Chapter 11
Polymers and Plastics

11.1 Introduction

A *polymer* is a large chain molecule of high molecular weight which is composed of a single molecule (monomer) that is repeated many times in the chain. In contrast, a macromolecule is a large molecule composed of many small molecules bound together with chemical bonds, e.g., a protein or DNA. An oligomer is a small polymer of only several monomer units.

Plastics are prepared by the melting, molding, extruding, or the compression of polymers. The word "polymer" implies a molecule consisting of a long chain of units of smaller molecules or monomers. Thus, the polymer is also called a macromolecule. Such large molecules exist in nature and common examples of these are cellulose, rubber, cotton, silk, wool, starch, and keratin.

The annual world production of polymers has increased from 11.5 Mt in 1940 to about 27 Mt in 1960, after which time production almost doubled every decade to more than 150 Mt in 1990. Fiber production at about 36 Mt is almost equally divided into natural and synthetic. The production of elastomers (flexible plastics) represents about one-tenth of the total polymers, with production of synthetic elastomers being about twice that of natural rubber.

11.2 Molecular Weight

Normally the number of monomers in a polymer molecule varies considerably, but the interesting range for the fabricator of plastics is generally between 10^3 and 10^6 units.

Since the precise number cannot be controlled, the molecular weight (MW) of a polymer is not a unique value, and the distribution can vary as a result of the method of preparation. There are two important average molecular weights of a polymer: the number average MW, $\bar{M}n$, and the weight average MW, $\bar{M}w$.

If we let w represent the total mass of a sample of polymer and w_i the weight of the ith species of MW M_i, then

$$n_i = \frac{w_i}{M_i} w_i \qquad \text{where } n_i \text{ is the number of moles of } i\text{th species} \tag{11.1}$$

$$\sum_{i=1}^{\infty} n_i = n_T \qquad \text{the total number of moles in the sample} \tag{11.2}$$

O.V. Roussak and H.D. Gesser, *Applied Chemistry: A Textbook for Engineers and Technologists*,
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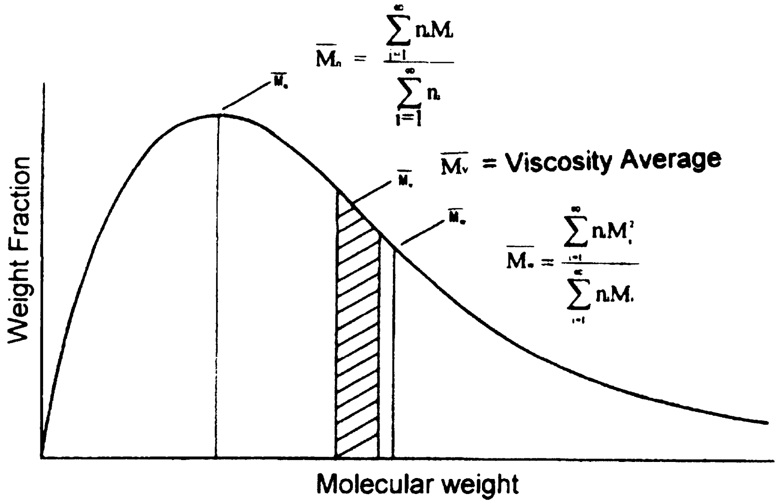


Fig. 11.1 Fraction of weight having an average MW

$$\text{the total weight,} \qquad w = \sum_{i=1}^{\infty} w_i = \sum_{i=1}^{\infty} n_i M_i \tag{11.3}$$

The number average MW $\bar{M}n$ is given by

$$\bar{M}_n = \frac{w}{\sum_{i=1}^{\infty} n_i} = \frac{\sum_{i=1}^{\infty} w_i}{\sum_{i=1}^{\infty} n_i} = \frac{\sum_{i=1}^{\infty} n_i M_i}{\sum_{i=1}^{\infty} n_i} \tag{11.4}$$

The weight average MW, $\bar{M}w$, is given by

$$\bar{M}_w = \frac{\sum_{i=1}^{\infty} w_i M_i}{\sum_{i=1}^{\infty} w_i} = \frac{\sum_{i=1}^{\infty} n_i M_i^2}{\sum_{i=1}^{\infty} n_i M_i} \tag{11.5}$$

A typical distribution of MW of a polymer is shown in Fig. 11.1.

The MW of a polymer is the single most important physical characteristic of the plastic since it determines its mechanical properties and even solubility among other properties.

Another related concept is the degree of polymerization (DP) which represents the number of monomer units in the polymer chain. Since the value of DP differs from one polymer chain to another, the value of the degree of polymerization is usually an average and is related to the MW by the relation

$$M_w = M(DP) \quad \text{and} \quad \overline{M}_w = M\left(\overline{DP}\right) \tag{11.6}$$

where M is the MW of the monomer.

The MW of a polymer can be determined by a variety of methods.

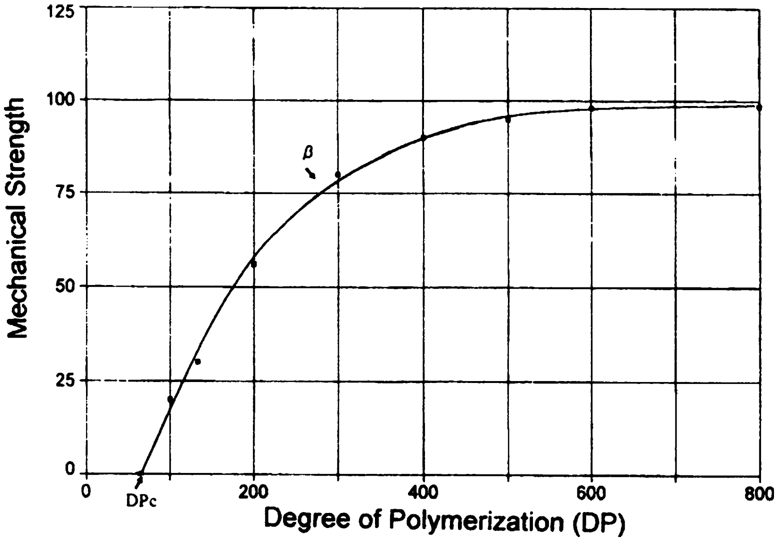


Fig. 11.2 Mechanical strength of a plastic as a function of degree of polymerization (DP)

The colligative properties of polymers in solution give rise to the number average MW, $\bar{M}n$. Thus, boiling point elevation and osmotic pressure measurement are commonly used though the latter method is much more sensitive, though restricted by the choice of suitable membranes. The weight average MW, $\bar{M}_w$, of a polymer in solution can be obtained by light scattering measurements.

The simplest and most commonly used method of measuring the MW of a polymer is by viscosity measurements of its solution. The relationship is

$$[\eta] = K\overline{M}_{\upsilon}^{\alpha} \tag{11.7}$$

where K and a are empirical constants dependent on the polymer, solvent, and temperature.

M_v is the average viscosity MW, and $[\eta]$ is the intrinsic viscosity defined as

$$[\eta] = \frac{\text{Limit}}{c \to 0} \frac{\eta sp}{c} \tag{11.8}$$

c is the concentration usually expressed as grams of polymer/100 g solvent and ηsp is the specific viscosity determined from the measurement of the viscosity of the pure solvent η_0, and viscosity of the solution η where $\eta/(\eta_0)$ is usually referred to as the viscosity ratio η_r and

$$\eta sp = \frac{\eta}{\eta_0} - 1 \tag{11.9}$$

Values of α and K are available from handbooks on polymers and range from 0.5 to 1 for α and 0.5 to 0.5×10^{-4} for K. The value of $\bar{M}_v$ is usually about 10 to 20% below the value of $\bar{M}_w$ (see Appendix B).

It is now well established that all important mechanical properties, such as tensile strength, elongation to break, impact strength, and reversible elasticity of polymers, depend on DP. When DP is relatively low, the polymer has little or no strength. As DP increases, the mechanical properties improve and tend toward a constant value. This is illustrated in Fig. 11.2 which shows the typical shape of the curve. The critical value DPc below which the polymer is essentially friable is different for each polymer, as is the bend over point β. However, plastics have little strength when DP < 30 and approach limiting strength at DP > 600.

11.3 Copolymers

When a polymer is formed from two or more monomers then the polymer is said to be a copolymer. The relative positions of the two monomers can be random or regular or in chunks. Figure 11.3 shows the different possible arrangements.

Blends of copolymers can be used to obtain specific properties of a plastic. Thus, polyethylene is brittle at temperatures below 0°C. However, when copolymers are formed with vinyl acetate (15 mol %), the resulting plastic is more flexible down to −40°C.

Another example of a copolymer is vinyl chloride with about 5% propylene. Polyvinyl chloride (PVC) is a hard brittle plastic which is made soft and flexible by dissolving a plasticizer into the PVC. Up to 30% by weight of plasticizers such as dioctyl phthalate is used to make plastic tubing. The propylene copolymer is soft without the plasticizer, or less plasticizer is required at lower concentrations in the propylene/PVC copolymer.

The loss of plasticizer from vinyl upholstery is the cause of cracking commonly observed in automobile seats and furniture.

11.4 Classification of Polymers

Many polymers occur naturally, e.g., cotton, wool, silk, gelatin, rubber, leather. Some are even inorganic such as sulfur, glass, and silicones. The thermal property of polymers is another important characterization. Thermoplastic polymers become soft and, without cross-linking, can be molded and shaped into various forms which are retained on cooling. The process is reversible, and the plastics can be reformed into other shapes when heated. Examples include polyethylene, PVC, nylon, and polystyrene. Thermosetting polymers cross-link on setting and once formed cannot be reshaped. Heating decomposes the plastic. Examples include Bakelite, melamine, phenol formaldehyde, and epoxy resins.

The manner in which polymers are formed is also a distinguishing feature. Two common methods are described.

