

Thermoplastics, Elastomers, and Thermosets

*A*s discussed in Chapter 1, polymers may be categorized as plastics (thermoplastics or thermosets), fibers, or synthetic rubber. Of the total synthetic polymer production in the United States, commodity thermoplastics account for the largest share of the market. Thermoplastics are followed by fibers (see Section 8.2), synthetic elastomers, and thermosets. The most commercially important thermoplastics include polyolefins (i.e., polyethylene and polypropylene), PVC, and the styrenics (e.g., PS, HIPS, SAN, and ABS). The principal feature of both thermosets and conventional elastomers that distinguishes them from thermoplastic materials is the formation of a network structure upon fabrication. This network may be formed by covalent or sometimes physical links that connect individual molecules. If only a few such links are formed, the material can be deformed but will return to its original shape upon release of the applied force, provided the force is less than required

to rupture the bonds. Polymers that have limited or no crystallinity, have low softening temperatures (glass-transition temperatures in the range from -50° to -70°C), and can be crosslinked in the above manner are candidates for elastomer applications. Polymeric materials that have a high density of crosslinks and are, therefore, infusible, insoluble, and dimensionally stable under load are thermosets.

9.1 Commodity Thermoplastics

Thermoplastics are polymers that can be melt processed by a variety of methods, including extrusion and molding. Thermoplastics are used for a wide range of applications, such as film for packaging, photographic and magnetic tape, beverage and trash containers, upholstery, and a variety of automotive parts. As shown by the data given in Table 9-1, the largest sales volume thermoplastics are the polyolefins followed by polypropylene, poly(vinyl chloride) and copolymers of vinyl chloride. Other important thermoplastics include poly(ethylene terephthalate), which is used for packaging applications (e.g., plastic bottles) and as an important fiber (i.e., polyester fiber) as discussed in Section 8.2.3. Engineering-grade polyesters that reach a more specialized market are reviewed in Section 10.1.8. The synthesis and properties of these important commercial thermoplastics are given in the following sections.

Table 9-1 U.S. Production of Thermoplastics in 2012^a

Thermoplastic	Thousands of Metric Tons ^{ba}	Annual Change %, 2002–12
Polyethylenes		
LDPE	3123	-1.5
LLDPE	6098	1.7
HDPE	8046	1.1
Polypropylene	7405	-0.4
Polystyrene	2473	-2.0
PVC and copolymers	6944	0.0

^a Adapted from Chemical and Engineering News, July 12, 2013, p. 65–66.

^b Conversion: 2206.6 lbs per metric ton.

9.1.1 Polyolefins

The polyolefins include various grades of polyethylene, differentiated on the basis of their crystallinity (i.e., density), and polypropylene. A comparison of the properties of polypropylene and the two extreme polyethylene grades—low-density (LDPE) and high-density polyethylene (HDPE)—are given in Table 9-2.

Table 9-2 Properties of Commodity Polyolefins

Property	ASTM	LDPE	HDPE	PP
Specific gravity	D792	0.91–0.93	0.94–0.97	0.90–0.91
Crystallinity, %	—	50–70	80–95	82
Melt temperature, °C	—	98–120	127–135	165–171
Tensile strength, MPa ^a	D638	4.1–16	21–38	31–41
Tensile modulus, GPa ^b	D638	0.10–0.26	0.41–1.24	1.10–1.55
Elongation-to-break, %	D638	90–800	20–130	100–600
Impact strength, notched Izod, J m ⁻¹ ^c	D256	No break	27–1068	21–53
Heat-deflection temperature, °C, at 455 kPa (66 psi)	D648	38–49	60–88	225–250

^a To convert MPa to psi, multiply by 145.

^b To convert GPa to psi, multiply by 1.45×10^5 .

^c To convert J m⁻¹ to lb_f in.⁻¹, divide by 53.38.

Polyethylene. Ethylene, one of the most important petrochemicals, may be polymerized by a variety of techniques to produce products as diverse as low-molecular-weight waxes and highly crystalline, high-molecular-weight polyethylene (HDPE). The first commercialized polyolefin (1939) was a low-crystallinity, low-density polyethylene (LDPE) produced in 1939 by ICI in England. The majority of LDPE produced today in the United States is used as thin film for packaging, while the remaining production finds use in wire and cable insulation, coatings, and injection-molded products.

Low-density polyethylene is produced by free-radical bulk polymerization using traces of oxygen or peroxide as the initiator. Polymerization is conducted either in high-pressure autoclaves or in continuous tubular reactors operating at temperatures near 250°C and pressures as high as 3000 atm. Since the heat of ethylene polymerization is high (105 kJ mol⁻¹), the exotherm needs to be carefully controlled. For this reason, the polymerization may be conducted in several stages, each employing low conversion.

Small amounts of polar comonomers such as acrylates, vinyl esters, and vinyl ethers may be added during the polymerization process to modify product properties, particularly to impart low-temperature flexibility through the reduction of crystallinity. For example, low-molecular-weight copolymers of ethylene and vinyl acetate (EVA) have been used as polymeric plasticizers for PVC (see Section 7.1.1). The incorporation of small amounts (<7%) of vinyl acetate results in polyethylene films (modified LDPE) having better toughness, clarity, and gloss. Copolymers of ethylene and vinyl alcohol (EVOH) provide better processability and moisture resistance and high gas-barrier properties for packaging applications. Films made from copolymers of ethylene and ethyl acrylate have outstanding tensile strength, elongation-to-break, clarity, resistance to stress cracking, and flexibility at low temperatures. Copolymers of ethylene and methacrylic acid, particularly neutralized in

the form of sodium or zinc salts, are called ionomers. Ionomers exhibit extreme toughness and abrasion resistance (see Section 10.2.2).

Molecular weights of LDPE typically fall in the range between 6000 and 40,000. Different molecular-weight grades are sold on the basis of their *melt index* (ASTM D1238). Melt index refers to the weight (in grams) of polymer extruded over a specified time interval and temperature through an extrusion die* in a plastometer that is fitted with a standard dead-weight piston and cylinder. For extrusion at 190°C in 10 min, typical melt indices of LDPE range from 0.1 to 109. In an oxygen-initiated polymerization, molecular weight can be reduced by simply increasing the oxygen concentration.

The free-radical polymerization of ethylene produces a highly branched molecule. The number of these branches may be as high as 30 per 500 monomer units. Most of these are short-chain alkyl groups such as ethyl and butyl, which are produced by an intramolecular “back-biting” mechanism illustrated in Figure 9-1A. At higher conversions and at lower pressures, long-chain branches (i.e., hexyl or longer) may be produced through a chain-transfer mechanism as illustrated in Figure 9-1B. Branching acts as defects that reduce crystallinity, as evidenced by the low density and low crystalline-melting temperature (T_m) of LDPE compared to HDPE (see Table 9-2). Branching can be reduced by increasing the pressure of the polymerization. For example, nearly linear polyethylene can be produced by free-radical polymerization at pressures approaching 5000 atm.

Alternatively, polyethylene with reduced branching can be obtained by polymerizing ethylene in the presence of a number of coordination catalysts (see Section 2.2.3). The first catalysts (Philips-type) consisted of chromium oxide (CrO_3) supported on aluminum oxide (Al_2O_3) or a silica–alumina base. Polymerization is conducted at 100 atm and 200°C in hydrocarbon solvents in which the catalysts are insoluble (i.e., heterogeneous solution polymerization). Alternative schemes employ Ziegler-type catalysts, which are typically complexes of aluminum trialkyls and titanium or other transition-metal halides, originally triethyl aluminum and titanium tetrachloride [1–3]. Compared to the Philips-type supported catalysts, Ziegler catalysts generally require lower temperatures and pressures, (i.e., 60° to 75°C and 1 to 10 atm) to obtain high-molecular-weight linear polymers.

* ASTM D1238 specifies a capillary die of 2.0955 mm in diameter and 8.0 mm in length.

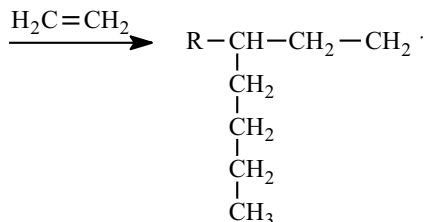
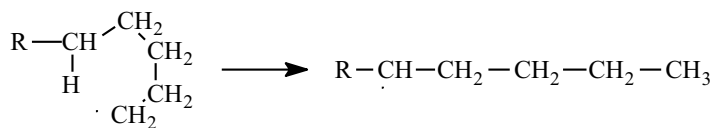
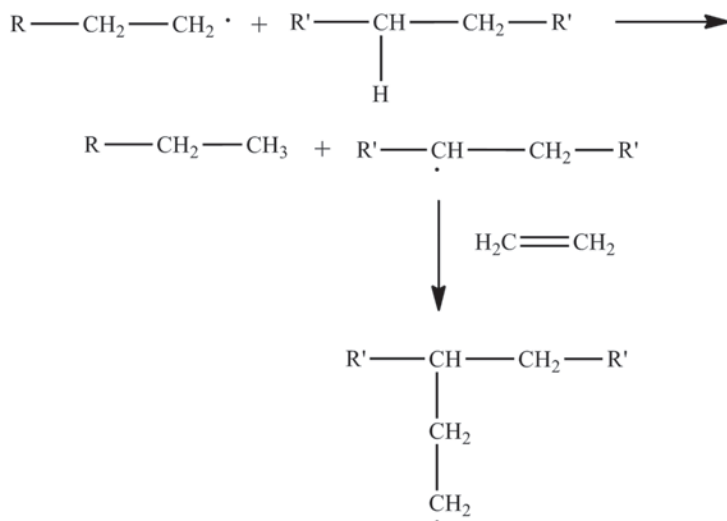
A**B**

Figure 9-1 Mechanisms of branching during the free-radical polymerization of low-density polyethylene. **A.** Formation of an *n*-butyl (C_4H_9) branch by an intramolecular “back-biting” mechanism. **B.** Formation of long-chain branches via an intermolecular chain-transfer mechanism. Long alkyl end chains are represented by R and R'.

