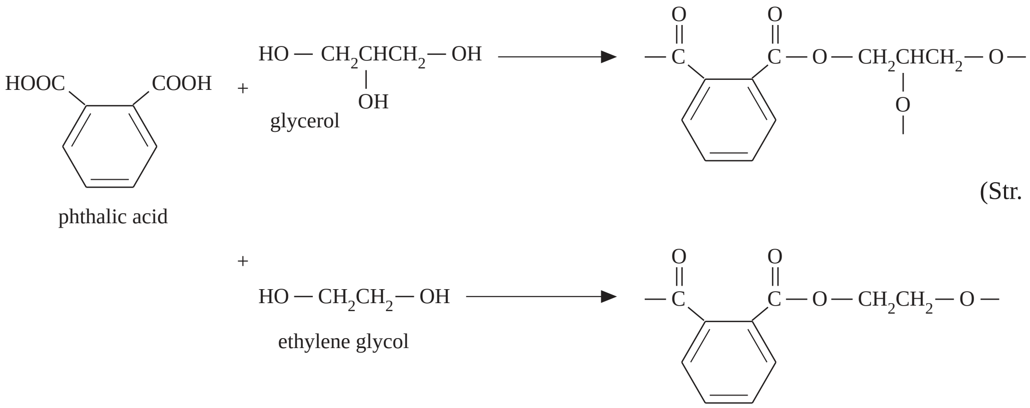


(Str. 17)

Even though the resulting polymer is linear, it can be cross-linked in a subsequent reaction due to the unsaturation on the main chain – for example, by using radical initiators.

Example 1.4: Explain the following observation. When phthalic acid reacts with glycerol, the reaction leads first to the formation of fairly soft soluble material, which on further heating yields a hard, insoluble, infusible material. If the same reaction is carried out with ethylene glycol instead of glycerol, the product remains soluble and fusible irrespective of the extent of reaction.

Solution:



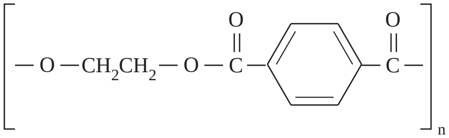
(Str. 18)

Phthalic acid and ethylene glycol are both bifunctional. Consequently, only linear polymers are produced from the reaction between these monomers. On the other hand, the reaction between phthalic acid and glycerol leads initially to molecules that are either linear, branched, or both. But since glycerol is trifunctional, cross-linking ultimately takes place between these molecules leading to an insoluble and infusible material.

---

2. Amorphous or Crystalline

Structurally, polymers in the solid state may be *amorphous* or *crystalline.* When polymers are cooled from the molten state or concentrated from the solution, molecules are often attracted to each other and tend to aggregate as closely as possible into a solid with the least possible potential energy. For some polymers, in the process of forming a solid, individual chains are folded and packed regularly in an orderly fashion. The resulting solid is a crystalline polymer with a long-range, three-dimensional, ordered arrangement. However, since the polymer chains are very long, it is impossible for the chains to fit into a perfect arrangement equivalent to that observed in low-molecular-weight materials. A measure of imperfection always exists. The degree of crystallinity, i.e., the fraction of the total polymer in the crystalline regions, may vary from a few percentage points to about 90% depending on the crystallization conditions. Examples of crystalline polymers include polyethylene (21), polyacrylonitrile (22), poly(ethylene terephthalate) (28), and polytetrafluoroethylene (29).



(Str. 19)

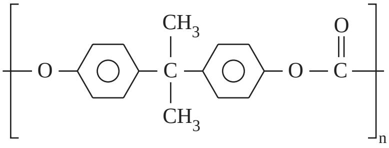
(28)

$$\left[\text{CF}_2 - \text{CF}_2 \right]_n$$

(Str. 20)

(29)

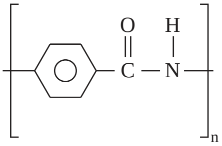
In contrast to crystallizable polymers, amorphous polymers possess chains that are incapable of ordered arrangement. They are characterized in the solid state by a short-range order of repeating units. These polymers vitrify, forming an amorphous glassy solid in which the molecular chains are arranged at random and even entangled. Poly(methyl methacrylate) (23) and polycarbonate (30) are typical examples.