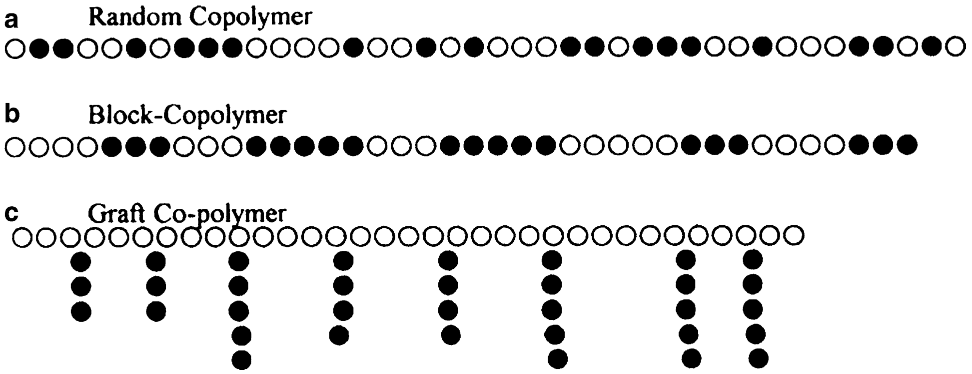


Fig. 11.3 Schematic arrangements of copolymers made from two monomers O and ©

11.4.1 Addition Polymers

The addition process where the monomer is converted into a free radical[1] which adds to another monomer. The process continues until the two growing chains combine, or one combines with a free radical. The process is as follows:

$$\text{Initiation}\quad \begin{cases} \text{Catalyst} \rightarrow \text{R}^* \\ \text{M} + \text{R}^* \rightarrow \text{R}-\text{M}^* \end{cases} \tag{11.10}$$

$$\text{Propagation}\quad \begin{cases} \text{R}-\text{M}^* + \text{M} \rightarrow \text{R}-\text{M}-\text{M}^* \\ \text{RM}_n^* + \text{M} \rightarrow \text{RM}_{n+1}^* \end{cases} \tag{11.11}$$

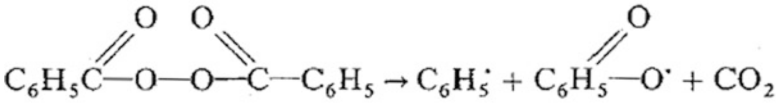
$$\text{Termination}\qquad \text{RM}_x^* + \text{R}^* \rightarrow \ \text{RM}_x\text{R}$$

$$\text{Recombination}\qquad \text{RM}_x^* + \text{R}^*\text{M}_y^* \rightarrow \ \text{RM}_x\text{M}_y\text{R} \tag{11.12}$$

$$\text{Disproportionate}\qquad \text{RM} + \ \text{RM} \rightarrow \ \text{RM}_x - \text{H} + \text{RM}_y\text{H}$$

where $\text{RM}_\text{X} = \text{H}$ is RM; which has lost a H-atom forming a C=C double bond.

The initiation process is usually by the thermal generation of free radicals from a peroxide such as benzoyl peroxide



$$\text{C}_6\text{H}_5\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-\text{O}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5^{\cdot} + \text{C}_6\text{H}_5\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}^{\cdot} + \text{CO}_2 \tag{11.13}$$

The peroxide or other azo initiators can also be decomposed when exposed to UV light. Such processes are used for the setting of polymers which function as fillings of tooth cavities.

11.4.2 Condensation Polymers

Condensation polymers are formed from the reaction of two different bifunctional monomers A and B which form AB by the reaction with the elimination of a product, usually water

$$\begin{aligned} &\text{A} + \text{B} \rightarrow \text{A} - \text{B} \\ &\text{AB} \ + \ \text{A} \rightarrow \text{ABA} \\ &\text{ABA} + \ \text{B} \rightarrow \text{BABA} \end{aligned} \tag{11.14}$$

and so on.

Thus, the polymer grows at both ends by condensing and stops when at least one of the reagents is fully consumed. Nylon 66 is a condensation polymer between a 6-carbon diamine and 6-carbon dicarboxylic acid.

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[1] A free radical is a molecule or fragment which has one or more unpaired.

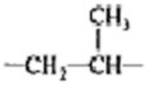
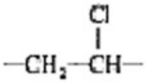
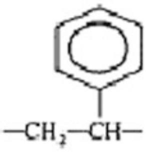
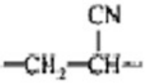
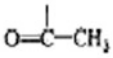
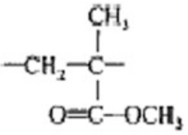
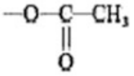
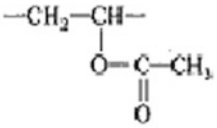
$$\begin{aligned}&NH_2-(CH_2)_6-NH_2+HOOC-(CH_2)_4COOH\\&\rightarrow NH_2-(CH_2)_6-NHOC(CH_2)_4COOH+H_2O\end{aligned}\qquad(11.15)$$

resulting in nylon 6,6 when the chain has grown sufficiently.

11.5 Vinyl Polymers

The vinyl radical is $CH_2{=}CH^{\bullet}$ and is the basis of a wide variety of monomers having the general formula $CH_2{=}CHX$. For example, when X=H, the molecule is ethylene and the polymer is polyethylene. The major vinyl polymers are listed in Table 11.1.

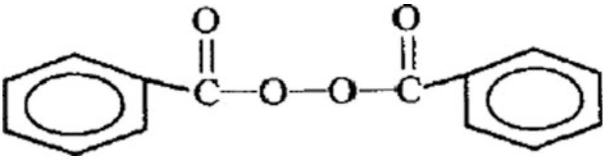
Table 11.1 Addition polymers for vinyl polymers $CH_2{=}CHX$

X	Monomer	Polymer	Uses
H	$CH_2{=}CH_2$ ethylene	$-CH_2-CH_2-$	Bottles, plastic tubing
CH_3	$CH_2{=}CHCH_3$ propylene	 $-CH_2-CH(CH_3)-$	Carpeting, textiles, ropes
Cl	$CH_2{=}CHCl$ vinyl chloride	 $-CH_2-CH(Cl)-$	Pipes, floor tiles, tubing
	$CH_2{=}CH(C_6H_5)$ styrene		Clear film, foam insulation, cups
CN	$CH_2{=}CHCN$ acrylonitrile	 $-CH_2-CH(CN)-$	Orion, ABS, carpet
 $O{=}C-CH_3$	Methyl methacrylate	 $-CH_2-C(CH_3)(C{=}O-OCH_3)-$	Windows, outdoor signs, lighting
 $-O-C({=}O)-CH_3$	Vinyl acetate	 $-CH_2-CH(O-C({=}O)-CH_3)-$	Paints, adhesives
$CF_2{=}CF_2$	Teflon	$-CF_2-CF_2-$	Electrical insulation, heat resistant, lubricant

11.5.1 Polyethylene

Also referred to as polythene, *polyethylene* is similar to polymethylene $(—CH_2)—_x$ which was prepared about 100 years ago by the decomposition of diazomethane (CH_2N_2), an explosive gas.

Polyethylene $({}^{\bullet}CH_2—CH_2—)_x$ was first produced commercially in 1939. The early process was under high pressure (1,000–3,000 atm) and at temperatures from 80 to 300°C. The polymerization mechanism is via free radical initiators such as benzoyl peroxide



which are added to the reaction mixture.

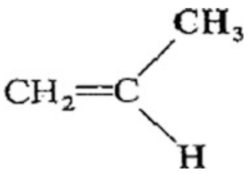
This process results in low-density polyethylene (0.915–0.94 g/mL).

High-density polyethylene is prepared at low pressure at about 70°C in the presence of a special catalyst (usually a titanium complex). The density is approximately 0.95 g/mL because of the higher degree of crystallinity and order in the polymer.

The original high-pressure process gave some branched polymers; polyethylene formed at low pressure has a higher melting point, higher density, and higher tensile strength. It is a linear crystalline polymer which costs approx. 1.5 times that of the high-pressure-low-density material.

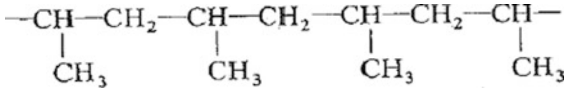
Polyethylene films are commonly used as vapor barriers in housing insulation. For greenhouse covering or window material, it is transparent enough but will slowly disintegrate due to the presence of residual carbon–carbon double bonds (C═C) which are split by ozone. Ultraviolet light will also degrade plastics unless a UV stabilizer is added which converts the absorbed UV light into heat. To make a plastic biodegradable, a substance is added which absorbs UV light from the sun and forms free radicals which attack the polymer chain.

11.5.2 Polypropylene



Polypropylene was first produced commercially in 1957. Early attempts resulted in very low MW polymers having poor plastic properties. The titanium complex used to prepare high-density polyethylene was found to be effective in polymerizing propylene. Because of the asymmetry of the propylene molecule, three different types of stereochemical arrangements can occur in the polymer chain.

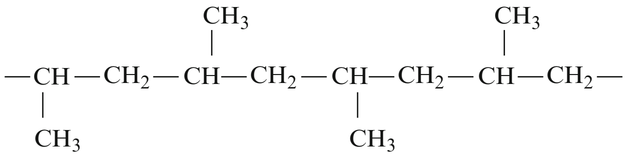
1. Isotactic



$$-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$$

(all methyl groups on one side)

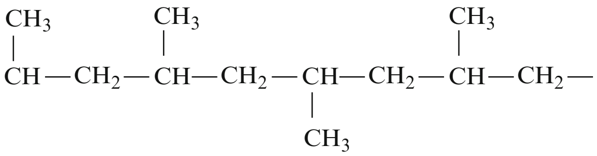
2. Syndiotactic



$$-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-$$

methyl groups alternate

3. Atactic



$$\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-$$

random orientation of CH_3 groups

Atactic polypropylene is completely amorphous, somewhat rubbery, and of little value. The isotactic and syndiotactic polymers are stiff, crystalline, and have a high melting point. Increasing the degree of crystallinity increases the tensile strength, modulus, and hardness.