Ethylene can also be polymerized by metallocene polymerization (see Section 2.2.3) [4–7]. Although metallocene catalysts are significantly more expensive than Ziegler–Natta catalysts, they can provide sufficiently high activity to be competitive. The first high-activity metallocene catalyst system for ethylene polymerization, bis(cyclopenta-dienyl)zirconium dichloride (Cp_2ZrCl_2)–MAO, was reported by Sinn

and Kaminsky in 1980 [8]. The process produced a linear high-density polyethylene with narrow-molecular-weight distribution and opened the way for the use of other metallocene and non-metallocene [3] transition-metal catalysts for olefin polymerizations. Metallocene catalysts are also able to incorporate comonomers, such as butene-1, hexene-1, and octene-1, much more efficiently than is otherwise possible [4].

Typical properties of HDPE were given in Table 9-2. The principal commercial applications for HDPE include blow-molded containers, crates, pails, drums, gas tanks, and blown film. Polyethylene with molecular weights as high as 5 million (i.e., ultrahigh-molecular-weight polyethylene, UHMW) has been used for specialty applications, particularly for medical use such as artificial hip replacements (see Section 10.2.3).

Approximately 30 years ago, another low-pressure process (Unipol) was developed for the polymerization of ethylene. This process produces what may be considered a third-generation hybrid polyethylene (see Section 2.3.5)—a linear low-density polyethylene (LLDPE) produced at low pressure. Branches are linear alkanes that are shorter than those of LDPE. One advantage of LLDPE over LDPE is a faster cycling time during the molding of containers and lids. LLDPE is frequently blended with LDPE for film and sheet production. In recent years, the production of LLDPE represents about one-third of the combined world production of both LDPE and LLDPE. LLDPE produced by metallocene polymerization (see Section 2.2.3) provides superior mechanical and heat-sealing properties compared to conventionally produced LLDPE [5]. In addition to LDPE, LLDPE, and HDPE, other commercial grades of polyethylene include medium-density polyethylene or MDPE and very-low-density polyethylene or VLDPE ($\rho < 0.915 \text{ g cm}^{-3}$).

Polypropylene. The polyolefin with the largest sales volume is polypropylene (PP), properties of which are included in Table 9-2. Polypropylene is a lightweight, moderately high- T_m plastic that finds use in the manufacture of pipe, sheet, and blow-molded containers and as a textile fiber (see Section 8.2.3). In general, α -olefins such as PP cannot be polymerized by either radical or ionic catalysts. While atactic PP can be produced by use of a Lewis acid or organometallic compound, the product is a branched, rubbery polymer ($T_g = -20^\circ\text{C}$) at ambient temperature with no important commercial applications. In the 1950s, Natta showed that Ziegler-type catalysts could be used to produce stereoregular PP with high crystallinity; however, in contrast to the polymerization of HDPE, the coordination polymerization of α -olefins is slower and more critically dependent on the nature of the catalyst. The commercial plastic, first introduced in 1957, was highly isotactic (i.e., *i*-PP). High-molecular-weight (150,000 to 1,500,000) *i*-PP can be obtained by using a heterogeneous catalyst of modified titanium (III) chloride with a co-catalyst or activator, usually an organoaluminum compound such as diethylaluminum chloride. Catalysts are slurried in a hydrocarbon mixture, which helps to facilitate heat transfer in batch or continuous reactors operating at temperatures of 50° to 80°C and pressures of 5

to 25 atm. Hydrogen, which acts as a chain-transfer agent, may be used to moderate molecular weight. Syndiotactic PP (*s*-PP) can be produced by using homogeneous Ziegler–Natta catalysts at lower temperatures; however, recent interest in *s*-PP has grown with the development of metallocene catalysts (see Section 2.2.3) [3–6]. Metallocene polymerization of propylene, using catalysts such as isopropyl(Cp)(fluorenyl)ZrCl₂–MAO [9], produces polypropylene with extremely high syndiotacticity ($[\text{rrrr}] > 90\%$) and a T_m near 150°C. Compared to its isotactic counterpart, *s*-PP has a slightly lower T_m and is more susceptible to solvent attack.

In comparison to HDPE, commercial grades of *i*-PP have a higher T_m , slightly lower crystallinity, and better crack resistance. Unlike polyethylene, whose lowest-energy conformation is the extended planar zigzag (see Chapter 1), the pendant methyl groups of PP require a more complicated conformation whereby three monomer units constitute a single turn in a helix. Its higher T_m allows PP to be used in products that must be steam sterilized. One disadvantage of PP is the susceptibility of its methyl groups to thermooxidative degradation.

9.1.2 Vinyl Polymers

Polystyrene. Polystyrene (PS) was first produced in quantity by Dow in 1938. Today, styrenic polymers, principally general-purpose (GP-PS) and impact grades of polystyrene (HIPS), constitute about 14% of the total thermoplastics market (see Table 9-1). Properties of different grades of PS are given in Table 9-3. Commercial (atactic) PS is produced by free-radical polymerization in bulk or suspension with peroxides or trace oxygen as initiators. Exotherm control in bulk polymerization can be achieved by using multiple-step polymerizations—an initial low conversion in a stirred-tank reactor followed by high conversion in a tubular reactor operating with an increasing temperature gradient.

The principal use for PS has been packaging, where it is receiving increasing competition from PP. An especially important application for styrenic polymers is the manufacture of foam and bead for insulation and packaging materials. The first expandable PS (EPS) was produced in England in 1943. Today, the worldwide consumption of EPS is estimated at 1.6 million tons. EPS is a closed-cell structure made from PS beads and a hydrocarbon propellant or blowing agent such as isopentane and butane (see Section 7.1.3). For construction use, flame-retardant grades of EPS can be produced by adding <1% of brominated aliphatic compounds such as hexabromocyclododecane (HBCD).

One advantage of PS for packaging and related applications is that it can be reprocessed fairly easily. For example, the use of 30% to 50% clean scrap is common practice in the manufacture of thermoformed packaging, and used coffee cups can be recycled as regrind for use in the core of three-layer sheet for new cup production.

Table 9-3 Properties of Styrenic Polymers

Property	ASTM	GP-PS	HIPS	ABS
Specific gravity	D792	1.04–1.05	1.03–1.06	1.03–1.58
Tensile strength, MPa ^a	D638	36.6–54.5	22.1–33.8	41.4–51.7
Tensile modulus, GPa ^b	D638	2.41–3.38	1.79–3.24	2.07–2.76
Elongation-to-break, %	D638	1–2	13–50	5–25
Impact strength, notched Izod, J m ^{-1 c}	D256	13.3–21.4	26.7–587	160–320
Heat-deflection temperature, °C at 455 kPa (66 psi)	D648	75–100	75–95	102–107

^aTo convert MPa to psi, multiply by 145.

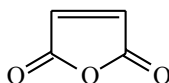
^bTo convert GPa to psi, multiply by 1.45×10^5 .

^cTo convert J m⁻¹ to lb_f in.⁻¹, divide by 53.38.

Polystyrene is especially susceptible to photooxidative degradation (see Section 6.1.2), which results in brittleness and yellowing. Degradation is initiated by the phenyl group, which absorbs UV radiation from sunlight. This energy is transferred to other sites along the polymer chain, resulting in bond cleavage, radical formation, and reaction with oxygen to form hydroperoxide and carbonyl groups.

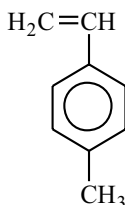
Stereospecific Polystyrene. As mentioned above, commercial-grade polystyrene is the atactic polymer (*a*-PS) produced by free-radical polymerization. An isotactic PS (*i*-PS) was first prepared by Natta in 1955 using a Z–N catalyst consisting of titanium tetrachloride and triethylaluminum [10]. Isotactic PS is moderately crystalline with a T_m of $\sim 230^\circ\text{C}$ but is more brittle and expensive than *a*-PS. For these reasons, *i*-PS was never commercialized. In 1986, syndiotactic PS (*s*-PS) was obtained by a metallocene polymerization (see Section 2.2.3) [11]. Unlike *i*-PS, *s*-PS has some advantages in properties over commercial-grade *a*-PS. These include better high-temperature performance ($T_m \approx 277^\circ\text{C}$), better toughness, lower permeability (i.e., improved barrier properties), and good chemical resistance. These advantages are offset by a higher price compared to commodity-grade PS. Current potential markets for *s*-PS include some electrical and electronics applications where *s*-PS can compete with poly(butylene terephthalate) (PBT) (see Section 10.1.8). Other areas may include some specialized products requiring thin walls and long, difficult flow paths during injection molding.

Styrene Copolymers. Disadvantages of GP-PS include its high brittleness and low T_g . To some extent, these limitations can be addressed through copolymerization. For example, copolymerization of styrene with maleic anhydride



provides slightly higher heat-distortion temperature, while copolymerization of styrene with acrylonitrile (i.e., SAN copolymer) provides higher strength and chemical resistance. Impact modification of PS can be obtained through the incorporation of polybutadiene. For example, high-impact PS (HIPS) is produced by the emulsion polymerization of styrene in a polybutadiene or styrene–butadiene (SBR) latex. The resulting toughened PS consists of a glassy matrix of PS in which are dispersed small domains (~ 0.005 -cm diameter) of polybutadiene. High interfacial adhesion, important for high strength, is achieved through graft polymerization of styrene, which occurs during the preparation of HIPS. ABS resins (see Section 10.1.2) are produced by blending latex emulsions of SAN and NBR (acrylonitrile–butadiene rubber) or by grafting styrene and acrylonitrile onto polybutadiene in latex form. Properties of SBR and NBR elastomers are reviewed in the following section. Polystyrene can be crosslinked by copolymerizing styrene with limited amounts of divinylbenzene. Applications of crosslinked PS beads include gel-permeation chromatography (see Section 3.3.4) and ion-exchange resins (see Section 2.4.1).

