Chapter 15

Polymer Properties and Applications

I. INTRODUCTION

Many of the products we enjoy every day are derived from polymers even though we may not readily appreciate this. Polymers influence the way we live, work, and play. The evidence is all around us. There is no room in our house, no vehicle we ride in, no sports activity we participate in that does not use products made from polymers; the list of polymer products is virtually endless. In fact, the products are so diverse, so prevalent, and so ingrained in our lifestyles that we tend to take them for granted.

There are currently more than 40 families of polymers, many of whose uses still go unrecognized because of their diversity. Most consumers many be familiar with polymers in the form of housewares, toys, appliance parts, knobs, handles, electrical fixtures, toothbrushes, cups, lids, and packages. But few are aware that

- the lifelines of communications — television, radio telephone, radar — are based on polymers for insulation and other vital components;
- foams made from polymers have changed modern concepts of cushioning and insulation;
- polymers are vital to the electrical/electronics industry; and
- the practice of replacing heart valves, sockets and joints, and other defective parts of the body owes it success to the availability of suitable polymer materials.[1]

Polymers are true man-made materials that are the ultimate tribute to man's creativity and ingenuity. It is now possible to create different polymers with almost any quality desired in the end product — some similar to existing conventional materials but with greater economic value, some representing significant property improvements over existing materials, and some that can only be described as unique prime materials with characteristics unlike any previously known.[1]

The use of polymers has permeated every facet of our lives. Polymers contribute to meeting our basic human needs, including food, shelter, clothing, health, and transportation. It is hard to imagine what the world was like before the advent of synthetic polymers. It is difficult to contemplate what the world, with all its luxury and comfort, would be like without polymers. In this chapter we discuss the properties and applications of a number of them. First, however, the structure of and the raw materials for the polymer industry are briefly highlighted.

II. THE STRUCTURE OF THE POLYMER INDUSTRY[1]

The polymer industry is generally made up of a large number of companies. Some of these companies produce basic raw materials, others process these materials into end-use products, and still others finish these products in some way that may sometimes make them unrecognizable as polymers. The activities or functions of these companies are not mutually exclusive; indeed, they frequently overlap. For example, automotive and packaging, which depend on polymer products for their operations, may themselves be large processors of polymers. In addition, within the industry itself, polymer materials manufacturers may also be engaged in processing and finishing operations. In any case, the structure of the polymer industry can be resolved essentially into the following categories.

A. POLYMER MATERIALS MANUFACTURERS

As has been discussed in Chapter 1, polymers are high-molecular-weight compounds (macromolecules) built up by the repetition of small chemical units. These units, or repeating units as they are called, are derived from monomers. Monomers, as we shall see in the Section III, are obtained largely from fractions of petroleum or gas recovered during the petroleum refining process. The reaction of monomers, referred to as polymerization, leads to the polymer formation. The polymer materials manufacturer or supplier is involved in the transformation of monomers or basic feedstocks into polymer materials, which are then sold in the form of granules, powder, pellets, flakes, or liquids for subsequent processing into finished products.

A number of polymerization techniques are used in the transformation of monomers into plastics (Chapter 10). These include bulk, solution, suspension, and emulsion polymerization processes. Each of these polymerization techniques has its advantages and disadvantages and may be more appropriate for the production of certain types of polymer materials. For example, bulk polymerization is ideally suited for making pure polymer products, as in the manufacture of optical-grade poly(methyl methacrylate) or impact-resistant polystyrene, because of minimal contamination of the product. On the other hand, solution polymerization finds ready application when the end use of the polymer requires a solution, as in certain adhesives and coating processes.

B. MANUFACTURERS OF CHEMICALS, ADDITIVES, AND MODIFIERS

Very frequently, the polymer material from the materials manufacturer does not go directly to the processor. There is often an intermediate step that involves the addition of other materials (chemicals, additives, modifiers) that serve to impart special properties or enhance the qualities of the polymers or resin. For example, polymers can be integrally colored (with polymers or dyes), made more flexible (with plasticizers), more heat and light resistant (with stabilizers), or stronger and more impact resistant (with fiber reinforcements). These modifiers may be supplied by the companies that manufacture the plastics themselves or by companies that specialize in the production of one or more modifiers.