Polypropylene is the lightest nonfoamed plastic, with a density of 0.91 g/mL. It is more rigid than polyethylene and has exceptional flex life. Polypropylene has found use in a wide variety of products which include refrigerators, radios, and TVs as well as monofilaments, ropes, and pipes.

11.5.3 Polyvinyl Chloride

Polyvinyl chloride is one of the cheapest plastics in use today. It is prepared by the polymerization of vinyl chloride (VCM) ($CH_2{=}CHCl$, B.P.—14°C) as a suspension or emulsion in a pressure reactor. The polymer is unstable at high temperatures and liberates HCl at $T > 200°C$. It can be injection molded or formed into a hard and brittle material. It can be readily softened by the addition of plasticizers such as diethylhexylphthalate to the extent of 30%. Plasticized PVC is used as an upholstery substitute for leather. Since the plasticizer is volatile to a small extent, it slowly leaves the vinyl which eventually becomes hard, brittle, and then cracks. This can be restored by replacing the plasticizer by repeated conditioning of the vinyl surface.

11.5.4 Polyvinylidene Chloride

Polyvinylidene chloride (PVDC) is prepared by free radical polymerization of vinylidene chloride ($CH_2{=}CCl_2$). This polymer, unlike PVC, is insoluble in most solvents. It forms copolymers with fiber forming polymers. Its films, known as Saran, have a very low permeability for O_2 and CO_2 and thus are used in food packaging. When heated to high temperatures, in the absence of oxygen, it liberates HCl, leaving a very active carbon with pores of about 1.6 nm. This “Saran carbon” has been used to double the storage capacity of CH_4 in cylinders. This is presently being considered for use in CH_4-fueled vehicles.

11.5.5 Polystyrene

Polystyrene (PS) is prepared by the polymerization of styrene (C_6H_5—CH═CH_2), also known as vinylbenzene. Commercial PS is mostly of the atactic variety and is therefore amorphous. The polymer, on decomposition, unzips and forms the monomer with some benzene and toluene. Its major defects are poor stability to weather exposure, turning yellow and crazing in sunlight. In spite of these drawbacks and its brittleness it has found wide use as molded containers, lids, bottles, electronic cabinets. As a foamed plastic it is used in packaging and insulation. The thermal conductivity of the expanded PS foam is about 0.03 $\mathrm{Wm^{-1}\,K^{-1}}$. The foam can absorb aromatic hydrocarbons usually found in the exhaust of automobiles and buses, causing the foam to disintegrate after long periods of normal exposure to a polluted environment.

The copolymerization of a small amount of divinylbenzene results in a cross-linked polymer which is less soluble and stronger. Cross-linking can sometimes be accomplished by γ-radiation which breaks some C—H and C—C bonds and on rearrangement form larger branched molecules. This is the case for polyethylene which, after cross-linking, will allow baby bottles to withstand steam sterilization.

11.5.6 Polyacrylonitrile

Polyacrylonitrile (PAN) is formed by the peroxide-initiated free-radical polymerization of acrylonitrile (CH_2═CH—CN). The major application of PAN is as the fiber Orion. When copolymerized with butadiene, it forms Buna N or nitrile rubber, which is resistant to hydrocarbons and oils. As a copolymer with styrene (SAN), it is a transparent plastic with very good impact strength used for machine components and for molding crockery. As a terpolymer of acrylonitrile–butadiene–styrene (ABS), the plastic is known for its toughness and good strength and finds applications in water lines and drains.

Polyacrylonitrile fibers are an excellent source for high-strength carbon fibers which are used in the reinforcement of composite (plastic) materials. The process was developed by the British Royal Aircraft Establishment and consists of oxidizing the atactic polymer at about 220°C while preventing it from shrinking. Further heating to 350°C results in the elimination of water and cross-linking of the chains which continues with loss of nitrogen. The fibers are finally heated to 1,000°C. The reactions are illustrated in Figs. 11.4, 11.5. The high tensile strength (3.2 $\mathrm{GNm^{-2}}$) and Young's modulus (300 $\mathrm{GNm^{-2}}$) are attributed to the alignment of the polymer chains and their cross-linking.

Carbon fibers have also been made from the pyrolysis of viscose (cellulose), rayon, and jute and from pitch. Though these methods produce slightly lower strength carbon fibers as compared to PAN, the lower cost ($\sim\frac{1}{5}$ to $\frac{1}{2}$) makes them excellent reinforcement materials for noncritical items such as golf clubs, tennis rackets, skis, and related sports goods.

11.5.7 Polymethyl Methacrylate

Polymethyl methacrylate (PMMA), also called *Plexiglas, Lucite,* or *Perspex*, is a colorless clear transparent plastic with excellent outdoor stability if UV absorbers are added to the polymer—otherwise, it yellows on exposure to sunlight. Like styrene, it also unzips on heating to reform the monomer. It has poor scratch resistance but was the plastic of choice for early contact lenses.

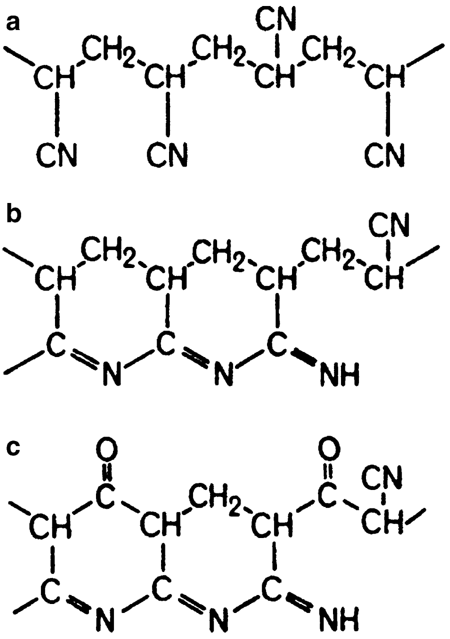


Fig. 11.4 Structure of (**a**) PAN, (**b**) PAN ladder polymer, (**c**) oxidized PAN ladder polymer

11.5.8 Polyvinyl Acetate, Polyvinyl Alcohol

Vinyl acetate ($CH_2{=}CH(OCOCH_3)$) is polymerized to polyvinyl acetate (PVAc) which is used in adhesives and lacquers. Its major use, however, is in the preparation of polyvinyl alcohol (PVA1) which cannot be prepared from vinyl alcohol ($CH_2{=}CHOH$) which isomerizes into acetaldehyde (CH_3CHO).

Polyvinyl alcohol is a water-soluble polymer which can be cross-linked into a gel by sodium borate ($Na_2B_4O_7$). This is shown in Fig. 11.6. Fibers made from PVAl can be made insoluble in water by cross-linking with formaldehyde, shown in Fig. 11.7. Such fibers are excellent substitutes for cotton because they absorb moisture (sweat) readily.

11.5.9 Polytetrafluoroethylene or Teflon

This polymer was discovered by accident. An old cylinder of gaseous tetrafluoroethylene (C_2F_4 B. P.—76°C) was found to have no gaseous pressure but still contained the original mass of material. When the cylinder was cut open, a white waxy hydrophobic powder was found. The polymerization process is highly exothermic, and it must be conducted with caution. The highly crystalline polymer is stable up to 330°C (its melting point) and is inert to strong acids, alkali, and organic solvents. It reacts with sodium leaving a carbon surface and NaF. This surface activation process allows Teflon to be bonded to other surfaces. The reaction of Teflon with hydroxyl free radicals (OH) can make the surface hydrophilic and bondable with ordinary adhesives (see Chap. 12).

Teflon tends to flow under pressure and is thus readily distorted. When filled with glass, the composite is stabilized and can be machined to precise dimensions.

Teflon cannot be injection molded because of the high viscosity of the melt and must therefore be formed by a compression of its powders. Another fluorinated polymer of comparable properties to

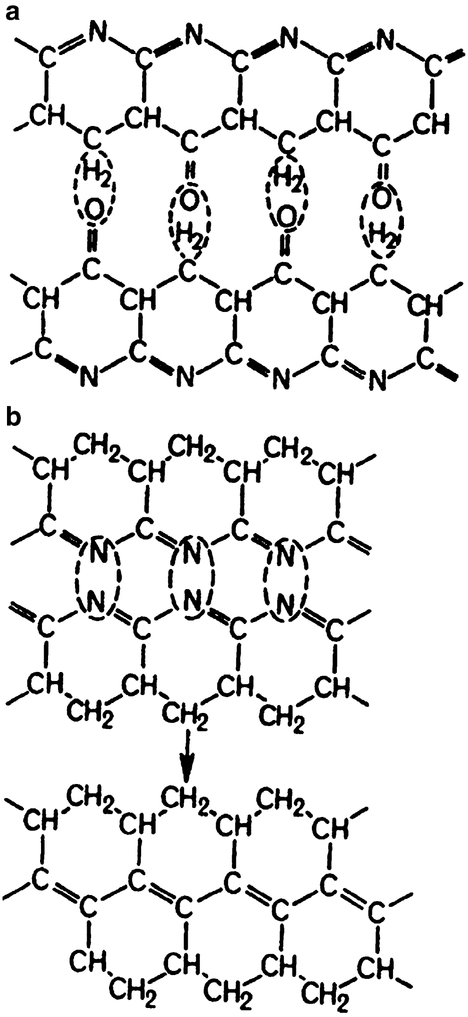


Fig. 11.5 (**a**) Cross-linking of PAN by intermolecular elimination of water, (**b**) cross-linking of dehydrated PAN by intermolecular elimination of nitrogen