Other Styrenic Polymers. The monomer *p*-methylstyrene (PMS)



can be synthesized from toluene and ethylene by a zeolite process in high yield. This monomer can be polymerized by techniques similar to those used for PS to give poly(*p*-methylstyrene) that has a lower density, a slightly higher heat-distortion temperature, better flame retardancy, and faster molding cycles than conventional GP-PS. Stereospecific poly(*p*-methylstyrene) can be polymerized using metallocene catalysts [4].

Poly(vinyl chloride). As Table 9-1 indicates, PVC and copolymers of vinyl chloride are among the largest-volume commodity thermoplastics. Annual U.S. production is estimated at about 69 million metric tons. Poly(vinyl chloride) (PVC) is available in two general grades, rigid and flexible. Rigid-grade PVC is used as sheet, pipe, and window profiles and for other molded parts. Flexible-grade PVC is obtained by blending PVC with low- T_g plasticizers as discussed in Section 7.1.1. Applications of plasticized PVC include wire coating, upholstery, floor coverings, film, and tubing. Commercial PVC is a clear, moderately tough, low-crystallinity ($T_g = 87^\circ\text{C}$; $T_m = 212^\circ\text{C}$) material with low to moderate molecular weight (25,000 to 150,000). Properties of rigid- and flexible-grade PVC are summarized in Table 9-4.

Table 9-4 Representative Properties of Commercial Grades of PVC

Property	ASTM	Rigid	Flexible
Specific gravity	D792	1.03–1.58	1.16–1.35
Tensile strength, MPa ^a	D638	41.4–51.7	22.1–33.8
Tensile modulus, GPa ^b	D638	2.41–4.14	1.79–3.24
Elongation-to-break, %	D638	2–80	13–50
Impact strength, notched Izod, J m ⁻¹ ^c	D256	21.4–1068	26.7–587
Heat-deflection temperature, °C at 455 kPa (66 psi)	D648	57–82	75–95

^a To convert MPa to psi, multiply by 145.

^b To convert GPa to psi, multiply by 1.45×10^5 .

^c To convert J m⁻¹ to lb_f in.⁻¹, divide by 53.38.

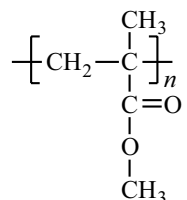
Polymerization of commercial-grade PVC is conducted by free-radical polymerization principally by suspension polymerization techniques, although emulsion polymerization and, more recently, bulk polymerization methods are also used. PVC is insoluble in its own monomer and, therefore, the polymer precipitates during bulk polymerization or within the monomer droplets in the case of suspension polymerization. If the suspension polymerization is performed under moderate pressure and then vented at the stage of high monomer conversion, a porous “dry-blend” resin is produced. Such resins are able to absorb large amounts of a plasticizer before becoming sticky and are, therefore, used in preparing flexible-grade PVC formulations.

The polymerization temperature is typically around 50°C for commercial PVC resins since higher temperatures can lead to minor branching and excessive formation of hydrochloric acid through dehydrochlorination, while lower temperatures result in polymers of high syndiotactic content. Dehydrochlorination, which starts at about 100°C, is also a serious problem when unstabilized PVC is heated above its T_g , as during melt processing (see Section 6.1.1). The thermally initiated dehydrochlorination reaction produces hydrochloric acid, which further accelerates dehydrochlorination, leading to intense color formation and eventual deterioration of polymer properties. It was for these reasons that the first commercial vinyl resins produced between 1928 and 1930 were copolymers of vinyl chloride with vinyl acetate, vinyl ethers, and acrylic esters. Today, thermal stability of the homopolymer is improved by adding organotin and other compounds.

Properties of PVC can be modified through chemical modification, copolymerization, or blending. For example, PVC may be chlorinated (i.e., CPVC) to increase its heat-distortion temperature for applications such as a hot-water pipe. A flexible film can be obtained by copolymerizing vinyl chloride with vinylidene chloride (Saran) or vinyl acetate. Vinyl acetate may also be grafted onto the PVC chain. The toughness of PVC can be improved by blending with high-impact resins

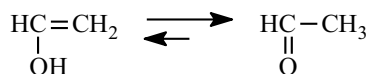
such as ABS (acrylonitrile–butadiene–styrene) and MBS (methyl methacrylate–butadiene–styrene) (see Section 7.2.2).

Poly(methyl methacrylate). Among other commercially important vinyl polymers are poly(methyl methacrylate) (PMMA) and to a lesser extent poly(vinyl acetate) and its derivatives. Commercial-grade PMMA



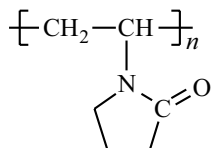
is an amorphous polymer of moderate T_g (105°C), with high light transparency and good resistance to acid and environmental deterioration. It is commercially polymerized by free-radical initiators such as peroxides and azo compounds in suspension or in bulk (e.g., cast polymerization) for sheet and molding compounds or for more specialized applications such as hard contact lenses. PMMA may also be polymerized anionically (see Section 2.2.2) at low temperatures to give highly isotactic ($T_g = 45^\circ\text{C}$; $T_m = 160^\circ\text{C}$) or highly syndiotactic ($T_g = 115^\circ\text{C}$; $T_m = 200^\circ\text{C}$) polymers. PMMA finds major applications in the automotive industry (e.g., rear lamps, profiles, and light fixtures), as acrylic sheet for bathtubs, advertisement signs, and lighting fixtures, and as composite material for kitchen sinks, basins, and bathroom fixtures.

Poly(vinyl acetate). Poly(vinyl acetate) (PVAC) ($T_g = 29^\circ\text{C}$), which may be polymerized by free-radical emulsion or suspension polymerization, finds limited applications in adhesives and also as the starting material for the production of poly(vinyl alcohol) (PVAL) and poly(vinyl butyral) (PVB), as discussed in Section 2.4.2. Poly(vinyl alcohol), which is used as a stabilizing agent in emulsion polymerization and as a thickening and gelling agent, cannot be directly polymerized because its monomer is isomeric with acetaldehyde, as shown below.



Commercially, PVAL is produced by the hydrolysis of PVAC in concentrated methanol. PVAL can be partially reacted with butyraldehyde to give PVB, which in its plasticized form is used as the inner layer of windshield safety glass. About 25% of the PVAL repeating units are left unreacted to provide strong adhesion to the glass.

Poly(*N*-vinyl-2-pyrrolidinone). Another interesting group of vinyl polymers are the polyvinylamides. As a class, they are highly polar, amphoteric polymers of which poly(*N*-vinyl-2-pyrrolidinone) (PVP)

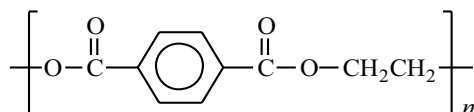


is the most commercially important. Poly(*N*-vinyl-2-pyrrolidinone) is an amorphous polymer with a glass-transition temperature ranging from 126° to 174°C for commercial grades. It has several very useful properties including very low toxicity, good film-forming and adhesive properties, and solubility in a broad range of solvents, including water, alcohols, and a number of other organic solvents. In addition, PVP is able to form complexes with a wide range of compounds through hydrogen-bond formation between its carbonyl group and the hydroxyl groups of water, alcohols, and hydroxyl-containing polymers like poly(vinyl alcohol). During World War II, PVP was used as a plasma extender, and copolymers of vinyl pyrrolidinone and hydroxyethyl methacrylate are used to manufacture soft contact lenses today.

Applications for PVP are diverse, including adhesives, coatings, controlled release of drugs, and the clarification of beer and wine in the food industry. PVP is also used as a protective colloid in emulsion and suspension polymerizations and for improving the dyeability of textile material. Vinyl pyrrolidinone is usually bulk polymerized by a free-radical mechanism employing peroxides or azo compounds as initiators and may be grafted or copolymerized with a number of different monomers, such as maleic anhydride, methyl methacrylate, acrylic acid, and acrylonitrile. PVP can be crosslinked in strong alkali, inorganic persulfates (e.g., potassium persulfate), and peroxides or can be crosslinked by irradiation with UV or γ -radiation.

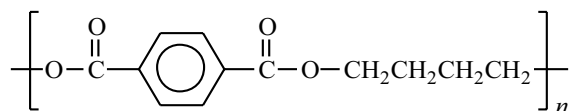
9.1.3 Thermoplastic Polyesters

The most industrially important polyester is poly(ethylene terephthalate) (PET)



which is principally recognized for its use as a consumer fiber dating back to 1953. Attempts to injection-mold PET in the mid-1960s were unsuccessful due to its slow crystallization rate, which translated into unacceptably low molding rates. At that

time, a promising alternative to PET for molding applications appeared to be poly(butylene terephthalate) (PBT)



which crystallized faster than the available grades of PET. Although much interest was directed toward developing PBT for molding (as well as fiber) use during the 1970s, the market for moldable PBT did not develop to the extent originally envisioned due to several issues, including problems with postmolding warpage. In the late 1970s, interest was directed toward the development of faster-crystallizing grades of PET suitable for molding applications such as packaging (soft drink and custom bottles and thermoformed trays). The current usage of PBT has been in the guise of an engineering thermoplastic along with several other polyesters, such as polyarylates (see Section 10.1.8) and liquid-crystalline polyesters (Section 10.2.6) for use in specialized applications.

The traditional route to the production of commercial PET is through two successive ester-interchange reactions, as shown in Figure 9-2. The first step (Figure 9-2A) is the ester interchange of dimethyl terephthalic acid (DMT) and ethylene glycol at temperatures near 200°C during which methanol is removed and an oligomeric product ($n = 1 - 4$) is obtained. In the second-stage esterification (Figure 9-2B), increasing temperature causes the formation of high-molecular-weight PET during which ethylene glycol is distilled off.

The total world production of PET was approximately \$23 billion in 2010 and is expected to increase to about \$48 billion by 2016. The largest segments of this market are fibers, plastic bottles, and films (magnetic recording tape and photographic). The market for molding grades of PET is particularly strong as a result of the relative ease with which PET can be recycled [12]. Although recycled PET cannot be used directly for beverage bottles, it can be used in the manufacture of other products, such as insulation boards, or can be thermally or chemically decomposed to its monomers, which can be used for the polymerization of virgin resin (see Section 6.2.1).