(Str. 21)

(30)

From the above discussion, it is obvious that the solid states of crystalline and amorphous polymers are characterized by a long-range order of molecular chains and a short-range order of repeating units, respectively. On the other hand, the melting of either polymer marks the onset of disorder. There are, however, some polymers which deviate from this general scheme in that the structure of the ordered regions is more or less disturbed. These are known as *liquid crystalline polymers.* They have phases characterized by structures intermediate between the ordered crystalline structure and the disordered fluid state. Solids of liquid crystalline polymers melt to form fluids in which much of the molecular order is retained within a certain range of temperature. The ordering is sufficient to impart some solid-like properties on the fluid, but the forces of attraction between molecules are not strong enough to prevent flow. An example of a liquid crystalline polymer is polybenzamide (31).



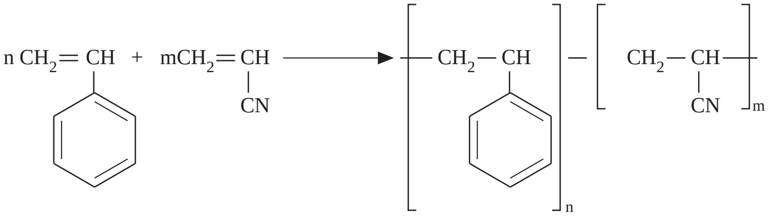
(Str. 22)

(31)

Liquid crystalline polymers are important in the fabrication of lightweight, ultra-high-strength, and temperature-resistant fibers and films such as Dupont’s Kevlar and Monsanto’s X-500. The structural factors responsible for promoting the above classes of polymers will be discussed when we treat the structure of polymers.

3. Homopolymer or Copolymer

Polymers may be either homopolymers or copolymers depending on the composition. Polymers composed of only one repeating unit in the polymer molecules are known as *homopolymers*. However, chemists have developed techniques to build polymer chains containing more than one repeating unit. Polymers composed of two different repeating units in the polymer molecule are defined as *copolymers.* An example is the copolymer (32) formed when styrene and acrylonitrile are polymerized in the same reactor. The repeating unit and the structural unit of a polymer are not necessarily the same. As indicated earlier, some polymers such as nylon 6,6 (5) and poly(ethylene terephthalate) (28) have repeating units composed of more than one structural unit. Such polymers are still considered homopolymers.



(Str. 23)

(32)

The repeating units on the copolymer chain may be arranged in various degrees of order along the backbone; it is even possible for one type of backbone to have branches of another type. There are several types of copolymer systems:

- **Random copolymer** — The repeating units are arranged randomly on the chain molecule. It we represent the repeating units by A and B, then the random copolymer might have the structure shown below:

—AABBABABBAAABAABBA— (Str. 24)

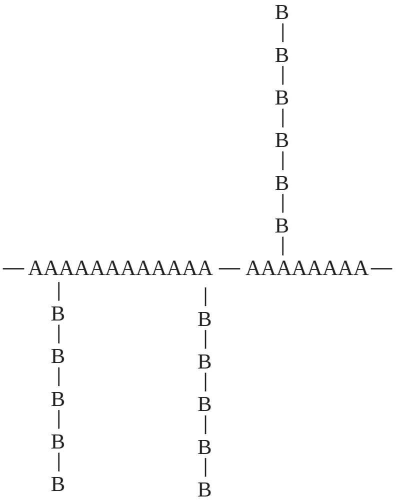
- **Alternating copolymer** — There is an ordered (alternating) arrangement of the two repeating units along the polymer chain:

— ABABABABABAB — (Str. 25)

- **Block copolymer** — The chain consists of relatively long sequences (blocks) of each repeating unit chemically bound together:

— AAAAA — BBBBBBBB — AAAAAAAAA — BBBB — (Str. 26)

- **Graft copolymer** — Sequences of one monomer (repeating unit) are “grafted” onto a backbone of the another monomer type:



(Str. 27)

4. Fibers, Plastics, or Elastomers

Polymers may also be classified as fibers, plastics, or elastomers. The reason for this is related to how the atoms in a molecule (large or small) are hooked together. To form bonds, atoms employ valence electrons. Consequently, the type of bond formed depends on the electronic configuration of the atoms. Depending on the extent of electron involvement, chemical bonds may be classified as either primary or secondary.

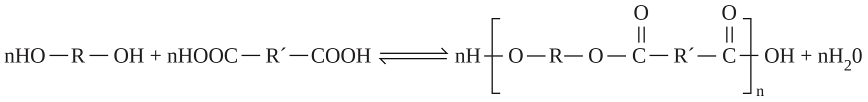
In primary valence bonding, atoms are tied together to form molecules using their valence electrons. This generally leads to strong bonds. Essentially there are three types of primary bonds: ionic, metallic, and covalent. The atoms in a polymer are mostly, although not exclusively, bonded together by covalent bonds.