C. COMPOUNDING/FORMULATING

As we said above, various types of modifiers, chemicals, and additives are compounded with the base resin or polymer material before processing. The compounding is usually done by the materials manufacturer; however, this is also performed by a group within the polymer industry. Such companies buy the base resin from the materials manufacturer and then compound it specially for resale to the processor. The processor may also buy the base polymer, modifiers, chemicals, and additives for in-house compounding.

D. THE PROCESSOR

The heart of the polymer industry is the processor, who is responsible for turning polymer materials into secondary products like film, sheet, rod and tube, component parts, or finished end products. Processors may be classified into three general categories depending on the target market for their products:

- Custom processors, who do processing on a custom basis for end users
- Proprietary processors, who manufacture polymer products such as housewares and toys for direct sale to consumers
- Captive processors, who possess in-house production facilities; they are usually manufacturers that consume large volumes of polymer parts

A number of processing techniques are employed in the plastics industry to shape the plastic material into the desired end product. In fact, processors are more often categorized on the basis of the type of processing operations they perform. Polymer processing operations include molding (injection, blow, rotational, compression, and transfer); extrusion; calendering; thermoforming; and casting (Chapter 11).

E. THE FABRICATOR

Some of the products from the processor are not directly usable by the consumer. The fabricator in the polymers industry is engaged in turning secondary products such as film, sheet, rods, and tubes into end products. Using conventional machine tools and simple bending techniques, the fabricator creates products like jewelry, signs, and furniture from rigid polymers. Similarly, products like shower curtains, rainwear, inflatables, upholstery, and packaging overwrap are obtained from flexible film and sheeting by employing various die cutting and sealing methods.

F. THE FINISHER

A number of uses of polymers are not easily recognizable as such because the appearance of polymers is similar to that of conventional materials. Examples of such polymer products include plastic furniture with integral wood grain patterns and plastic automotive grilles that can be electroplated with a metallic surface. Production of such polymer products, including the large-volume printing of plastic film and sheets, is done by the finisher. The finishing of polymers includes the different methods of adding either decorative or functional surface effects to the polymer product. Color and decorative effects can be added to polymers prior to and during manufacturing.

Also, polymer parts, whether film and sheeting or rigid products, can be postfinished in a number of ways. Some companies within the polymers industry specialize in various finishing techniques. On the other hand, finishing, decorating, and assembly of the polymer end product can be done in-house by the processor or fabricator.

III. RAW MATERIALS FOR THE POLYMER INDUSTRY[2,3]

A finished polymer article may be made entirely from the neat or pure resin. More often, however, it is necessary to compound the resin with additives to improve its processing behavior and/or enhance product quality and service performance. In this section we examine, in a global way, the various feedstocks for the polymers industry. The raw materials can be divided essentially into the base polymers and the various additives. Polymer additives and reinforcements have been treated in Chapter 9. Therefore, only base polymers are discussed here.

The first plastic made was cellulose nitrate, which is a derivative of cellulose, obtained from wood pulp. The first truly synthetic polymer material was phenolic resin, which was synthesized from phenol and formaldehyde derived from coal. Today, the source of organic chemicals for the production of polymers has shifted from these traditional sources to petroleum and natural gas. Petroleum as a raw material for organic chemicals (petrochemicals) is relatively cheap, readily available in large tonnages, and more easily processed than the other main source of organic chemicals — coal.

There are two stages involved in the production of petrochemicals from petroleum. The first is the separation of petroleum, which is a mixture of hydrocarbons, into various fractions (mainly liquid fuels) by a process called fractional distillation. The second is the further refinement of certain fractions from the distillation process to form petrochemicals. Most petrochemicals are derived from three sources:

1. Various mixtures of carbon monoxide and hydrogen, known as synthesis gas, obtained from steam reforming of natural gas (methane) or, in a few cases, steam reforming of naphtha.
2. Olefins obtained by steam cracking (pyrolysis) of various feedstocks, including ethane, propane–butane (LPG), distillates (naphtha, gas oil), and even crude oil.
3. Aromatics — benzene, toluene, and xylene (BTX) — obtained from catalytic reforming.

These routes are the sources of the eight building blocks — ammonia, methanol, ethylene, propylene, butadiene, benzene, toluene, and xylene — from which virtually all large tonnage petrochemicals are derived. Figure 15.1 represents a simplified version of the production of these chemicals from petroleum and natural gas. Simplified flow diagrams for the production of some polymers from these basic petrochemicals are shown in Figures 15.2–15.9.