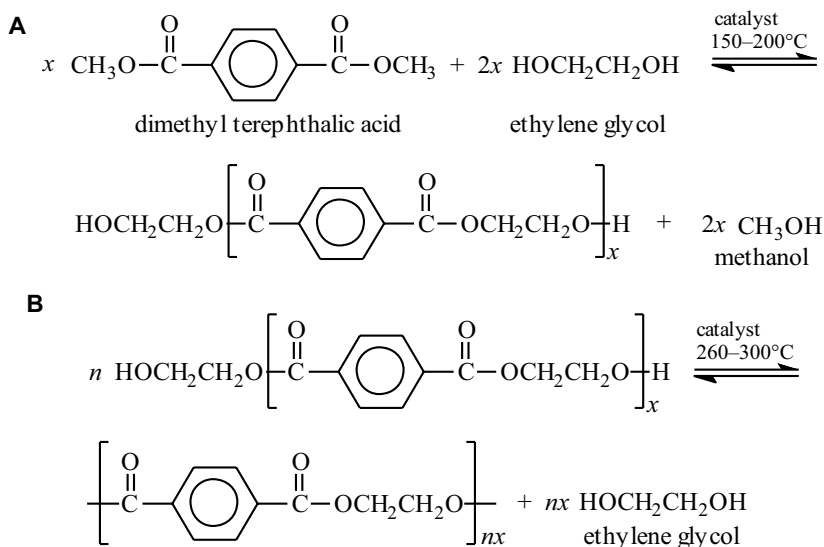
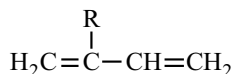


Figure 9-2 Two steps in the polymerization of poly(ethylene terephthalate). **A.** Ester interchange of dimethyl terephthalic acid and ethylene glycol. **B.** High-temperature esterification to yield high-molecular-weight polymer and ethylene glycol as a by-product.

9.2 Elastomers

Elastomers can be broadly classified as belonging to one of three groups: diene elastomers, nondiene elastomers, and thermoplastic elastomers. Diene elastomers such as polybutadiene, polyisoprene, and polychloroprene are polymerized from monomers containing two sequential double bonds (a diene) having the structure



where R represents a substituent group such as a hydrogen atom (in the case of polybutadiene), a chlorine atom (in polychloroprene), or a methyl group (in polyisoprene). As discussed in the following section, polymerization results in a repeating unit containing a single double bond that can provide a site for subsequent crosslinking (i.e., vulcanization). Typically, the most significant segment of the U.S. market for synthetic rubber is styrene-butadiene rubber (SBR), followed by polybutadiene and EP rubber.

Nondiene elastomers include polyisobutylene, polysiloxanes (silicone rubber), and a number of specialty elastomers, such as polyurethane (Spandex), and fluoroelastomers, such as Viton. Nondiene elastomers have no unsaturated sites and, therefore, crosslinking requires alternative methods to vulcanization, such as the use of trifunctional monomers in the case of condensation polymerizations (e.g., polysiloxanes), by the use of free-radical initiators, or by copolymerization with a small amount of a diene monomer (e.g., butadiene).

Thermoplastic elastomers such as SBS terpolymer are thermoplastics that contain rigid (“glassy”) and soft (“rubbery”) segments that can be thermally processed, unlike chemically crosslinked elastomers. Upon cooling, the soft and rigid segments phase-separate into physically distinct domains whereby the rigid domains serve as physical anchors for the rubbery segments and, thereby, provide a restoring force when the thermoplastic elastomer is stretched. The methods of synthesis and the properties of these three classes of elastomers are reviewed in the following sections. Principles of rubber elasticity were developed in Section 5.2.

9.2.1 Diene Elastomers

One way to form an elastomeric network is by the chemical bonding of two unsaturated carbons located on adjacent polymer molecules. Elastomers containing unsaturated sites include some of the most important synthetic rubbers, such as polybutadiene, polyisoprene, and polychloroprene. As shown in Figure 9-3, conjugated dienes such as isoprene and chloroprene can be polymerized to give either a 1,2-, 3,4-, or 1,4-polymer. In the case of 1,4-polymers, both *cis* and *trans* configurations are possible. In the case of the polymerization of 1,3-butadiene, for which there is no asymmetric substitute group, the 1,2- and 3,4- structures are identical. The proportion of each type of structure incorporated into the polymer chain influences both thermal and physical properties and is controlled by the conditions and method of polymerization. For example, butadiene can be polymerized by free-radical addition (see Chapter 2) at low temperature to give a polymer that is mostly *trans*-1,4- with only about 20% 1,2- structure. As the polymerization temperature is increased, the amount of *cis*-1,4- structure increases, while the proportion of 1,2- structure remains about the same.

Dienes can also be prepared by anionic polymerization using lithium or organolithium initiators like *n*-butyllithium in nonpolar solvents like pentane or hexane to yield polymers with high *cis*-1,4 content. The proportion of *cis*-1,4 structure decreases when higher alkali-metal initiators or more polar solvents are employed. Stereoregularity can also be controlled by use of selective coordination catalysts like Ziegler–Natta (see Section 2.2.3) or heterogeneous Alfin catalysts, which are combinations of alkenyl sodium compounds, alkali metal halides, and an alkoxide. Use of the latter system gives high-molecular-weight, high *trans*-1,4-content polymers.

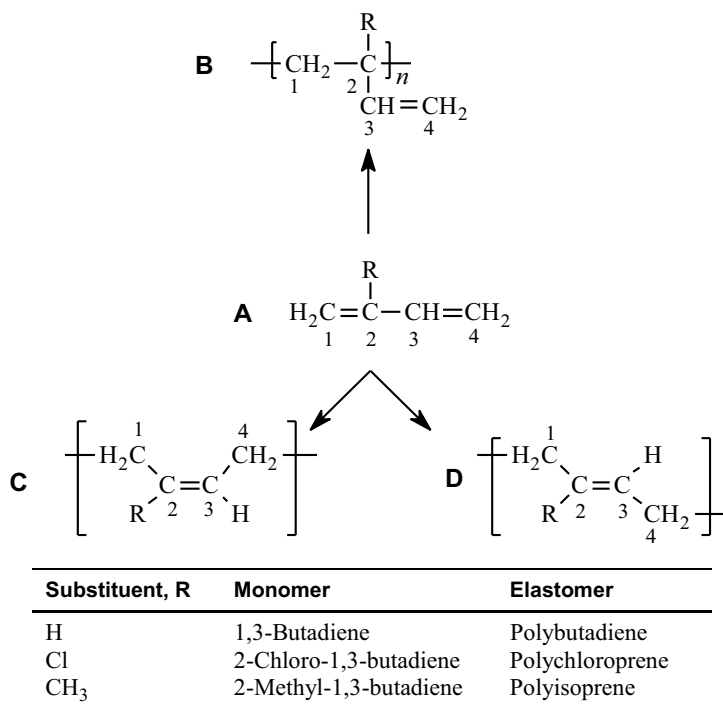


Figure 9-3 Polymerization of diene monomer (A) to yield 1,2- (B), *cis*-1,4- (C), and *trans*-1,4- structures (D). Different elastomers are obtained depending upon the substituent group, R.

Butadiene-Based Elastomers. Of all synthetic elastomers, polybutadiene (BR) and butadiene copolymers enjoy the largest sales share. In particular, styrene-butadiene copolymers (SBR) now have the largest share of the entire synthetic elastomer market in the United States. The principal use of both BR and SBR is in the production of tires and tire products, which are typically blends of both natural and synthetic rubbers. Polybutadiene has good resilience and abrasion resistance and low heat buildup—important properties for tire applications.

SBR is a highly random copolymer of butadiene and 10% to 25% styrene. The addition of styrene results in a lower price and contributes to the good wearing and bonding characteristics of SBR. In addition, strength, abrasion resistance, and blend compatibility are improved over BR alone. Like BR, SBR can be polymerized by a free-radical mechanism in emulsion either at 30° to 60°C (hot rubber) or near 0°C (cold rubber). A typical composition of the butadiene portion of SBR is approximately 70% of *trans*-1,4-polybutadiene, 15% to 20% of *cis*-1,4-polybutadiene, and 15% to 20% of 1,2-polybutadiene. Coordination copolymerization in solution yields

an SBR product (stereo SBR) that has a higher molecular weight, narrower molecular-weight distribution, and higher *cis*-1,4- content than emulsion-polymerized SBR.

Butadiene can also be copolymerized with 15% to 40% acrylonitrile in either hot or cold free-radical emulsion polymerization. The resulting elastomer, NBR or *nitrile rubber*, has improved oil and aromatic solvent resistance and, therefore, can be used as material for gaskets, tubing, O-rings, and gasoline hose. NBR, whose production was 180 million pounds in the United States during 2001, can also be used as a blend component in tire manufacture.

Polyisoprene. As discussed in Section 8.1.4, polyisoprene occurs in nature but can also be produced synthetically. Natural rubber (NR) or Hevea rubber used in tire manufacture is nearly all *cis*-1,4-polyisoprene. The synthetic equivalent of *cis*-1,4-polyisoprene (IR) can be obtained by polymerizing 2-methyl-1,3-butadiene (Figure 9-3) with Ziegler–Natta and Alfin catalysts. High *trans*-content polyisoprene may also be obtained by appropriate catalyst selection. IR has many of the good properties of its naturally occurring counterpart including high resilience, strength, and abrasion resistance. As in the case of most other diene-based elastomers, IR has poor resistance to attack by ozone, gasoline, oil, and organic solvents.

Polychloroprene. Another important diene-based elastomer is polychloroprene (neoprene), or CR. Compared to the other elastomers in this class, CR exhibits good resistance to attack by oxygen, ozone, oil, and gas. For these reasons, CR is used primarily as material for gaskets, tubing, O-rings, seals, and gasoline hose. The commercial material is mostly *trans*-1,4-polychloroprene produced by free-radical emulsion polymerization of 2-chloro-1,3-butadiene (Figure 9-3).