$$Na_2B_4O_7 \rightarrow 2Na^+ + B_4O_7^{2-}$$

$$B_4O_7^{2-} + 9H_2O \rightleftharpoons 4B(OH)_4^- + 2H^+$$

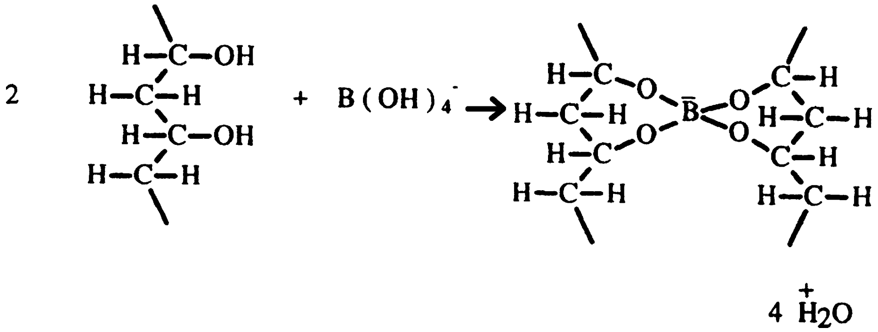


Fig. 11.6 The cross-linking of polyvinyl alcohol by borax

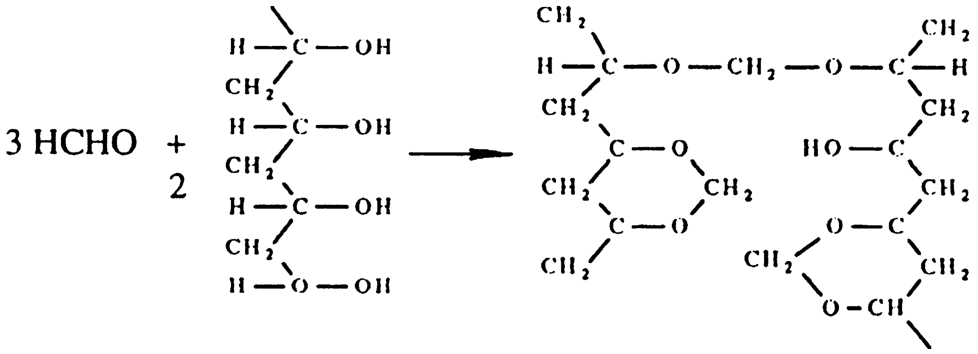


Fig. 11.7 The cross-linking of polyvinyl alcohol with formaldehyde

Teflon is a blend of PTFE and polyhexafluoropropylene (FEP) made by polymerization of perfluoropropylene (C_3F_6). This plastic is not as thermally stable as Teflon (M.P.=290°C), but it is less opaque than Teflon and can be extruded, injection molded, or blow molded and thus presents some advantage over Teflon in particular applications.

A Teflon-like surface is made when polyethylene bottles are blown with nitrogen containing about 1% F_2. This makes the bottles less permeable to organic solvents and thus increases its usefulness.

11.6 Condensation Polymers

Some condensation polymers are listed in Table 11.2.

11.6.1 Nylon

Nylon is classed as a polyamide polymer prepared by the condensation of a dicarboxylic acid [HOOC—$(CH_2)_n$—COOH] and a diamine [H_2N—$(CH_2)_m NH_2$]. The plastic is characterized by the values of n and m, i.e., nylon m, n. Thus, nylon 6,6 (M.P.=250°C) has good tensile strength, elasticity, toughness, and abrasion resistance and has use as a fiber as well as a plastic. The melting temperature range of nylon is from 250° to 300°C. The aromatic polyamides have very high melting points (>500°C) and unusually high strength/weight ratio, of which the fiber Kevlar is an example.

11.6.2 Polyester

A condensation of a dicarboxylic acid and a diol results in a polyester.

$$\begin{gathered}\mathrm{HOOC-(CH_2)}_x\mathrm{-COOH\ +\ HO-CH_2-(CH_2)}_y\mathrm{-CH_2-OH} \rightarrow \mathrm{-OCH_2-(CH_2)}_y \\ \mathrm{-CH_2O}\left(\mathrm{OC-(CH_2)}_x\mathrm{-COOCH_2(CH_2)}_y\mathrm{-CH_2-O}\right)_n\mathrm{OC-(CH_2)}_x - +n\mathrm{H_2O}\end{gathered} \tag{11.16}$$

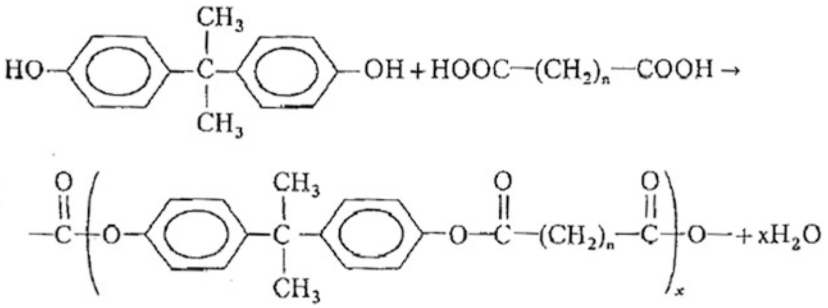
The aliphatic polyester has a melting point of about 65°C, whereas the aromatic substituted dicarboxylic acid has a melting point of 265°C. Thus, the polyester polyethylene terephthalate (PETP) is commercially one of the most popular polymers marketed as Terylene or terene.

Table 11.2 Some condensation polymers

Nylon 66	$HOOC(CH_2)_4COOH + HN,—(CH,)_6—NH_2$ ↓ $-[—NH–(CH_2)_6\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_a)_4–\underset{\underset{O}{\|}}{C}–]-$
Polyester	$HO—CH_2—CH,—OH + HOOC—(C_6H_4)—COOH$ ↓ $HO—CH_2—CH_2—O—[—\underset{\underset{O}{\|}}{C}—(C_6H_4)—\underset{\underset{O}{\|}}{C}—0—CH_2—CH_2 \sim 0—]—\underset{\underset{O}{\|}}{C}—$
Polyurethane	$H—[—O— CH_2— CH_2—]—OH + CH_3—(C_6H_3)—(NCO)_2$ ↓ $(CH_3)(NCO)(C_6H_3)\ —NH—C—[—O— CH_2— CH_2—]—O—C—NH—(C_6H_3)(CH_3)(NCO)$

11.6.3 Polycarbonates and Epoxides

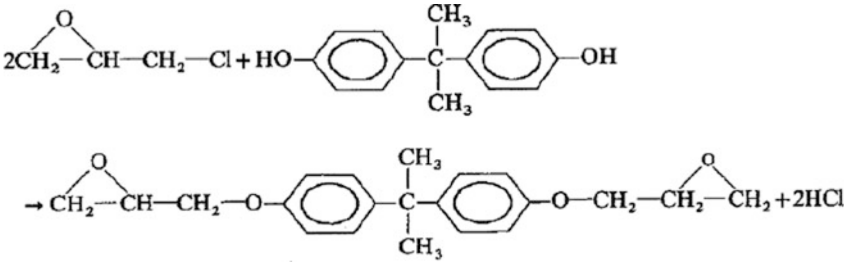
The condensation of a diphenol, (bisphenol-A), with dicarboxylic acid



(11.17)

forms the polycarbonate. These polymers melt at about 265°C and have very high impact strength, making them useful for helmets and safety shields.

The reaction of epichlorohydrin with bisphenol-A forms the diepoxy or diglycidyl ether.



(11.18)

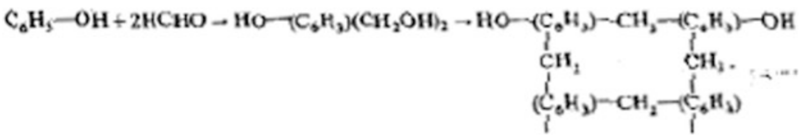
The reaction of the diglycidyl bis-phenyl ether with a polydiol or polydiamine will result in a hardened thermosetting resin. Other thermosetting polymers are discussed in the next section.

11.7 Thermosetting Polymers

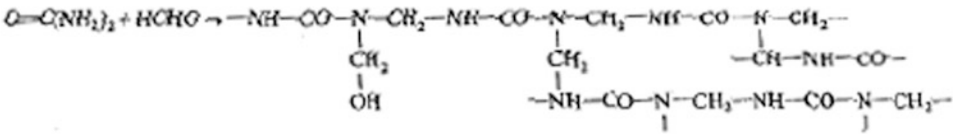
Polymers which form 3D network solids are thermosetting and decompose when heated and thus cannot be reshaped once they have set. A selection of the common polymers is listed in Table 11.3.

Table 11.3 Some thermosetting resins

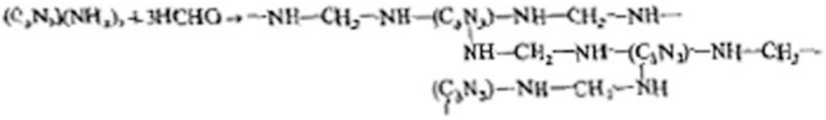
Phenol-formaldehyde



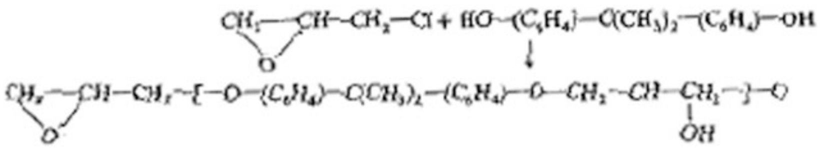
Urea-Formaldehyde



Melamine-formaldehyde

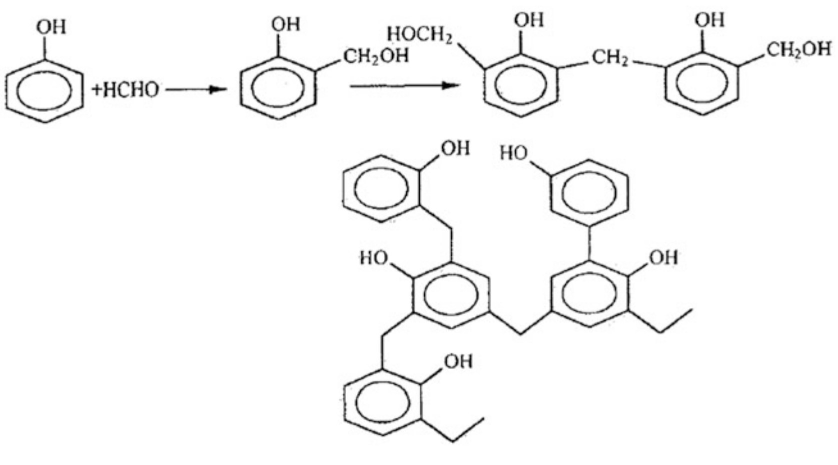


Epoxy polymer



11.7.1 Phenol Formaldehyde (Bakelite)

The first industrial plastic was developed by Baekeland in about 1907 and was called Bakelite. This was prepared by the reaction of phenol and formaldehyde in the presence of catalysts.