IV. POLYMER PROPERTIES AND APPLICATIONS

The rapid growth and widespread use of polymers are due largely to the versatility of their properties. As we saw in Chapter 3, polymer properties are attributable to their macromolecule nature and the gross configuration of their component chains as well as the nature and magnitude of interactions between the constituent chain atoms or groups. The major uses of polymers as elastomers, fibers, and plastics are a consequence of a combination of properties unique to polymers. For example, the elasticity of elastomers, the strength and toughness of fibers, and the flexibility and clarity of plastic films reflect their different molecular organizations. Throughout the discussion in the previous chapters, we have consistently emphasized the structural basis of the behavior of polymeric materials. We have discussed the variables necessary to define the mechanical, physical, and other properties of polymers. We now focus attention on the properties and applications of polymers. We start the discussion with the large-volume polymers — so-called general-purpose or commodity thermoplastics. The selection of polymers for discussion is based on convenience rather than on a consistent classification scheme.

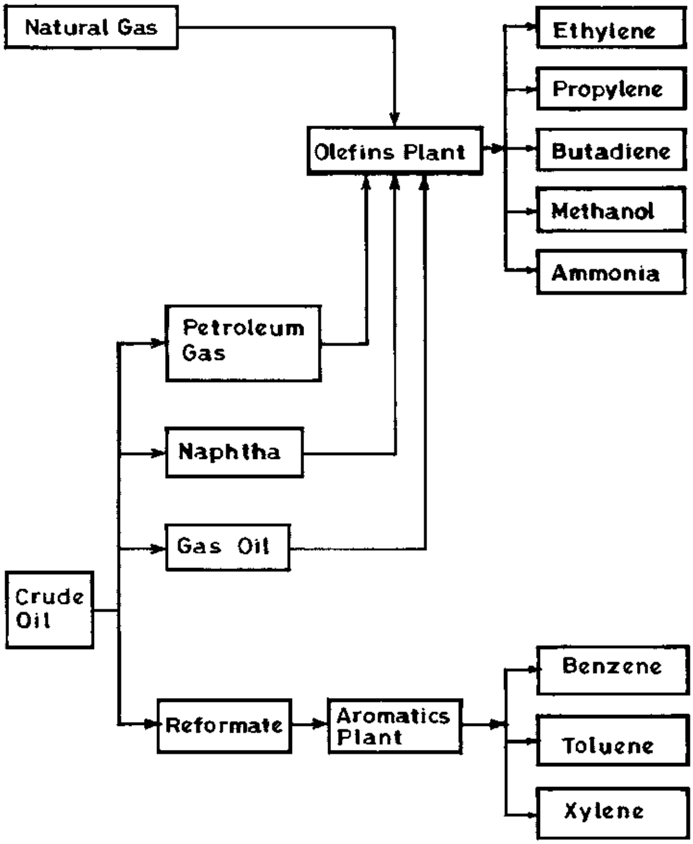


Figure 15.1 *Base petrochemicals from petroleum and gas.*

A. POLYETHYLENE

$$\left[CH_2 - CH_2 \right]_n \qquad \text{(Str. 1)}$$

Ethylene may be polymerized by a number of processes to produce different varieties of polyethylene. The most commercially important of these polymers are low-density polyethylene (LDPE); high-density polyethylene (HDPE); and, more recently, linear low-density polyethylene (LLDPE) and ultra-high-density polyethylene (UHDPE).

The first commercial ethylene polymer (1939) was low-density, low-crystalline (branched) polyethylene (LDPE), which is the largest of the thermoplastics produced in the U.S. LDPE is produced by free-radical bulk polymerization using traces of oxygen or peroxide (benzoyl or diethyl) and sometimes hydroperoxide and azo compounds as the initiator. To obtain a high-molecular-weight product, impurities such as hydrogen and acetylene, which act as chain transfer agents, must be scrupulously removed from the monomer. Polymerization is carried out either in high-pressure, tower-type reactors (autoclaves) or continuous tubular reactors operating at temperatures as high as 250°C and at pressures between 1000 and 3000 atm (15,000 to 45,000 psi). The exothermic heat of polymerization (about 25 kcal/mol) is controlled by conducting the polymerization in stages of 10 to 15% conversion. Solution polymerization of ethylene with benzene and chlorobenzene as solvents is also possible at the temperatures and pressures employed.