Metathesis Elastomers. At present, polynorbornene and polyoctenamer are two commercial elastomers produced by ring-opening metathesis polymerization (see Section 2.5.1). These specialty elastomers offer high oil absorptivity (polynorbornene) and high strength (polyoctenamer). Recent advances have shown that other elastomers, including polybutadiene as well as block and graft copolymers, can be made by metathesis [13, 14].

Vulcanization. Uncrosslinked rubber products such as natural rubber obtained from the latex of the *Hevea brasiliensis* tree are tacky, gummy materials, much like chewing gum, having none of the resiliency and permanent set we normally associate with commercial rubber products such as rubber bands, rubber hose, and tires. To obtain a network structure, diene elastomers are crosslinked by use of peroxides, ionizing radiation, and especially sulfur or sulfur-containing compounds. An illustration of a crosslinked elastomeric network is shown in Figure 9-4.

In the traditional method of vulcanization, which dates back to 1839, the rubber compound is heated with elemental sulfur. Sulfur bridges between individual elastomer molecules are formed by what is believed to be an ionic mechanism involving addition to the double bond. Concentration of sulfur in the vulcanized prod-

uct is typically 3 parts per hundred (pph) parts of elastomer compared to about 30 pph in highly crosslinked, hard rubber such as ebonite. The traditional vulcanization process is slow and inefficient as long sulfur bridges and cyclic sulfur structures can form. The process is improved by addition of accelerators such as thiuram disulfides, dithiocarbamates, and benzothiazoles. Activators such as zinc oxide and stearic acid serve to reduce the concentration of cyclic sulfide units and promote the formation of shorter-chain sulfide bridges. In addition to these additives, typical formulations for commercial rubber may include antioxidants and reinforcing fillers (see Section 7.1).

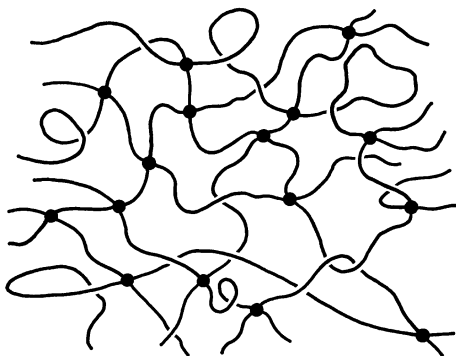
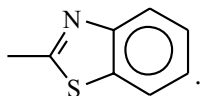


Figure 9-4 Idealized representation of a crosslinked elastomeric network. Filled circles indicate crosslink points (e.g., polysulfide bridges). Reproduced from J. E. Mark and B. Erman, *Rubberlike Elasticity—A Molecular Primer*. 1988, New York: John Wiley & Sons, with permission of James E. Mark.

A typical formulation for the vulcanization of a diene is given in Table 9-5. In this formulation, the fatty acid (e.g., stearic acid) and zinc oxide serve as the vulcanization activators. It is believed that the activators form a salt that complexes with the accelerator. Through this process, the accelerator forms a monomeric polysulfide as illustrated in Figure 9-5. The Ac group indicated in Figure 9-5 is an organic radical derived from the accelerator. An example is the benzothiazolyl group



This monomeric polysulfide then reacts with an unsaturated site of an elastomer chain to produce a rubber polysulfide and finally with another chain to form a polysulfide bridge. Typical molecular weight between crosslink points ranges from approximately 4000 to 10,000 where the molecular weight of individual chains is on the order of 100,000 to 500,000.

Table 9-5 Typical Vulcanization Ingredients for a Polydiene

Component	Phr
Accelerator	0.5–2
Sulfur	0.5–4
Fatty acid	1–4
Zinc oxide	2–10

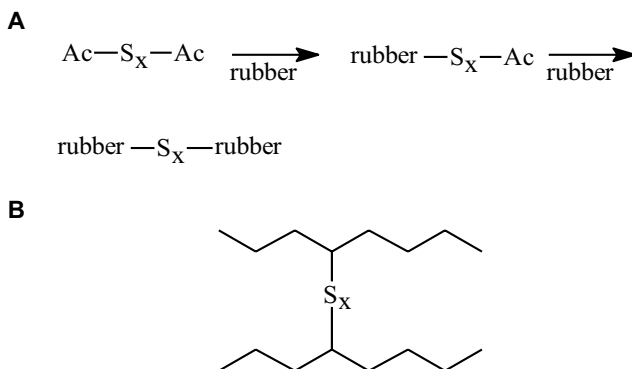


Figure 9-5 Vulcanization process. **A.** A polysulfide formed by reaction of elemental sulfur with an accelerator reacts with individual rubber chains to form polysulfide bridge. **B.** Polysulfide bridge between two rubber chains.

9.2.2 Nondiene Elastomers

A number of important elastomers do not have the unsaturated chain structure characteristic of the diene elastomer. These nondiene elastomers include polyisobutylene (butyl rubber), polysiloxane (silicone rubber), fluoroelastomers such as Viton, polyurethane elastomers such as Spandex, and elastomers derived from ethylene and propylene (EP and EPDM elastomers). In two cases—butyl rubber and EPDM—a small amount of diene monomer that provides a site for vulcanization is included by means of copolymerization. For the other nondiene elastomers, free-radical initiators or polyfunctional monomers are used for network formation. The absence or low concentration of double bonds in the main chain of these elastomers results in high resistance to attack by oxygen and ozone and superior chemical resistance of these specialty rubbers compared to diene elastomers.

Polyisobutylene. Polyisobutylene or butyl rubber is produced as a copolymer (IIR rubber) containing about 0.5% to 2% isoprene, which provides the necessary unsaturation sites for vulcanization. Butyl rubber exhibits outstanding resistance to attack by oxygen and ozone and exhibits low gas permeability. For these reasons, it finds principal usage in weather stripping and inner tubes. High-molecular-weight

butyl rubber may be prepared by low-temperature cationic polymerization using Lewis acids like aluminum chloride in chlorocarbon solvents such as chloromethane.

Polysiloxanes. Silicone elastomers have both high-temperature and oxidative stability, flexibility at low temperatures, good electrical properties, and resistance to weathering and oil. Typical applications include wire and cable insulation, surgical implants, gasket material and seals, and aircraft tubing. Polysiloxanes can be prepared by the hydrolysis of dichlorosilanes such as dimethyldichlorosilane, as shown in Figure 9-6. This process is unsatisfactory for obtaining high-molecular-weight polymer because of a tendency to form cyclic siloxanes, typically trimers and tetramers. High-molecular-weight polymer suitable for elastomer applications can be obtained by subsequent base-catalyzed ring-opening polymerization of the cyclic products. Crosslinked siloxane elastomers may be obtained by cohydrolysis of dichlorosilanes with alkyl-trichlorosilanes, which provide an additional functional group for polymerization. Alternatively, polydimethylsiloxane can be crosslinked by the use of peroxides. The efficiency of the vulcanization step is greatly enhanced by incorporation of unsaturated sites through copolymerization with vinyl-group-containing siloxanes such as vinylmethylsilanol.

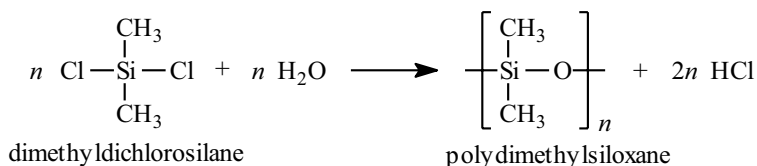


Figure 9-6 Polymerization of polydimethylsiloxane by the hydrolysis of dimethyldichlorosilane.

Fluoroelastomers. Most fluoroelastomers are obtained by high-pressure, free-radical emulsion polymerizations using organic or inorganic initiators. Most are copolymers of fluorinated polyolefins (tetrafluoroethylene and hexafluoropropylene) with vinylidene fluoride. Examples of common fluoroelastomers are given in Table 9-6. Fluorocarbon elastomers are capable of meeting demanding service applications, including operation over a broad temperature range and exposure to a wide range of chemicals and petroleum products. Uses include hose, tubing, O-rings, and gaskets in automotive, petrochemical, petroleum, and hydraulic applications. Fluoroelastomers are compounded with various fillers, processing aids, accelerators, and curatives and then extruded into the desired form such as tubing or O-ring cord. The extrudate is then postcured at 200° to 260°C for up to 24 h to achieve maximum mechanical properties.

Table 9-6 Examples of Fluoroelastomers

Fluoroelastomer	Trademarks
Poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene)	Viton, Fluorel
Poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene- <i>co</i> -tetrafluoroethylene)	Viton, Fluorel
Poly[vinylidene fluoride- <i>co</i> -tetrafluoroethylene- <i>co</i> -perfluoro(methyl vinyl ether)]	Viton
Poly[tetrafluoroethylene- <i>co</i> -perfluoro(methyl vinyl ether)]	Kalrez
Poly(tetrafluoroethylene- <i>co</i> -propylene)	Aflas
Poly(vinylidene fluoride- <i>co</i> -chlorotrifluoroethylene)	Kel-F

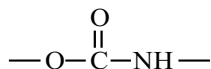
Polyurethanes. Polyurethanes (PUR) were developed by Otto Bayer and coworkers at I. G. Farbenindustrie in 1937. These polymers have high strength, good resistance to gas, oil, and aromatic hydrocarbons, high abrasion resistance, and excellent resistance to oxygen and ozone but are susceptible to microbial attack. Applications include shoe soles, solid tires, and impellers. Although the majority of polyurethane usage is for rigid and flexible foams first produced in the 1950s, about 15% of polyurethane production is targeted for elastomer applications. Basics of urethane chemistry and the preparation of polyurethane elastomers are discussed in this section.

In general, polyurethanes can be prepared either by the step-growth polymerization of diisocyanates with dihydroxyl (diol) compounds or, less commonly, by the reaction of bischloroformates with diamines. Both routes are illustrated in Figure 9-7. As shown, the step-growth polymerization of a diisocyanate with a diol, unlike the bischloroformate reaction, occurs without liberation of a low-molecular-weight by-product. The high reactivity of the isocyanate group enables polyurethanes to be processed by reaction injection molding (RIM) as discussed in Section 11.1.2.