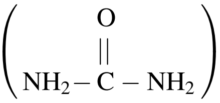


(11.19)

When heated in excess formaldehyde, cross-linking occurs, and the resin novolac is formed for P/F ~ 1.25.

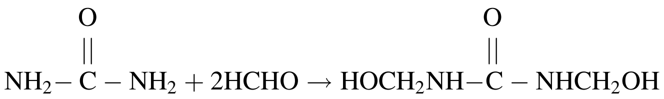
11.7.2 Urea Formaldehyde

Urea



$$\left(\mathrm{NH_2}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NH_2}\right)$$

reacts with formaldehyde to form a cross-linked resin which is an inexpensive adhesive.



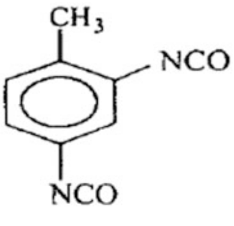
$$\mathrm{NH_2}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NH_2}+2\mathrm{HCHO}\rightarrow \mathrm{HOCH_2NH}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NHCH_2OH} \tag{11.20}$$

On further addition of urea and HCHO, $H(NHCO—NH—CH_2)_n—OH$ is formed. With an acid catalyst, it is possible to produce a foam product known as urea formaldehyde foam insulation (UFFI) having a thermal conductivity, K, of about 0.022 $Wm^{-1}\ K^{-1}$.

In 1977 the Canadian government subsidized the introduction of UFFI in older homes to conserve energy.[2] The UFFI proved to be unstable in some cases due to improper installation, and as a result formaldehyde levels in some homes exceeded the threshold limit value (TLV) of 0.10 ppm (120 $\mu g/m^3$). Ammonia was able to neutralize the acid, and it was also shown that the water-soluble polymeric amine, polyethyleneimine, could remove the liberated formaldehyde. Nonetheless, the Canadian government then paid the homeowners an estimated $272 million ($5,000 to 57,700 homes) to remove the UFFI. The urea formaldehyde resin is commonly used as the adhesive resins in plywood and particle board and will initially release formaldehyde if not sealed. As more composite wood products find their way into buildings, greater concern about indoor air is warranted.

11.7.3 Polyurethane

This condensation polymer is unique insofar as it can be a coating and varnish, a soft or hard foam, a resilient or rigid elastomer (rubber) as well as an adhesive. It is prepared by the reaction of a diisocyanate (OCNRNCO) with a diol (HOR′OH) where R can be an aromatic radical such as toluene (TDI-2,4, toluene diisocyanate).



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[2] Each of the 100,000 homeowners was given $500 toward the cost of adding UFFI.

and R′ is an aliphatic radical $(CH_2)_n$ where the length n determines strength, toughness, and elasticity of the plastic. The reaction is

$$\mathrm{OCN-R-NCO} + \mathrm{HO-R'-OH} \rightarrow \mathrm{-R'-[OCO-NH-R-NH-CO-OR'-]_{\mathit{x}}O-CO} \tag{11.21}$$

For the preparation of foams, the R component is a polyether or polyester with reactive end groups of hydroxyl and carboxyl. The reaction is

$$\mathrm{-RCOOH} + \mathrm{OCN-R'-} \rightarrow \mathrm{-R-CO-NH-R'} + \mathrm{CO_2} \tag{11.22}$$

where the liberated CO_2 foams the plastic into an open or closed cell sponge with densities of 25–50 g/dm^3 and which is often used in upholstery. The hard and rigid foams, having a density of 50–300 g/dm^3, are used as insulation and elastomers.

It is possible to replace the air in inflatable tires by *polyurethane* foam. This is feasible for low-speed vehicles used in road construction, service equipment, snowplows, street sweepers, as well as many other applications. The two components are blended together to produce the resilient foam in the tire which is then not susceptible to flats or punctures, a feature which reduces downtime and tire replacement costs. Polyurethane foam (closed cell) has a thermal conductivity of 0.022 $Wm^{-1}\,K^{-1}$ and is usually covered with aluminum foil to reduce the heat loss due to the transmission of radiation.

11.8 Glass Transition Temperature

The melting point of a polymer is not a unique value unless it can be formed into a crystalline solid. The amorphous glassy solid is really a supercooled liquid. A polymer which does not have long-range order cannot exist in a crystalline state. As the temperature of an amorphous plastic is increased, the polymer chains begin to achieve segmental mobility. This is called the *glass transition temperature (T_g)*, and the material is in a rubbery state. On further heating, the polymer chains begin to move and have molecular mobility— the plastic begins to flow. A graph showing the transition in terms of the variation of the specific volume (the reciprocal of density) as a function of temperature is shown in Fig. 11.8. The T_g and melting points of some polymers are listed in Table 11.4.

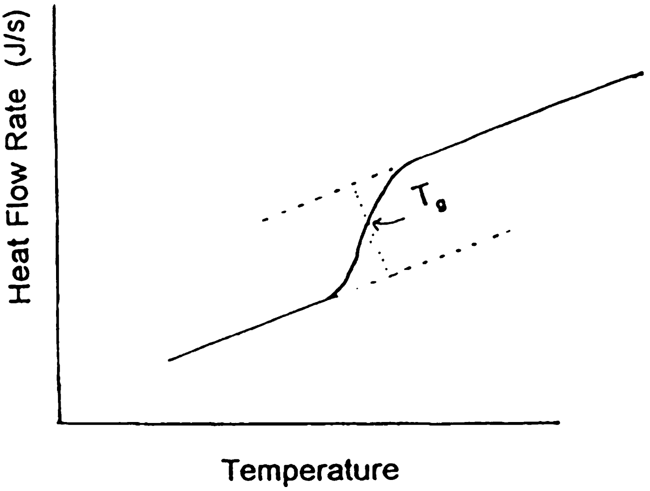
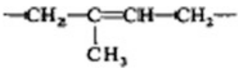
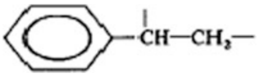
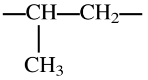
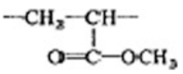
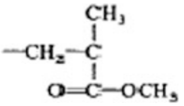
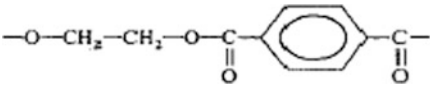
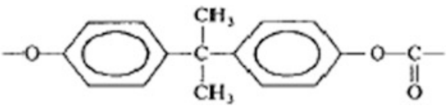


Fig. 11.8 The glass transition temperature is indicated by a change in heat flow of the material while the temperature increases linearly with time

Table 11.4 Theglass transition temperature (T_g) and melting temperature (T_m) of selected polymers

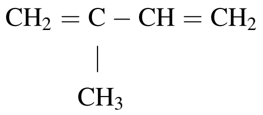
Polymer	Structural unit	Tg, °C	Tm, °C
1. Polybutadiene	$—CH_2—CH = CH—CH_2—$	Cis-102	6
		trans-58	100
2. Polyisoprene		−75	65
3. Polystyrene		100	240
4. Nylon 6,6	$—NH—(CH_2)_6—NH—O—CO—(CH_2)_4CO—O—$	50	270
5. Polyethylene	$—CH_2—CH_2—$	High density −125	140
6. Polypropylene	 $—\underset{\underset{CH_3}{\vert}}{CH}—CH_2—$	Atactic-13	
		Isotactic-8	200
7. Poly methylacrylate		5	
8. Polymethyl methacrylate		72	
9. Polyvinylchloride	$—CH_2—CHCl—$	80	310
10. Polyethylene terphthalate		70	260
11. Polycarbonate-basphenol A		150	225

Tg is dependent on degree of cross-linking area and molecular weight. The value of T_g increases as molecular weight of a polymer increases or as the branching or cross-linking increases. Thus, for PS #3, Table 11.4, $T_g = 100°C$ which is much higher than for PE #5, $T_g = -125°C$. Similarly, the difference in T_g between polybutadiene (−102°C) #1 and #2 polyisoprene (−75°C) shows the effect of replacing a H by CH_3 in the side of a chain.

The T_g of a polymer can be reduced by the addition of a plasticizer to the solid plastic. This reduces the van der Waals interaction between the polymer chains and allows the molecules to move. The plasticizer may be considered as an internal lubricant. The plasticizer can also be considered to increase the free volume of the polymer by allowing increased motion of the chain ends, the side chains, or even the main chain. Another possible mechanism by which the plasticizer lowers the T_g is in terms of the solvent/ solute system that forms when the plasticizer can be considered to solubilize the polymer. The plasticizer is usually a low volatile, low molecular weight organic compound which is compatible with the polymer.