Polyethylene with limited branching, that is, linear or high-density polyethylene (HDPE), can be produced by the polymerization of ethylene with supported metal–oxide catalysts or in the presence of

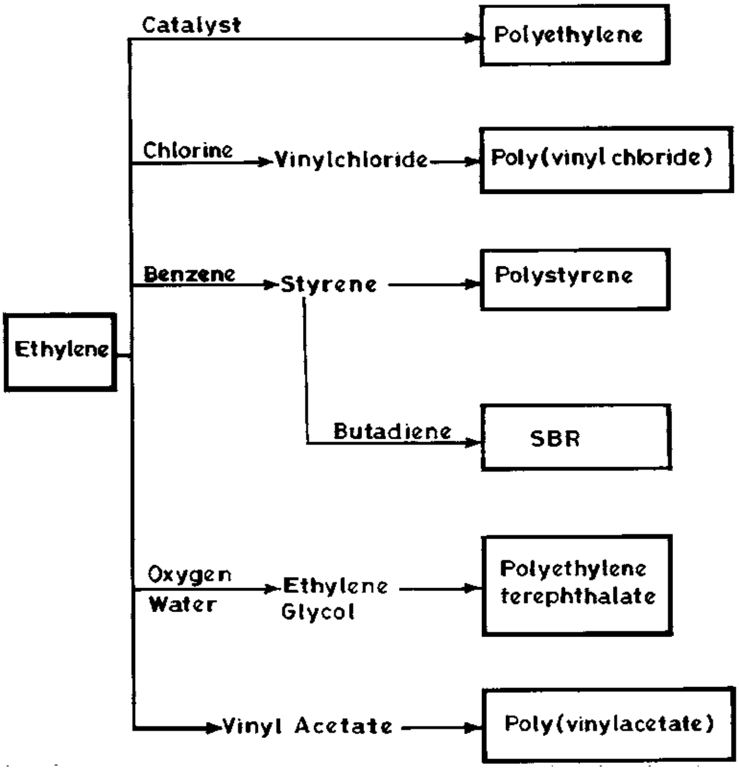


Figure 15.2 *Some polymers from ethylene.*

coordination catalysts. The first class of metal–oxide catalyst (Phillips type) consisted of chromium oxide (CrO_3) supported on alumina (Al_2O_3) or silica–alumina base. Polymerization is carried out at 100 atm and 60 to 200°C in hydrocarbon solvents in which the catalysts are insoluble using either fixed-bed, moving bed, fluidized-bed, or slurry processes. The coordination polymerization of ethylene utilizes Ziegler-type catalysts. These are complexes of aluminum trialkyls and titanium or other transition-metal halides (e.g., $TiCl_4$). Coordination polymerization of ethylene generally requires lower temperatures and pressures than those that involve the use of supported metal–oxide catalysts, typically 60 to 70°C and 1 to 10 atm. Linear, low-to-medium-density polyethylene (LLDPE) with shorter chain branches than LDPE is made also by a low-pressure process (Dow Chemical).

Low-density polyethylene is a partially crystalline solid with a degree of crystallinity in the 50 to 70% range, melting temperature of 100 to 120°C, and specific gravity of about 0.91 to 0.94 (Table 15.1). Free-radical polymerization of ethylene produces branched polymer molecules. Branches act as defects, and as such the level of side chain branching determines the degree of crystallinity, which in turn affects a number of polymer properties. The number of branches in LDPE may be as high as 10 to 20 per 1000 carbon atoms. Branching is of two different types. The first and predominant type of branching, which arises from intermolecular chain transfer, consists of short-chain alkyl groups such as ethyl and butyl. The second type of chain branching is produced by intermolecular chain transfer. This leads to long-chain branches that, on the average, may be as long as the main chain. High-density polyethylene, on the other hand, has few side chains, typically 1 per 200 carbon main chain atoms. Linear polyethylenes are highly crystalline, with a melting point over 127°C — usually about 135°C — and specific gravity in the 0.94 to 0.97 range.