Isocyanates, the esters of isocyanic acid (HNCO), can be aliphatic, cycloaliphatic, or polycyclic. Typical diisocyanates include methylene-4,4'-diphenyl-diisocyanate (MDI), toluene-2,4-diisocyanate (TDI),* and hexamethylene diisocyanate (HMI), whose structures are shown in Table 9-7. Diols are typically low-molecular-weight (e.g., 2000 to 3000) hydroxyl-terminated polyesters or polyethers such as polytetrahydrofuran (PTHF). Isocyanates or hydroxyl compounds with functionalities greater than 2 can be used to introduce branched groups or cross-links. Characteristic of all polyurethanes is the presence of the carbamate group†

* Often used as a mixture with its 2,6-isomer.

† An early term for polyurethanes was polycarbamate, from carbamic acid (RNHCO₂H).



in the chain backbone. Depending upon the chemical composition of the reactants (i.e., R, R'), the polyurethane chain may also include ester, ether, amide, or urea groups.

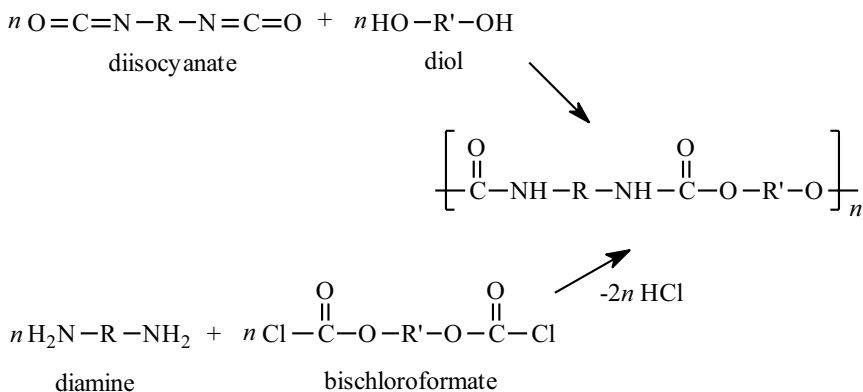
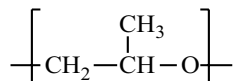
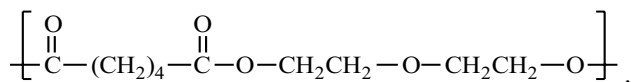


Figure 9-7 Routes to the synthesis of polyurethanes from diisocyanates (top) and bischloroformates (bottom).

Polyurethane elastomers can be obtained by the formation of (AB)_n-block copolymers consisting of alternating “soft” and “hard” segments. Typically, polyurethane elastomers are prepared by reacting an excess of an aromatic diisocyanate (e.g., MDI or TDI) with a hydroxy-terminated polyether or polyester (2000 to 3000 molecular weight) to yield an isocyanate-terminated prepolymer. An example of a commonly used polyether is poly(propylene glycol)



while a typical polyester is poly(diethyleneglycol adipate)



Polyester-based polyurethanes are less expensive and have better oxidative and high-temperature stability than do polyether-based polyurethanes, which have better hydrolytic stability and better low-temperature flexibility. As illustrated in Figure 9-8, the prepolymer can then be reacted with a diamine, such as ethylenediamine,

which acts as a chain extender to give the high-molecular-weight elastomer through a urea linkage as shown below.

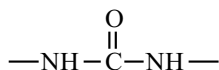
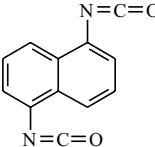
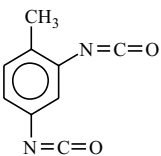


Table 9-7 Examples of Typical Diisocyanates

Diisocyanate	Abbrev.	Structure
Hexamethylenediisocyanate	HMI	$\text{O}=\text{C}=\text{N}-(\text{CH}_2)_6-\text{N}=\text{C}=\text{O}$
4,4'-Methylene-bis(cyclohexylisocyanate)	H_{12}MDI	$\text{O}=\text{C}=\text{N}-\text{C}_6\text{H}_{10}-\text{CH}_2-\text{C}_6\text{H}_{10}-\text{N}=\text{C}=\text{O}$
Methylene-4,4'-diphenyldiisocyanate	MDI	$\text{O}=\text{C}=\text{N}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{N}=\text{C}=\text{O}$
Naphthalene-1,5-diisocyanate	NDI	
Toluene-2,4-diisocyanate	TDI	

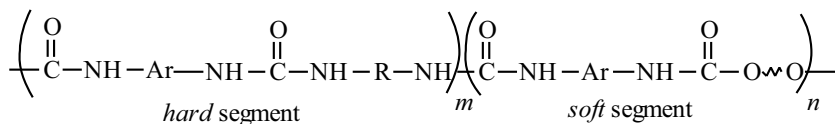
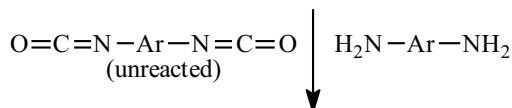
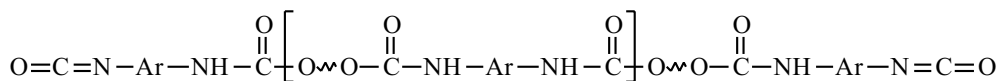
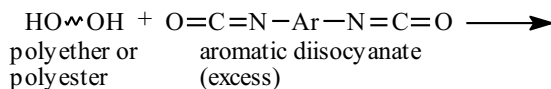
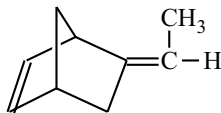


Figure 9-8 Synthesis of an elastomeric polyurethane for fiber applications.

The soft blocks of the copolymer are the flexible polyether/polyester segments, which constitute the bulk of the elastomer and form an amorphous continuous phase whose T_g is below normal-use temperature. Intermolecular hydrogen bonding between urethane groups results in domain association of hard blocks ($T_g > T_{use}$), which serve as physical anchor sites or crosslinks providing a restorative force when these elastomers are stretched. When the polyurethane elastomer is stretched, the soft segments elongate and crystallize until tension is released. Polyurethane elastomers are easily dyed and have high strength and chemical resistance, good abrasion and mar resistance, and elastic recovery. They are stable to attack by hydrocarbons and oxygen, although they are susceptible to strong acids and oxygenated solvents like ketones. Uses for polyurethane elastomers include foundation garments, surgical hose, and swimsuits.

Elastomers from Polyolefins. Random copolymers of ethylene and propylene (EPM rubber) can be prepared by use of soluble Ziegler–Natta catalysts (see Section 2.2.3) at controlled ethylene-propylene monomer concentration. The random placement of monomer units limits crystallinity and results in a rubbery material that can be crosslinked with peroxides through hydrogen abstraction and subsequent radical combination. Alternatively, an unsaturated terpolymer (EPDM rubber) can be prepared from ethylene, propylene, and unconjugated dienes like dicyclopentadiene, cyclooctadiene, 1,4-hexadiene, and ethylidene norbornene



These unsaturated terpolymers may be vulcanized by traditional means. EPM and EPDM have good resistance to acids, good weatherability and color stability, and good electrical stability. They can be used as substitutes for SBR and neoprene in automotive applications such as in tires, radiator hose, gaskets, and seals. EPM and EPDM are also used in wire and cable insulation, weather stripping, and in footwear. Blends of polypropylene and EPDM are used as material in the manufacture of car bumpers.

9.2.3 Thermoplastic Elastomers

Commercial elastomers can be made without the formation of the permanent crosslinks that are normally created through vulcanization. In place of covalent bonds, rigid-domain structures are used to create a network structure, as illustrated in Figure 9-9. These are typically the crystalline or glassy phases associated with the crystalline or glassy blocks of block copolymers or result from associations formed through the creation of secondary bonds such as hydrogen bonding between chemical groups in different molecules. Since these domains are physical in nature, they

are normally reversible and therefore elastomers belonging to this class are thermoplastic and can be fabricated by conventional molding techniques. Thermoplastic elastomers can be made from polyurethanes (discussed in Section 9.2.1), polyesters, polyolefins, and styrenic block copolymers. The absence of a separate vulcanization step and easy recycling of these materials have led to rapid commercialization of thermoplastic elastomers over the past 30 years.

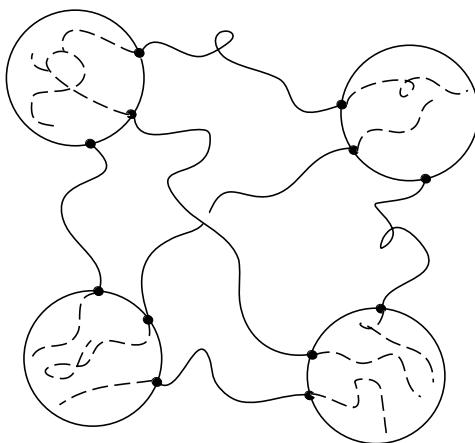


Figure 9-9 Representation of glassy domains in a thermoplastic elastomer such as SBS, polystyrene-*block*-polybutadiene-*block*-polystyrene. Circles represent physically separated domains of high glassy polymer (e.g., polystyrene) content that serve as physical crosslinks. Glassy domains are interconnected by the elastomeric (e.g., polybutadiene) segments. Adapted from L. H. Sperling, *Introduction to Physical Polymer Science*. Copyright © 1986 John Wiley & Sons. This material is used by permission of John Wiley & Sons, Inc.

SBS Elastomers. The most commercially important thermoplastic elastomers are ABA block copolymers composed of a high-molecular-weight (50,000 to 100,000) polystyrene end block and a central block of low-molecular-weight (10,000 to 20,000) polybutadiene (YSBR) or other olefins such as isoprene and ethylene-butylene. When cooled from the melt to below their glass-transition temperature, the polystyrene blocks phase-separate to form rigid glassy domains that act as physical crosslinks for the elastomeric olefin blocks. These block copolymers are prepared by anionic “living” polymerization as discussed in Section 2.2.2. As a class, they have higher tensile strength than SBR rubber but have limited heat resistance. YSBR can be hydrogenated to improve weather and temperature resistance. Blends of styrenic thermoplastic elastomers are used in rubber bands, toy products, shoe soles, and gasket material. YSBR containing 30% polybutadiene content may be blended with PS to produce a resin suitable for thermoforming plas-

tic drinking cups. PS alone is too brittle to withstand the high extension resulting from thermoforming (see Section 11.1.2).