11.9 Elastomers

Flexible plastics composed of polymers with T_g well below room temperature are classed as elastomers or rubbers. Natural rubber was known to the natives of South America for centuries, though it was not until Goodyear's discovery of vulcanization in 1839 that it became a practical product. Prior to this, rubber was used for waterproofing boots, clothing, and other weatherproofing surfaces. Goodyear showed that sulfur cross-linked the rubber and made it a manageable product. The polymer is based on the monomer isoprene



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

which results in *cis* and *trans* forms (see Fig. 11.9). Of the two forms, the *trans* is less elastic because of the more ordered structure and more close packing of the molecules. In general, *elastomers* differ from plastics only because the elastomer is in a mobile "liquid" state whereas the plastic is in a glassy state. The transition between these two states occurs at the glass transition temperature T_g when the glassy state changes into the rubbery state. Below this temperature, the molecules are frozen into position and held in place by van der Waals forces.

Because of the residual carbon–carbon double bonds ($\mathrm{C{=}C}$) in natural rubber, it is readily degraded by ozone, which adds to double bonds forming ozonides that eventually decompose, splitting the polymer chain.

Synthetic rubbers are made from chloroprene and butadiene which form neoprene and buna, respectively. The copolymer of acrylonitrile with butadiene (1,3) is known as nitrile rubber and styrene with butadiene (1,3) is Buna S. The combination of acrylonitrile, butadiene, and styrene in various formulations is used to form the thermoplastic ABS.

Some fluorinated polymers which show exceptional thermal stability and chemical inertness are Kel-F elastomers, made of a copolymer of chlorotrifluoroethylene-vinylidene fluoride $\mathrm{ClCF{=}CF_2/CH_2{=}CF_2}$, and Viton, a copolymer of hexafluoropropylene and vinylidene fluoride $\mathrm{CF_2{=}CF{-}CF_3/CH_2{=}CF_2}$.

Though stable at high temperature, these fluorocarbons show limited low-temperature flexibility. Silicone rubbers are made from dimethyldichlorosilane which under controlled hydrolysis form oils, gels, and rubbers.

Silicone rubber is more permeable to oxygen and carbon dioxide than most other polymers. A comparison of the permeability of these gases and water through various plastics is given in Table 11.5.

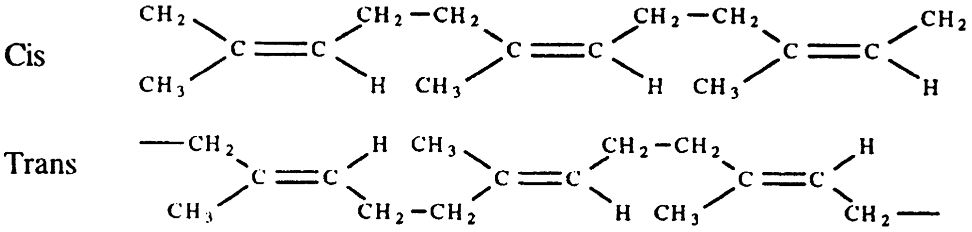


Fig. 11.9 Structures of natural rubber: *cis*, natural, herea and *trans*; gutta, percha, balata

Table 11.5 The gas permeability of various plastics at 25°C

	$P_r = \left(\frac{\text{mL gas (NTP) cm}}{\text{sec, cm}^2,\ \Delta\text{P(cm Hg)}} \times 10^9\right)$		
Film	O_2	CO_2	H_2O
1. Polyvinylidene chloride (Saran)	6.3×10^{-4}	4.8×10^{-4}	5.3
2. Monochlorotrifluoroethylene (Trithene A)	9.2×10^{-4}	0.010	0.8
3. Polyester (Mylar)	6.7×10^{-3}	0.012	32
4. Cellulose acetate	0.067	0.35	1,900
5. Opaque high density polyethylene	0.087	0.218	5.3
6. Polypropylene	0.115	0.400	15
7. Clear high density polyethylene	0.14	0.845	
8. Polystyrene	0.1	0.98	152
9. Low density polyethylene	0.35	1.09	25
10. Tetrafluoroethylene (Teflon)	0.67	1.88	67
11. Ethyl cellulose (Ethocel)	0.98	4.07	1,600
12. Natural rubber	2.5	13	
13. Fluorosilicone	1.1	64	
14. Nitrile silicone	8.5	67	
15. Silicone rubber (Silastic 372)	60	325	3,600
16. MEM-213 (G.E. Silicone Block Copolymer)	$16_{(N_2 7)}$	$97_{(H_2 21)}$	

Saran plastic shows the lowest permeability to O_2, CO_2, and very low for water. This feature makes Saran wrap an excellent packaging material for food in which freshness and flavor are to be preserved.

Silicone rubber, however, shows the highest permeability rates for these gases, and in fact, silicone rubber is used in blood oxygenators required for open heart surgery. It is also used in extended wear contact lenses since the transport of O_2 and CO_2 through the lens allows the cornea to respire. Thus, cloudiness and rainbows are not generally experienced, even after continuous wear for a month.

The permeability of various gases through silicone rubber is given in Table 11.6 and shows a broad variation. The permeability *(P_r)* of a gas through a plastic film is usually considered as equal to the product of the solubility (S) of the gas in the plastic and the rate of diffusion *(D)* of the gas in the plastic (actually the diffusion coefficient). Thus,

$$P_r = \frac{D(\text{cm}^2/\text{sec}) \times 10^6 \times S\left(\frac{\text{mL NTP}}{\text{mL atm}}\right)}{76\,\text{cm/atm}} \tag{11.23}$$

Some values of P_r, D, and S for O_2 and CO_2 at various temperatures are given in Table 11.7. When comparison is made for other gases and other plastic films, it becomes obvious that the solubility of gases in silicone rubber is not much different from other elastomers. Hence, the higher permeability of gases such as O_2 and CO_2 in silicone rubber is primarily due to higher diffusion coefficients due to more flexible O—Si—O bonds and to a much lower T_g (T_g, silicone rubber, is -123°C).

The high permeability of oxygen and CO_2 through silicone rubber suggests its possible use as an artificial gill. This is demonstrated in Fig. 11.10 in which a hamster lived in a (0.03 m^2) silicone rubber lined cage (30 L) submersed in air saturated water. When 35 L/min of the air saturated water is pumped around the cage, oxygen can be supplied to the 30 g hamster at a rate of 2.5 mL/min which is enough for its needs. The *CO_2* is removed by the water flow and though the experiment could be continued for days, the molding of the food limited the duration of the experiment.

It may be noted in Table 11.6 that the permeability of O_2 is about twice that of nitrogen. Hence, it is possible to obtain air enriched in oxygen by collecting the gases which pass through several large

Table 11.6 The permeability of various gases through dimethyl-silicone rubber at 25°C

		$P_r = \frac{\text{mL gas (NTP) cm}}{\text{sec, cm}^2, (\Delta\text{P}) \text{ cm Hg}} \times 10^9$	
Gas	P_r	Gas	P_r
H_2	65	C_3H_8	410
He	35	n-C_4H_{10}	900
NH_3	590	n-C_5H_{12}	2,000
H_2O	3,600	n-C_6H_{14}	940
CO	34	n-C_8H_{18}	860
N_2	28	n-$C_{10}H_{22}$	430
NO	60	Freon 11	1,500
O_2	60	Freon 12	138
H_2S	850	H_2CO	1,110
Ar	60	CH_3OH	1,390
CO_2	325	Acetone	1,980
N_2O	435	Pyridine	1,910
NO_2	760	Benzene	1,080
SO_2	1,500	Toluene	913
CS_2	9,000	$COCl_2$	1,500
CH_4	95	Phenol	2,100
C_2H_6	250	Freon 22	382
C_2H_4	135	Freon 114	211
C_2H_2	2,640	Freon 115	51
CCl_4	5,835	Xe	171

Table 11.7 Effect of temperature on P_r, D, and S for O_2 and CO_2 in silicone rubber

Temp. (°C)		$P_r \times 10^9$	$D \times 10^6$	S
O_2	28	62	16	0.31
	−40	20	3.9	0.39
	−75	0.74	0.0012	47
CO_2	8	323	11	2.2
	−40	293	2.7	8.2
	−75	22	0.0022	770

Note: Unit for $P_r = \frac{\text{mL gas (NTP) cm}}{\text{sec, cm}^2(\Delta P \text{ cm Hg})} \times 100$

$$D = \frac{\text{cm}^2}{\text{sec}} \times 10^6$$

$$S = \frac{\text{mL (NTP)}}{\text{mL atm}}$$

membranes. The use of oxygen instead of air is advantageous in many processes such as combustion, steel manufacture, heating, welding and many others. For example, the removal of N_2 from the air used in the burning of natural gas results in a higher temperature and therefore more heat for the same amount of gas burnt. This is because when nitrogen is present, some of the heat of combustion is used to heat up the nitrogen which is both reactant and product.

This effect is even more pronounced if the nitrogen were to be removed from the air used in an internal combustion engine. The result would be a higher temperature of combustion and less work expended in the compression of the gases (see Exercise 11.8).