Secondary bonds on the other hand, do not involve valence electrons. Whereas in the formation of a molecule atoms use up all their valence bonds, in the formation of a mass, individual molecules attract each other. The forces of attraction responsible for the cohesive aggregation between individual molecules are referred to as secondary valence forces. Examples are van der Waals, hydrogen, and dipole bonds. Since secondary bonds do not involve valence electrons, they are weak. (Even between secondary bonds, there are differences in the magnitude of the bond strengths: generally hydrogen and dipole bonds are much stronger than van der Waals bonds.) Since secondary bonds are weaker than primary bonds, molecules must come together as closely as possible for secondary bonds to have maximum effect.

The ability for close alignment of molecules depends on the structure of the molecules. Those molecules with regular structure can align themselves very closely for effective utilization of the secondary intermolecular bonding forces. The result is the formation of a *fiber.* Fibers are linear polymers with high symmetry and high intermolecular forces that result usually from the presence of polar groups. They are characterized by high modulus, high tensile strength, and moderate extensibilities (usually less than 20%). At the other end of the spectrum, there are some molecules with irregular structure, weak intermolecular attractive forces, and very flexible polymer chains. These are generally referred to as *elastomers.* Chain segments of elastomers can undergo high local mobility, but the gross mobility of chains is restricted, usually by the introduction of a few cross-links into the structure. In the absence of applied (tensile) stress, molecules of elastomers usually assume coiled shapes. Consequently, elastomers exhibit high extensibility (up to 1000%) from which they recover rapidly on the removal of the imposed stress. Elastomers generally have low initial modulus in tension, but when stretched they stiffen. *Plastics* fall between the structural extremes represented by fibers and elastomers. However, in spite of the possible differences in chemical structure, the demarcation between fibers and plastics may sometimes be blurred. Polymers such as polypropylene and polyamides can be used as fibers and as plastics by a proper choice of processing conditions.

C. POLYMERIZATION MECHANISM

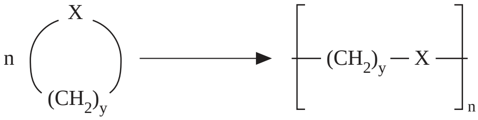
Polymers may be classified broadly as *condensation, addition,* or *ring-opening* polymers, depending on the type of polymerization reaction involved in their formation. *Condensation* polymers are formed from a series of reactions, often of condensation type, in which any two species (monomers, dimers, trimers, etc.) can react at any time leading to a larger molecule. In condensation polymerization, the stepwise reaction occurs between the chemically reactive groups or functional groups on the reacting molecules. In the process, a small molecule, usually water or ammonia, is eliminated. A typical condensation polymerization reaction is the formation of a polyester through the reaction of a glycol and a dicarboxylic acid (Equation 1.8). Examples of condensation polymers include polyamides (e.g., nylon 6,6) (5); polyesters (e.g., poly(ethylene terephthalate) (28); and urea-formaldehyde and phenol–formaldehyde resins.

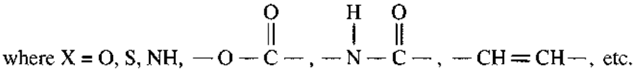


$$nHO-R-OH + nHOOC-R'-COOH \rightleftharpoons nH\left[O-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}\right]_n OH + nH_{2}0 \qquad (1.8)$$

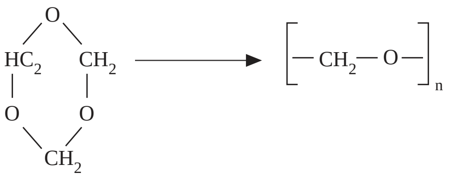
Addition polymers are produced by reactions in which monomers are added one after another to a rapidly growing chain. The growing polymer in addition polymerization proceeds via a chain mechanism. Like all chain reactions, three fundamental steps are involved: initiation, propagation, and termination. Monomers generally employed in addition polymerization are unsaturated (usually with carbon-carbon double bonds). Examples of addition polymers are polystyrene (2), polyethylene (21), polyacrylonitrile (22), poly(methyl methacrylate) (23), and poly(vinyl chloride) (24).

As the name suggests, ring-opening polymerization polymers are derived from the cleavage and then polymerization of cyclic compounds. A broad generalization of ring-opening polymerization is shown in Equation 1.9.