Olefinic Elastomers. Olefinic thermoplastic elastomers, prepared by use of Ziegler–Natta catalysts (see Section 2.2.3), include *polyallomers*, which are block copolymers of polypropylene (the hard, crystalline block) and a second olefinic block, usually ethylene or ethylene and a diene (EPDM). EPDM block copolymers are attractive replacements for neoprene in oil-resistant wire and cable insulation due to their superior processability and coloration properties.

Copolyesters. Thermoplastic copolyesters consist of a hard (crystalline) polyester block, such as that formed by the reaction of terephthalic acid and butanediol, and a soft block of an amorphous long-chain polyester (e.g., polytetramethylene ether glycol) soft block. Like thermoplastic polyurethanes, thermoplastic copolyesters have good hydrocarbon and abrasion resistance. Applications include wire and cable insulation, gaskets, seals, hose, and automotive parts.

9.3 Thermosets

Principal commercial thermosets include epoxies, polyesters, and formaldehyde-based resins (i.e., phenol–formaldehyde, urea–formaldehyde, and melamine–formaldehyde). Typically, phenol resins constitute the largest segment of the thermoset market, followed by urea resins, unsaturated polyesters, and melamine resins.

9.3.1 Epoxies

Epoxies are formed by a two-stage process. Initially, a low-molecular-weight prepolymer is prepared by a base-catalyzed step-growth reaction of a dihydroxy compound such as bisphenol-A with an epoxide, typically epichlorohydrin, as illustrated in Figure 9-10. The prepolymer molecular weight is increased and the network is formed during a separate cure step, as shown in Figures 9-11 and 9-12. Amines, usually aromatic, may be used to cause ring opening of the end epoxide groups through nucleophilic addition (Figure 9-11). Carboxylic acid anhydrides such as phthalic acid anhydride can react with pendant hydroxyl to give ester acids, which can then react with epoxide or other hydroxyl groups to create additional ester groups (Figure 9-12). Epoxy resins have high chemical and corrosion resistance, outstanding adhesion properties, low shrinkage upon cure, and good electrical properties. Principal applications for these resins include protective coatings, composite matrices, and adhesives.

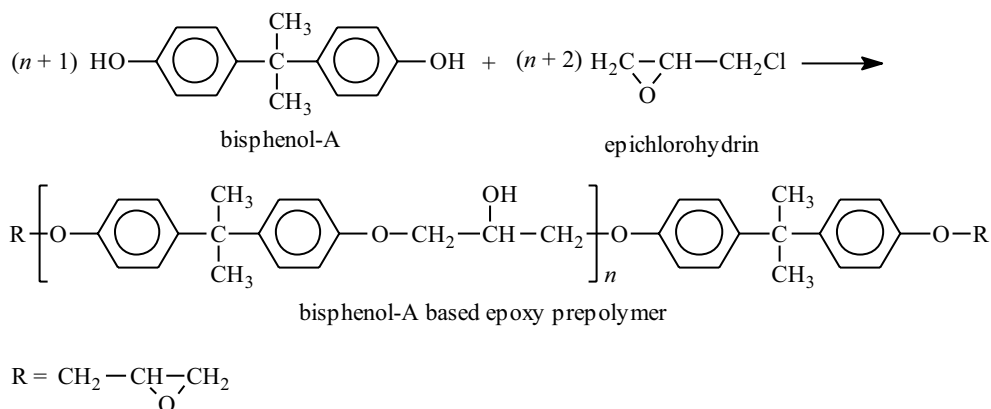


Figure 9-10 Epoxy prepolymer formed from bisphenol-A and epichlorohydrin.

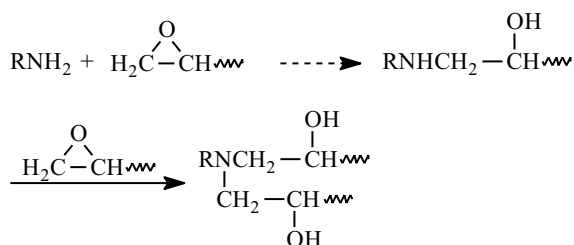


Figure 9-11 Cure of an epoxy resin by reaction of the prepolymer with an amine.

9.3.2 Unsaturated Polyesters

Polyester resins are widely used in construction and marine applications. Network formation distinguishes polyester resins from linear (thermoplastic) polyesters such as PET. Crosslinking is achieved either by use of polyols such as glycerol, as in the case of saturated polyesters (glyptal), or by the use of unsaturated dicarboxylic acids, such as maleic anhydride in the case of unsaturated polyester resins. Glyptal, which is used mainly as an adhesive or modified with natural or synthetic oils (oil-modified alkyds) for coatings, is formed by the reaction of glycerol and phthalic anhydride, as shown in Figure 9-13. The reaction is allowed to continue until a viscous liquid is obtained. The liquid can then be transferred to a mold for further network development (hardening).

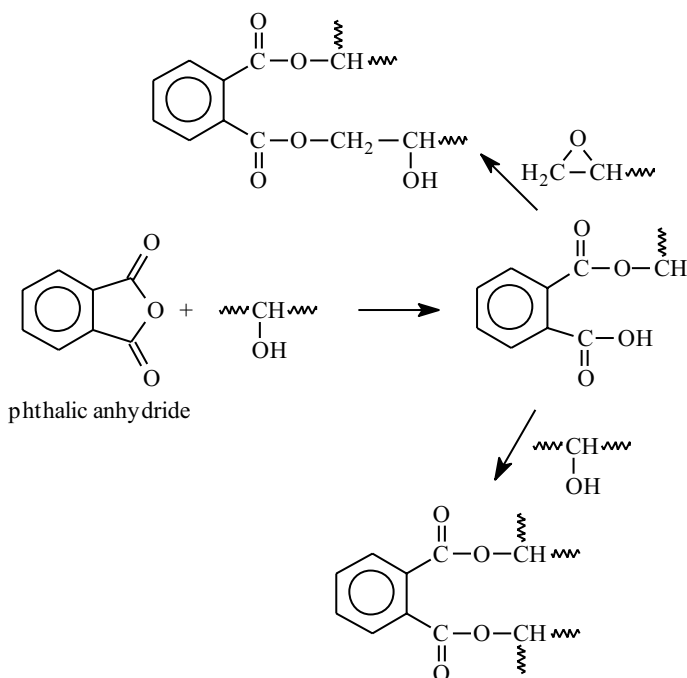


Figure 9-12 Cure of an epoxy resin by reaction of the prepolymer with an anhydride.

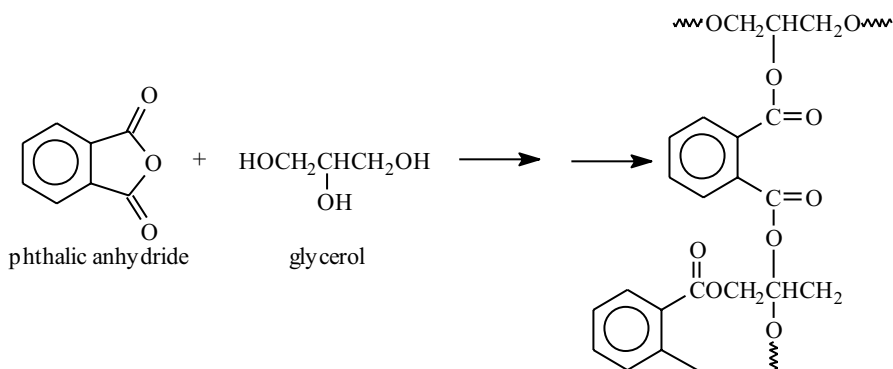


Figure 9-13 Formation of a glyptal resin.

Unsaturated polyester resins, which are used as the matrix component of glass-fiber composites, can be obtained by copolymerization of both saturated acids (e.g., phthalic anhydride) and unsaturated acids (e.g., maleic anhydride) with a diol such

as propylene glycol or diethylene glycol, as illustrated in Figure 9-14. Incorporation of the saturated acid serves to decrease crosslink density and consequently resin brittleness. Fumaric acid may be used in place of maleic acid to increase impact resistance. The low-molecular-weight product is soluble in styrene, which can then polymerize in the presence of peroxides at the double-bond sites of the prepolymer.

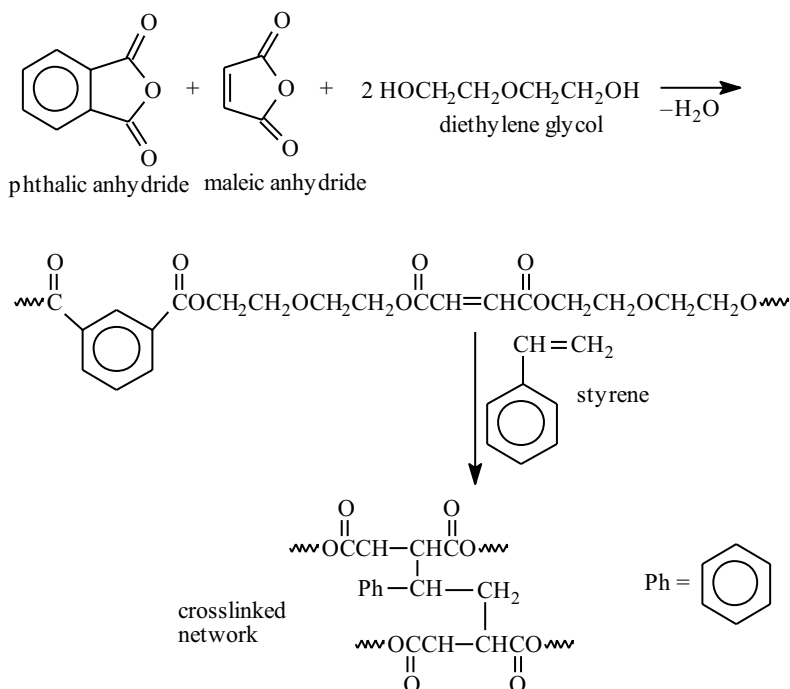


Figure 9-14 Formation of an unsaturated polyester resin.