It is difficult to obtain continuous sheets of silicone rubber having a large area free of holes. It is, however, easier to draw capillary tubes and to stack these together giving very large areas. However, silicone rubber is not a thermoplastic and capillary tubing cannot be extruded. To get around this difficulty, General Electric prepared a block copolymer of silicone rubber and polycarbonate and

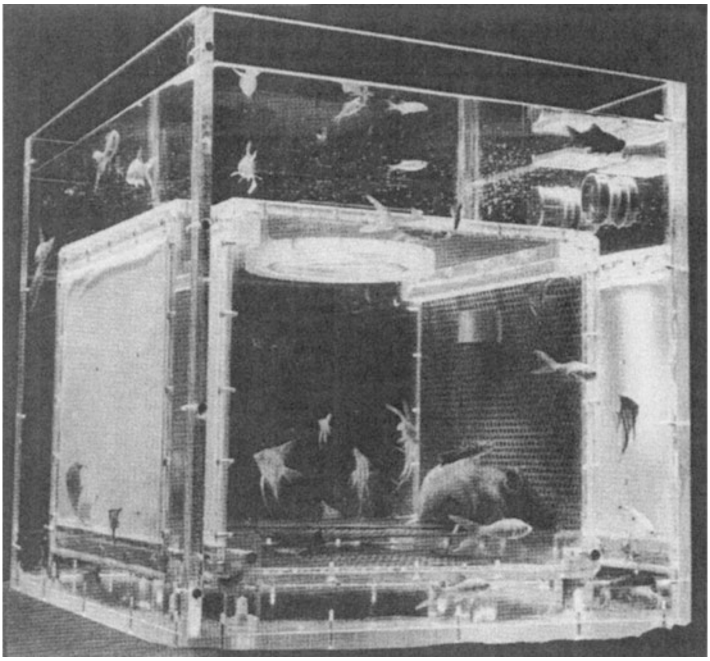


Fig. 11.10 Hamster in submerged cage fitted with silicone rubber membrane sides

because the polycarbonate is thermoplastic—the plastic (MEM 213) made from the copolymer can be molded and small bore capillary tubing can be readily fabricated. The polymer has most of the properties of pure silicone rubber with permeability rates of about 60% of the pure material.

Many modifications of the elastomers above have been developed chiefly by copolymerization with various synthetic resins. These modified elastomers furnish the engineer with a wide selection of materials suitable for special uses. An example of a relatively new hydrocarbon rubber is a copolymer of ethylene and propylene, EPR. This rubber has outstanding resistance to ozone weathering. It has lower tear resistence and higher air permeability than Buna S (SBR), but can be lined with butyl to correct the latter property.

11.10 Mechanical Strength of Plastics

The mechanical properties of materials are usually studied by means of tensile testing machines or dynamometers. The stress–strain curve obtained characterizes the plastic and determines its usefulness for specific applications.

Some design properties of common plastics are shown in Fig. 11.11. Shown also are relative costs as well as useful temperature range. Many of these properties can be improved by incorporating solid fillers into the plastics. Fillers which increase the mechanical strength are called *active fillers,* and include carbon black, titania, limestone, kaolin, silica, and mica. Their application to rubber and elastomers has been practiced for many years. The T_g of elastomers are usually increased by the addition of fillers. Good wetting of the filler by the polymer is essential for maximum effect. Thus, coupling agents are used (see Chap. 12) which bond to the solid and can react with the polymer. The size and shape of the filler particles also has an influence on its effectiveness. Thus, mica, which is a

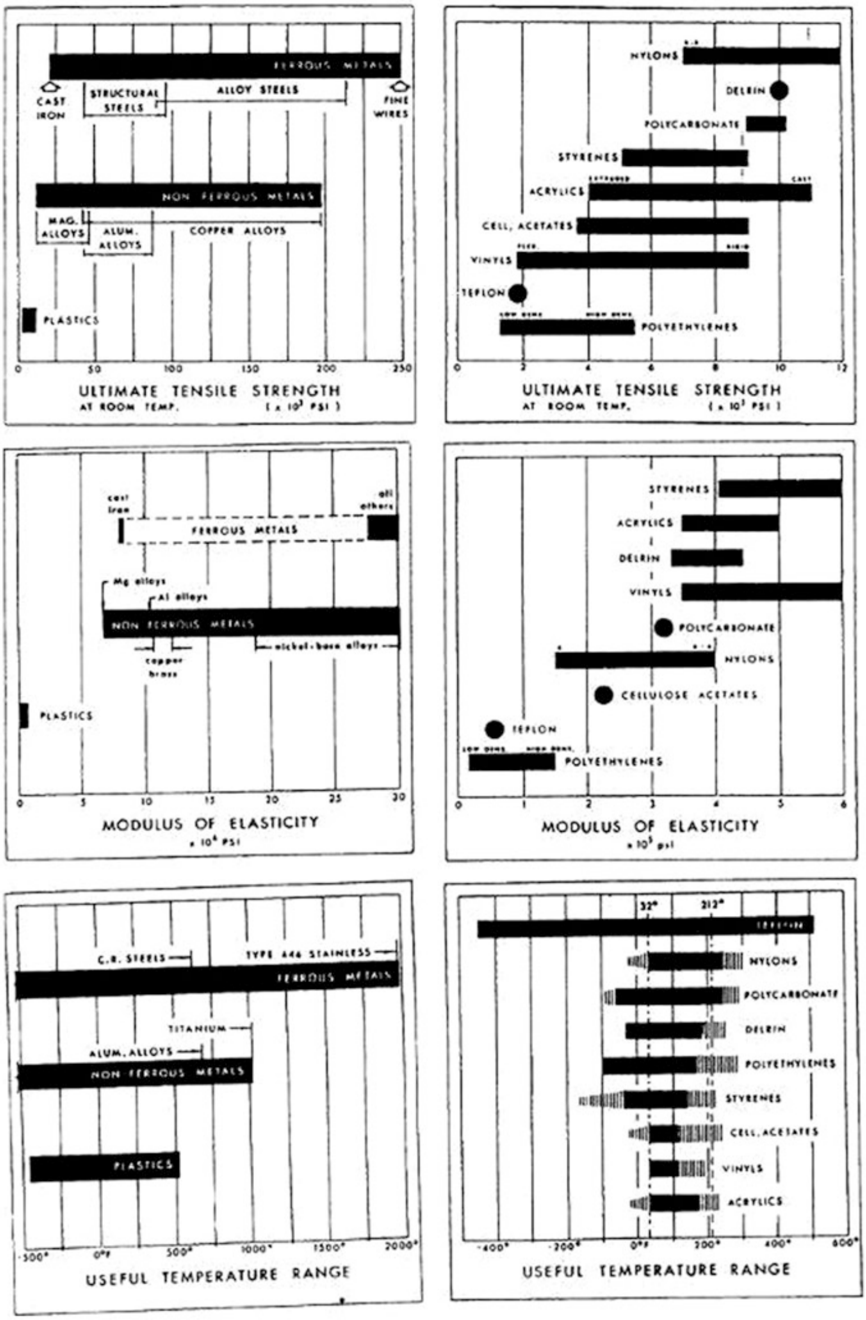


Fig. 11.11 Selected design properties or some plastics as compared to other common materials

layer lattice, is not spherical particles but thin platelets which can be split into thinner particles by ultrasonics. The length to thickness dimensions is called the *aspect ratio*. High aspect ratio (HAR) mica is much superior as a filler to ordinary mica or comparable amounts of silica or other fillers. The role of reinforcing fibers and binders in composite materials is discussed in Chap. 16.

11.11 Fire Retardants in Plastics

Plastics composed of polymer which have carbon and hydrogen are combustible. During the flammable process both thermal decomposition and combustion occur. A substance is classified as noncombustible if it does not produce flammable vapors when heated to 750°C. Few organic polymers can pass this test. Hence, most plastics burn, producing combustion products which can be toxic. Some of these gases are listed in Table 11.8. In the case of hydrogen cyanide (HCN), the amount produced is from 20 to 50% of the nitrogen present in the polymer. The major fire hazard is not the toxic gases but the smoke and lack of oxygen. Thus, smoke and fire retardants are essential ingredients in the formulation of plastics. The relative decrease in light transmission or degree of obscuration for some materials as determined in a specific apparatus is given in Table 11.9. The addition of flame retardants to materials may reduce fire but can at times increase the formation of smoke. The ease with which a substance will burn is determined by the minimum O_2 concentration (in N_2 as %) which will support combustion. This is called the limiting oxygen index (LOI) and some selected valves are given in Table 11.10. Thus, those materials with LOI ≤ 21 are combustible in air and must be treated to increase the LOI values

Fire retardants are additives to plastics and are usually based on some of the following elements: Al, B, Br, Cl, Mg, N, P, Sb, Sn, Zn. Halogen compounds (RX) produce halogen atoms (X) which act as chain terminators in the reacting vapors. Bromine compounds are often used but the formation of HBr in a fire makes it a corrosive retardant. A more inert fire retardant is alumina trihydrate ($Al_2O_3{\cdot}3H_2O$) which also acts as a smoke suppressant. It absorbs heat while liberating water at 230° to 300°C. Another inorganic fire retardant is zinc borate ($ZnO{\cdot}B_2O_3{\cdot}H_2O$) which liberates water

Table 11.8 Toxic degradation products from combustible materials in air

CO and CO_2	From all substances containing carbon
NO_x	Polyurethanes
HCN	Wool (150), silk, nylon (100), polyurethanes (40), polyacrylonitrile (200)
SO_2	Rubber
Hydrohalides	PVC, fluorinated plastics, polyvinylidene chloride
Phosgene	Chlorohydrocarbons
NH_3	Melamine, nylon, urea formaldehyde
Benzene	Styrene
Phenol	Phenol formaldehyde
CO	PUF (600), nylon (450), wool (300)

Values in parentheses are average values in mg/g of material

Table 11.9 Relative obscurance due to smoke formation during the combustion of various materials

Material	Obscuration (%)
Oak	2
Pine	48
Acrylic	2
Polystyrene	100
PVC	100
Polyester	90
Plaster board	1
Flame-retardant acrylic	97
Polyester	99
Plywood	15

Table 11.10 Limiting oxygen index (LOI) values of selected materials

Material	LOI
Polyurethane foam	16.5
Polymethyl methacrylate	17.3
Polyethylene	17.4
Polypropylene	17.4
Polystyrene	18.0
Acrylic fiber	18.2
Cotton	18.4
Nylon fiber	20.1
Polyester fiber	20.6
Oak	23
Polycarbonate	25.0
Wool	25.2
Nylon 6,6	28.7
Kevlar	29
Polyvinylidene fluoride	43.7
Polyvinyl chloride	47
Teflon	95
Polyvinylidene chloride	60
Carbon	65

Table 11.11 Selected fire retardants

$Al_2O_3–3H_2O$	Alumina trihydrate
$ZnOB_2O_3–H_2O$	Zinc borate
Sb_2O_3	Antimony oxide
NH_2CONH_2	Urea
$(NH_4)_2HPO_4$	Diammonium hydrogen phosphate
$Mg(OH)_2$	Magnesium hydroxide
$Br_3C_6H_4—CH{=}CH_2$	Tribromostyrene
$C_6Br_5—CH_2—O—CO—CH{=}CH_2$	Pentabromobenzyl acrylate
MoO_3	Molybdenum trioxide
CuC_2O_4	Cupric oxalate

at 245°–380°C and is used to supplement halogen retardants. A list of selected fire retardants is given in Table 11.11. The increase in LOI of 10% (from 18% to 28%) represents an effective application of retardants.