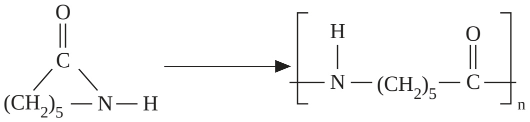

(1.9)


$$\text{where } X = O, S, NH, -O-\overset{\overset{O}{\|}}{C}-, -\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-, -CH{=}CH-, \text{etc.}$$

The nature of the cyclic structure is such that in the presence of a catalyst it undergoes equilibrium ring-opening to produce a linear chain of degree of polymerization, n. X is usually a heteroatom such as oxygen or sulfur; it may also be a group such as lactam or lactone. A number of commercially important polymers are obtained via ring-opening polymerization. Thus, trioxane (33) can be polymerized to yield polyoxymethylene (34), the most important member of the family of acetal resins, and caprolactam (35) undergoes ring-opening to yield nylon 6 (36), an important textile fiber used especially for carpets.


(33) (34)

(Str. 28)


(35) (36)

(Str. 29)

We will discuss the various polymerization mechanisms in greater detail in Chapter 2. The original classification of polymers as either condensation or addition polymers as proposed by Carothers does not permit a complete differentiation between the two classes or polymers, particularly in view of the new polymerization processes that have been developed in recent years. Consequently, this classification has been replaced by the terms *step-reaction* (condensation) and *chain-reaction* (addition) *polymerization.* These terms focus more on the manner in which the monomers are linked together during polymerization.

D. THERMAL BEHAVIOR

For engineering purposes, the most useful classification of polymers is based on their thermal (thermo-mechanical) response. Under this scheme, polymers are classified as *thermoplastics* or *thermosets*. As the name suggests, thermoplastic polymers soften and flow under the action of heat and pressure. Upon cooling, the polymer hardens and assumes the shape of the mold (container). Thermoplastics, when compounded with appropriate ingredients, can usually withstand several of these heating and cooling cycles without suffering any structural breakdown. This behavior is similar to that of candle wax. Examples of thermoplastic polymers are polyethylene, polystyrene, and nylon.

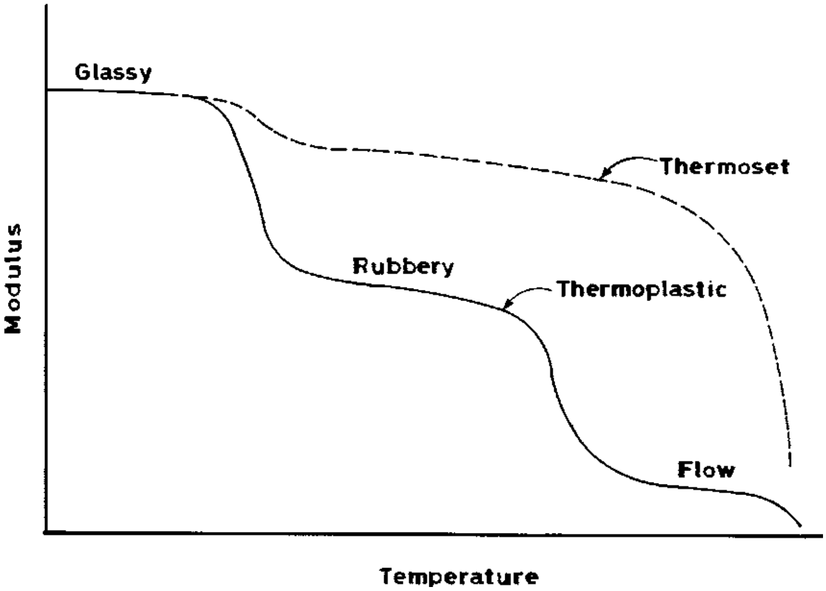


Figure 1.3 *Idealized modulus–temperature curves for thermoplastics and thermosets.*

A thermoset is a polymer that, when heated, undergoes a chemical change to produce a cross-linked, solid polymer. Thermosets usually exist initially as liquids called prepolymers; they can be shaped into desired forms by the application of heat and pressure, but are incapable of undergoing repeated cycles of softening and hardening. Examples of thermosetting polymers include urea–formaldehyde, phenol–formaldehyde, and epoxies.

The basic structural difference between thermoplastics and thermosets is that thermoplastic polymers are composed mainly of linear and branched molecules, whereas thermosets are made up of cross-linked systems. Recall from our previous discussion that linear and branched polymers consist of molecules that are not chemically tied together. It is therefore possible for individual chains to slide past one another. For cross-linked systems, however, chains are linked chemically; consequently, chains will not flow freely even under the application of heat and pressure.