9.3.3 Formaldehyde Resins

Formaldehyde is used in the production of two different but related classes of thermosets—phenoplasts and aminoplasts. *Phenoplasts*, or phenolic (PF) resins, are produced by the condensation of phenol (or resorcinol) and formaldehyde. These were the first synthetic thermosets. About 41% of PF resins are used in plywood manufacture and about 14% in insulation. Other applications include lacquers and varnishes, molding compounds, and laminates (e.g., wall panels and table tops).

Aminoplasts are prepared from the condensation of either urea (UF resins) or melamine (MF resins) with formaldehyde. Applications of aminoplasts are similar to those of phenoplasts; they also include the treatment of textile fibers for improv-

ing their shrink and crease resistance and their use to increase the wet strength of paper. In terms of sales volume, UF resins are the most important. Like phenolic resins, they can be used in molding, laminating, and adhesive applications, especially where the darker color of phenolics may be objectionable, such as in interior-grade plywood. They also find use in the manufacture of electrical switches and plugs and insulating foam. MF resins are harder and more chemical, temperature, and moisture resistant than UF resins but are more expensive. Typical applications for MF resins include decorative plastic dinnerware, laminated worktops, and electrical fittings. Formaldehyde-based resins may be used as unmodified compounds or may be compounded with additives such as wood flour or glass fibers that serve as reinforcing fillers.

Phenoplasts. Phenolic resin was the first totally synthetic coating material. It was commercialized in 1909 as Bakelite, a replacement for cellulose nitrate [15, 16]. Phenolic resins may be prepared by either a base-catalyzed addition of formaldehyde to phenol (resole formation) or by an acid-catalyzed reaction (novolac formation). The first step in resole formation is the reaction of phenol and excess formaldehyde under basic conditions to form mono-, di-, and trimethylolphenols. The formation of monoethylolphenol is illustrated in Figure 9-15. Under these conditions, phenol is present as a resonance-stabilized anion, and substitution is exclusively *ortho* and *para*. Upon heating, the methylolphenols condense to give a low-molecular-weight prepolymer called a *resole* (see Figure 9-16), which contains a large number of free methylol groups and is soluble in base. Further heating of the resole at elevated temperatures and under basic, neutral, or slightly acidic conditions yields the final high-molecular-weight network called the *resite*.

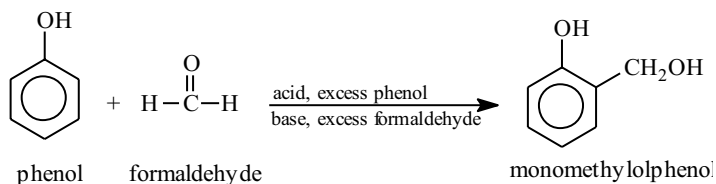


Figure 9-15 Reaction of phenol and formaldehyde to yield monomethylolphenol. Formation of dimethylolphenols and trimethylolphenols is also possible.

Resole formation can also be obtained by an initial acid-catalyzed reaction of formaldehyde with excess phenol. The mechanism involves protonation of the carbonyl group of formaldehyde, followed by electrophilic aromatic substitution at the *ortho* and *para* positions of phenol. Under acidic conditions, further reaction yields a low-molecular-weight, fusible but insoluble prepolymer called a *novolac* whose structure is illustrated in Figure 9-17. Unlike resole (Figure 9-16), novolac contains no residual hydroxymethyl groups. The high-molecular-weight network, the *resite*,

is obtained from the novolac by heating with additional formaldehyde, paraformaldehyde, or hexamethylenetetramine.

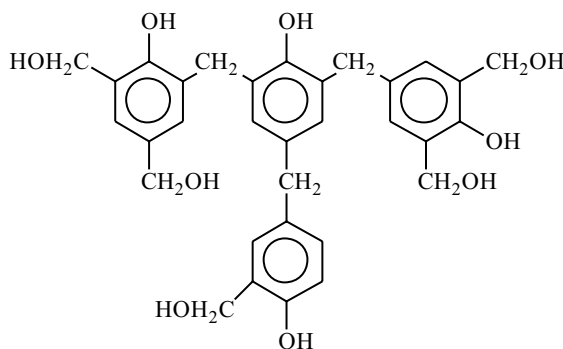


Figure 9-16 Representative structure of a resole.

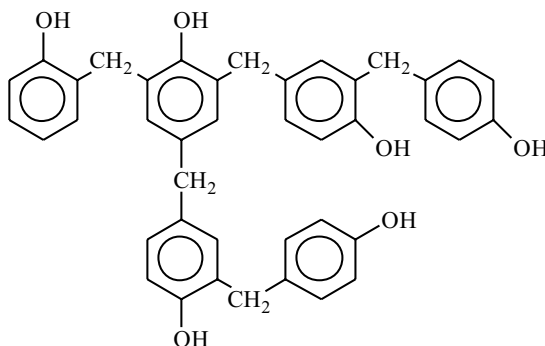


Figure 9-17 Representative structure of a novolac.

Aminoplasts. The first step in the production of UF resins is the nucleophilic addition of urea to formaldehyde to give methylol derivatives, as illustrated in Figure 9-18, in a manner similar to the initial stages of phenolic-resin production. Subsequent condensation of these derivatives gives the final high-molecular-weight resin. The UF resin may be a true network structure, such as that shown in Figure 9-19A, or a colloidal dispersion of UF condensates (Figure 9-19B), which are stabilized by association with excess formaldehyde.

As illustrated by Figure 9-20, the initial step in the preparation of MF resin is a condensation of formaldehyde and melamine similar to that of urea and formaldehyde (Figure 9-18). A difference is that the majority of amino groups of melamine form *dimethylol* derivatives rather than monomethylol derivatives, as in the case of UF resins. In the final stage of resin production, methylol groups condense with

amino groups to form methylene bridges, which link the prepolymer chains in a rigid network structure, as illustrated in Figure 9-21.

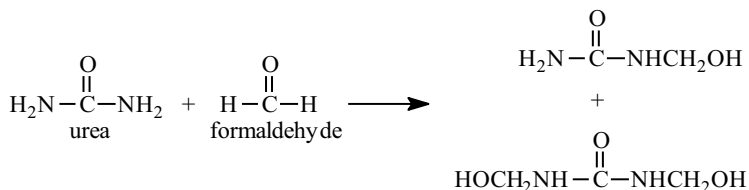


Figure 9-18 Reaction of urea and formaldehyde to yield methylol derivatives as the first step in the production of urea-formaldehyde resins.

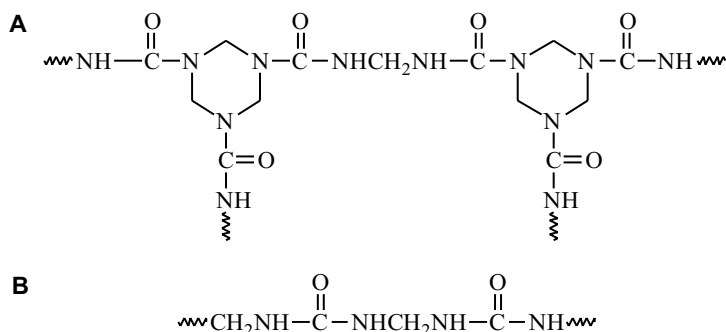


Figure 9-19 Structures proposed for a fully cured UF resin. **A.** Network model. **B.** Oligomeric UF condensates in the colloidal dispersion mode.

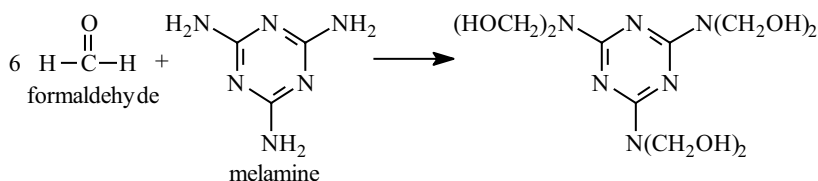


Figure 9-20 Condensation of melamine and formaldehyde to yield the dimethylol derivative of melamine.

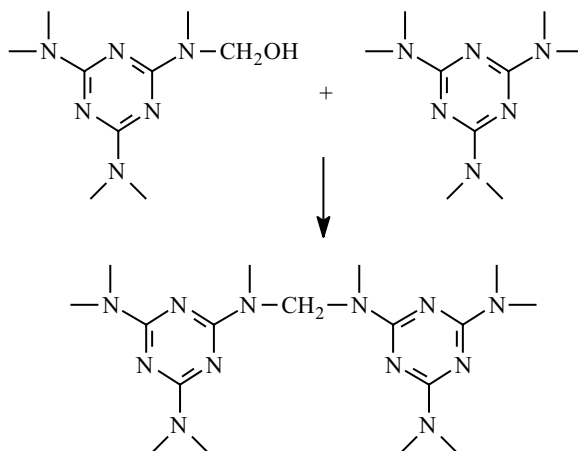


Figure 9-21 Formation of MF-resin network.

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PROBLEMS

- 9.1 Discuss the uses of thermosets in the construction industry.
- 9.2 Natural rubber is sometimes epoxidized. Describe the reaction and the use of epoxidized rubber.
- 9.3 Compare the mechanical and thermal properties and costs of PET and poly(trimethylene terephthalate) (PTT).^{*} Can PTT be used as a substitute for PET in engineering thermoplastic applications?
- 9.4 Describe the chemical routes to obtain the following monomers:
 - (a) bischloroformates from dihydroxy compounds
 - (b) hexamethylene diisocyanate from hexamethylene diamine
 - (c) naphthalene diisocyanate from naphthalene

^{*} See Section 8.2.3.

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