The flame characteristics of a plastic and a measure of its density can often be used to identify the polymer. Polymers can conveniently be identified by a quick test of IQ infrared absorption spectra. A short list of tests of a few plastics is given in Table 11.12. In general, aromatic substances burn with smoky flames. Chloride can be tested with the plastic-coated copper wire which shows a green color in the colorless part of a Bunsen flame.

The growth of the polymers and plastics industries has meant that a major fraction of the workforce in developed countries is either directly or indirectly employed by plastic-related jobs. As more stable and less costly plastics are developed, more applications are found and growth continues. Because polymers and plastics are based on petroleum and since petroleum is a limited resource, it is essential that continued efforts be made to recycle our plastic wastes—something that is slowly being realized.

Table 11.12 Combustion and density tests for plastics identification

Polymer	Density[a] (g/cm^3)	Type	Odor	Color	Character
PE	0.91–0.98	TP	Candle	Yellow	Burns, melts, drips
PP	0.89–0.92	TP	Wax, candle, wax	Yellow	Burns, melts, drips
PS	1.05–1.07	TP	Styrene	Smoky	Burns
PMMA	1.24	TP	Methanol	Yellow	Burns slowly
PET	1.39	TP	Aromatic	Smoky	Slightly acidic fumes
PC	1.2	TP	Benzene	Smoky	Neutral vapors, difficult to ignite, SE
PAN	1.2	TP	HCN	Smoky	
PF	1.28	TS	Phenol	Yellow smoky	Basic fumes, SE, difficult to ignite
PU	1.2	TS	Acid	Yellow	Acidic or basic fumes
PVC	1.39	TP	Acid	Yellow	Acidic fumes, SE
N	1.14	TP	Ammonia	Bluish	Burns, basic fumes, SE
ABS	1.0	TP	Styrene	Yellow	Burns

[a] Values ±0.1 to 0.2, *SE*, self-extinguishing, *TP* thermoplastic, *TS* thermosetting, *PE* polyethylene, *PP* polypropylene, *PS* polystyrene, *PMMA* polymethyl methacrylate, *PET* polyethylene terephthalate, *PC* polycarbonate, *PAN* polyacrylonitrile, *PF* phenol formaldehyde, *PU* polyurethane, *PVC* polyvinyl chloride, *N* nylon, *ABS* acrylonitrile–butadiene–styrene

Exercises

1. From the data given in Sect. 11.1, calculate the annual production of rubber in 1990.
2. The table below gives the fraction of molecules of a polymer sample having a given average molecular weight. Calculate the number average molecular weight, $\overline{M}_n$ and the weight average MW, $\overline{M}_w$.

MW	10,000	14,000	16,000	19,000	22,000	24,000	28,000	32,000
Fraction	0.12	0.14	0.16	0.22	0.12	0.1	0.08	0.06

3. What conclusion can you reach if both $\overline{M}_w$ and $\overline{M}_n$ are determined to be identical?
4. The MW of a polymer dissolved in a solvent was determined from viscosity measurements at 25°C for various concentrations

C(g/100 mL)	0.25	0.50	1.00	2.00
η/η_Q	1.36	1.8	2.8	6.1

The ratio η_{sp}/C is to be plotted against C and extrapolated to zero concentration in order to obtain the intrinsic viscosity $[\eta]$. The constants for Eq. (11.7) are K=3.8 × 10^{-4} and $\alpha = 0.92$ for this polymer-solvent-temperature system when the concentration is in g/100 mL Calculate the MW of the polymer.

5. Polyvinyl alcohol (PVA) is soluble in water. What will be the freezing point of a 3% solution of PVA (MW 50,000 g/mol) in water? [*Note:* 1 molal solution depresses the F.P. by 1.86°C]
6. Write the chemical reaction showing the formation of the following polymers from initial reactants: (a) nylon, (b) lexan, (c) terylene, (d) polyurethane.
7. Floor tiles of plasticized PVC can be made more flexible, more scratch resistant, to have a longer lifespan and have increased color fastness when treated with γ-radiation. Explain.
8. The permeability equation of a gas through a membrane is

$$N = A(P_iX_i - P_0X_0)P_r/l$$

where N = mL/s (NTP) gas flow; l = film thickness in cm; P_r = permeability; P_i = pressure of feed gas in cmHg; X_i = mole fraction of diffusing component in feed gas; P_0 = pressure of product gas in cm of Hg; X_0 = mole fraction of component in product gas; A = area in cm^2. For air $P_0 = 76$ cm, X_i=0.2.

(a) If we assume l = 1 miL (0.025 mm), P_0—38 cm, X_0—0.3, calculate the area required for an internal combustion engine burning up to 150 mL/min of gasoline.
(b) If P_i is increased to 3 atm, would the required area be reduced significantly?

9. A man at rest uses 300 mL O_2/min. Seawater contained 4 mL O_2/L. What area of membrane is required to act as an artificial gill if water is initially saturated at 160 mmHg of O_2 and can be depleted to 100 mm? What volume of water must be passed over the membrane each minute to achieve this oxygen Mow to support a man under water?
10. It has been suggested that polymeric membranes be used to separate alcohol from water. What advantage would this have over distillation?
11. Distinguish between thermosetting plastics, thermoplastics, and elastomers.
12. How is polyvinyl alcohol prepared?
13. How much dioxygen is used by an automobile engine:
(a) idle; (b) moving 50 km/h?

Further Reading

1. Kacapio, Norton IT, Ubbink JB (2009) Modern biopolymer science, 5 edn.
2. Brydson JA (1999) Plastic materials, 7th edn. Butterworth-Heinemann, Newton
3. Strong AB (1999) Plastics, 2nd edn. Prentice-Hall, Upper Saddle River
4. Elias HG (1997) An introduction to polymer science. VCH, New York
5. Harper CA (ed) (1996) Handbook of plastics, elastomers, and composites, 3rd edn. McGraw-Hill, New York
6. Luise RR (1996) Applications of high temperature polymers. CRC Press, Boca Raton
7. Mark JE (ed) (1996) Physical properties of polymers handbook. American Institute of Physics, Cincinnati
8. Salamone JC (ed) (1996) Polymeric materials encyclopedia. CRC Press, Boca Raton
9. Fried JR (1995) Polymer science and technology. Prentice-Hall, Englewood Cliffs
10. Ravve A (1995) Principles of polymer chemistry. Plenum, New York
11. Osswald TA, Menges G (1995) Materials science of polymers for engineers. Hanser-Gardner, Cincinnati
12. Santappa M (1995) State of the art in polymer science and engineering. International Special Book, Portland
13. Zaikov GE (ed) (1995) New approaches to polymer materials. Nova Science, Commack
14. Zaikov GE (ed) (1995) Polymers in medicine. Nova Science, Commack
15. Zaikov GE (ed) (1995) Flammability of polymeric materials. Nova Science, Commack
16. Zaikov GE (ed) (1995) Kinetic and thermodynamic aspects of polymer stability. Nova Science, Commack
17. Zaikosv GE (ed) (1994) Degradation and stabilization of polymers: theory and practice. Nova Science, Commack
18. Ward IM, Hadley DW (1993) An introduction to the mechanical properties of solid polymers. Wiley, New York
19. Domininghaus H (1993) Plastics for engineers: materials, properties, applications. Hanser-Gardner, Cincinnati
20. Rosen SL (1993) Fundamental principles of polymeric materials, 2nd edn. Wiley, New York
21. Ulrich H (1993) Introduction to industrial polymers. Hanser-Gardner, Cincinnati
22. Sperling LH (1992) Introduction to physical polymer science, 2nd edn. Wiley, New York
23. Vieth WR (1991) Diffusion in and through polymers: principles and applications. Hanser-Gardner, Cincinnati
24. Brandrup J, Immergut EH (eds) (1989) Polymer handbook, 3rd edn. Wiley, New York
25. Gowariker VR, Viswanathan NV, Sreedkar J (1986) Polymer science. Wiling Eastern, New Delhi
26. Billmeyer FW (1984) Textbook of polymer science, 3rd edn. Wiley-Interscience, New York
27. Rudin A (1982) The elements of polymer science and engineering. Academic, Toronto
28. J Chem Educ (1981) Full issue devoted to polymer chemistry
29. Brydson JA (1980) Plastic materials, 2nd edn. Newnes-Butterworths, London
30. MacGregor EA, Greenwood CT (1980) Polymers in nature. Wiley, New York
31. Tager A (1978) Physical chemistry of polymers, 2nd edn. (English). MIR, Moscow
32. Lee H, Neville K (1971) Handbook of biomedical plastics. Pasadena Technology Press, Pasadena
33. Palin GR (1967) Plastics for engineers. Pergamon Press, Oxford

34. American Plastic Council, http://www.ameriplas.org/
35. History of plastics, http://www.polymerpIastics.com
36. About silicone rubber, http://www.chemcases.com/silicon/
37. Sources of polymers, http://www.polymer-search.com
38. Chemical searcher, http://www.chemconnect.com
39. Polymer processing, http://www.polymerprocessing.com/sites.html
40. http://www.plastics.com/
41. http://www.canplastics.com/
42. Polymers in industry, http://www.chemindustry.com/
43. www.wikipedia.org