The differences in the thermal behavior of thermoplastics and thermosets are best illustrated by considering the change in modulus with temperature for both polymers (Figure 1.3). At low temperatures, a thermoplastic polymer (both crystalline and amorphous) exists as a hard and rigid glass. As the temperature is increased, it changes from a glass to a rubbery elastomer to a viscous melt that is capable of flowing — hence this phase is also known as the flow region. (The transitions between the different phases or regions of thermal behavior are characterized by drops in the magnitude of the modulus — usually two to three orders. As we shall see later, differences exist between amorphous and crystalline thermoplastics in the details and nature of these transitions). For the thermosetting polymer, on the other hand, the modulus remains high in the rubbery region, while the flow region disappears.

E. PREPARATIVE TECHNIQUE

Polymers can be classified according to the techniques used during the polymerization of the monomer. In *bulk polymerization,* only the monomer (and possibly catalyst and initiator, but no solvent) is fed into the reactor. The monomer undergoes polymerization, at the end of which a (nearly) solid mass is removed as the polymer product. As we shall see later, bulk polymerization is employed widely in the manufacture of condensation polymers, where reactions are only mildly exothermic and viscosity is mostly low thus enhancing ready mixing, heat transfer, and bubble elimination. *Solution polymerization* involves polymerization of a monomer in a solvent in which both the monomer (reactant) and polymer (product) are soluble. *Suspension polymerization* refers to polymerization in an aqueous medium with the monomer as the dispersed phase. Consequently, the polymer resulting from such a system forms a solid dispersed phase. *Emulsion polymerization* is similar to suspension polymerization but the initiator is located in the aqueous phase (continuous phase) in contrast to the monomer (dispersed phase) in suspension polymerization. Besides, in emulsion polymerization the resulting polymer particles are considerably smaller (about ten times smaller) than those in suspension polymerization.

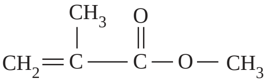
F. END USE

Finally, polymers may be classified according to the end use of the polymer. In this case, the polymer is associated with a specific industry (end use): diene polymers (rubber industry); olefin polymer (sheet, film, and fiber industries); and acrylics (coating and decorative materials).

IV. PROBLEMS

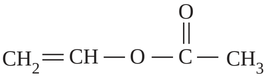
1.1. Show the structural formulae of the repeating units that would be obtained in the polymerization of the following monomers. Give the names of the polymers.

$$CH_2{=}CH{-}COOH \qquad \text{(Str. 30)}$$



$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_3$$

(Str. 31)



$$CH_2{=}CH{-}O{-}C({=}O){-}CH_3$$

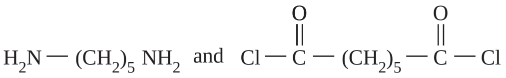
(Str. 32)

$$CH_2{=}CH{-}CH_3 \qquad \text{(Str. 33)}$$

$$CH_2{=}CH{-}CN \qquad \text{(Str. 34)}$$

1.2. Show the repeating units that would be obtained from the reaction of the following monomer(s).

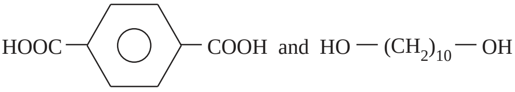
a.



$$H_2N{-}(CH_2)_5\,NH_2 \text{ and } Cl{-}C({=}O){-}(CH_2)_5{-}C({=}O){-}Cl$$

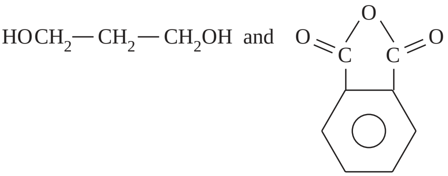
(Str. 35)

b.



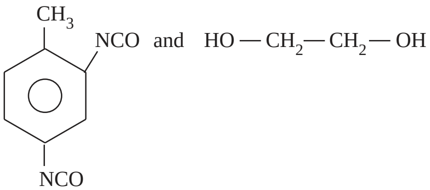
(Str. 36)

c.



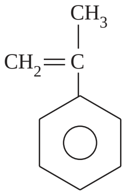
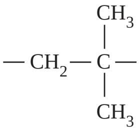
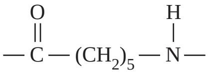
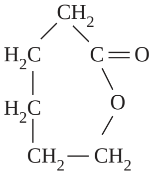
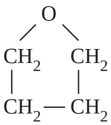
(Str. 37)

d.

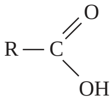
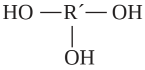
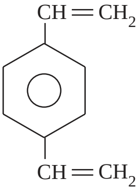
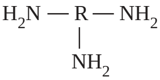
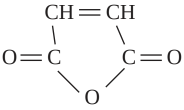
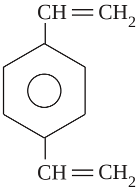
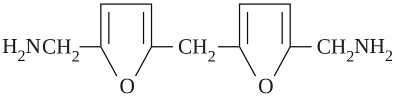
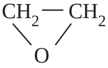


(Str. 38)

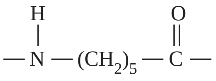
1.3. Complete the following table.

Monomer	Repeat Unit	Polymer
a.		Poly(ethyl acrylate)
b. 		
c.	 $-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-$	
d.		Poly(vinylidene chloride)
e.	 $-\overset{O}{\overset{\Vert}{C}}-(CH_2)_5-\overset{H}{\overset{\vert}{N}}-$	
f. 		
g.		Poly(dimethylsiloxane)
h. 		

1.4. Complete the table by indicating whether the monomer(s) will form a polymer and, if so, whether the polymer formed will be linear or branched/cross-linked.

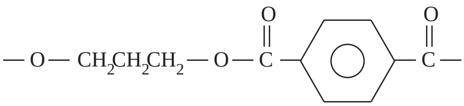
		Polymer		
			Yes	
Monomer A	**Monomer B**	**No**	**Linear**	**Branched/ Cross-linked**
a. 	 $HO-R'(OH)-OH$			
b. $HOOC-R-COOH$	$HO-R'-OH$			
c. $HO-R-OH$	$R'-N{=}C{=}O$			
d. 				
e. $HO-(CH_2)_5COOH$				
f.  $H_2N-R(NH_2)-NH_2$	$HOOC-R'-COOH$			
g. 				
h. $H_2N-R-NH_2$	$OCN-R'-NCO$			
i. $CH_2{=}CHCOOH$				
j. CH_2O				
k. 				

1.5. What is the molecular weight of the following polymers if the degree of polymerization is 1000?

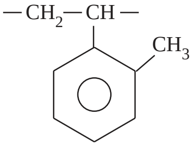
a. 

$$-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C}-$$

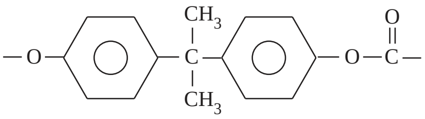
(Str. 39)

b. 

(Str. 40)

c. 

(Str. 41)

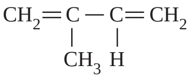
d. 

(Str. 42)

1.6. Draw the structural formulae of the repeating units of the following polymers.

a. Poly(ethylene succinate)
b. Poly(ethylene sebacate)
c. Poly(hexamethylene phthalate)
d. Poly(tetramethylene oxalate)

1.7. A polyester is formed by a condensation reaction between maleic anhydride and diethylene glycol. Styrene is then added and polymerized. Describe the chemical composition and molecular architecture of the resulting polymer. What would be the effect if maleic anhydride were replaced with adipic acid?

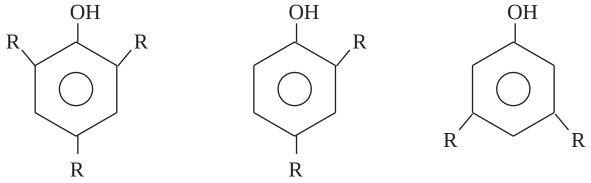
1.8. Natural rubber is a polymer of isoprene 

$$CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}-\underset{\underset{\displaystyle H}{|}}{C}{=}CH_2$$

(Str. 43)

a. Show what structures can form as it polymerizes.
b. What feature of the polymer chain permits vulcanization?

1.9. An industrialist wants to set up a phenol–formaldehyde adhesive plant. He has approached you with the following phenolic compounds.



(a) (b) (c)

(Str. 44)

Which of the compounds (a, b, or c) would you choose for reaction with formaldehyde? Explain your choice.

1.10. The following structure represents the general formula for some aliphatic amines.

$$H_2N\left[(CH_2)_2-NH\right]_n-(CH_2)_2-NH_2$$ (Str. 45)

What is the functionality of the corresponding amine in its reaction with diglycidyl ether of bisphenol A (DGEBA) if n = 1, 2, 3, 4?

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