The physical properties of LDPE depend on three structural factors. These are the degree of crystallinity (density), molecular weight (MW), and molecular weight distribution (MWD). The degree of crystallinity and, therefore, density of polyethylene is dictated primarily by the amount of short-chain branching. Properties such as opacity, rigidity (stiffness), tensile strength, tear strength, and chemical

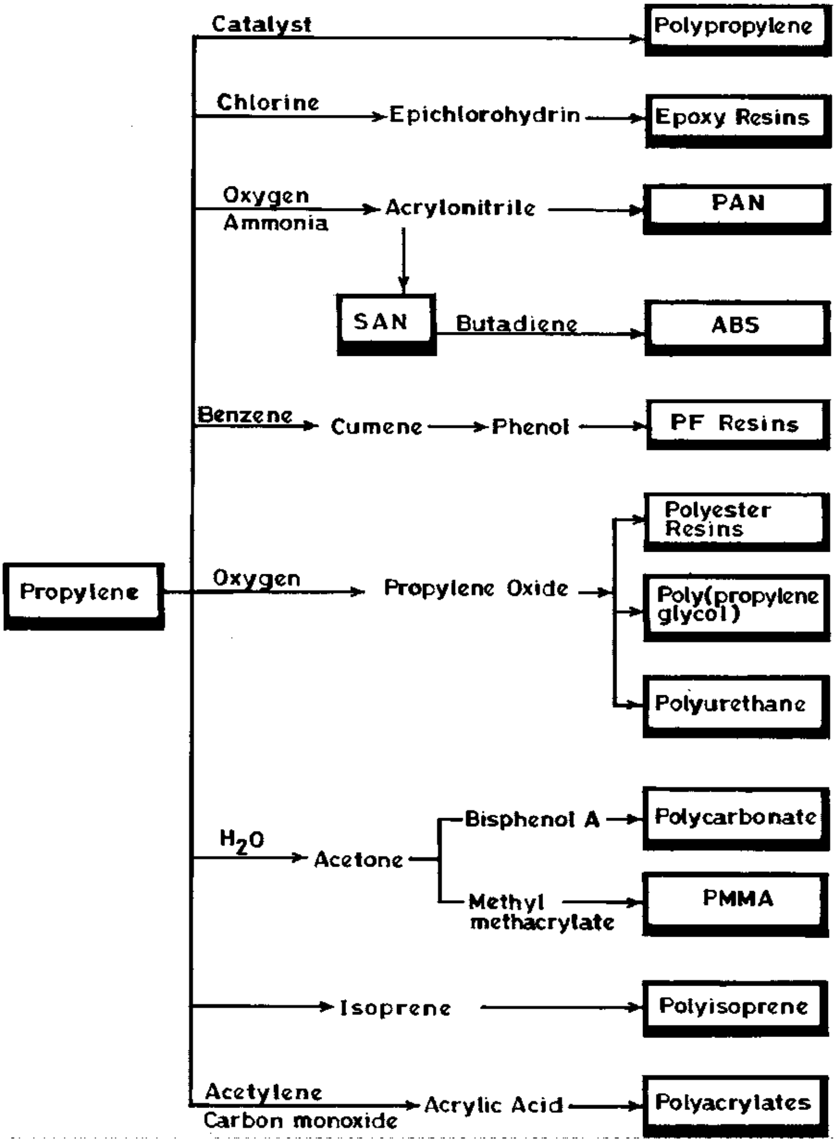


Figure 15.3 *Some polymers from propylene.*

resistance, which depend on crystallinity, increase as density increases (i.e., the amount of short-chain branching decreases). On the other hand, permeability to liquids and gases decreases and toughness decreases with increasing crystallinity.

Copolymerization with polar monomers such as vinyl esters (e.g., vinyl acetate, acrylate esters, carboxylic acids, and vinyl ethers) can be used to adjust crystallinity and modify product properties. Ester comonomers provide short-chain branches that reduce crystallinity. For example, LDPE films with increased toughness, clarity, and gloss have been obtained by the incorporation of less than 7% vinyl acetate. Films made from ethylene and ethyl acrylate (EEA) copolymers have outstanding tensile strength, elongation at break, clarity, stress cracking resistance, and flexibility at low temperatures. As we shall see later, ionomers display extreme toughness and abrasion resistance and improved tensile properties. With HDPE, control of branching is usually achieved by adding comonomers such as propylene, butene, and hexene during polymerization.

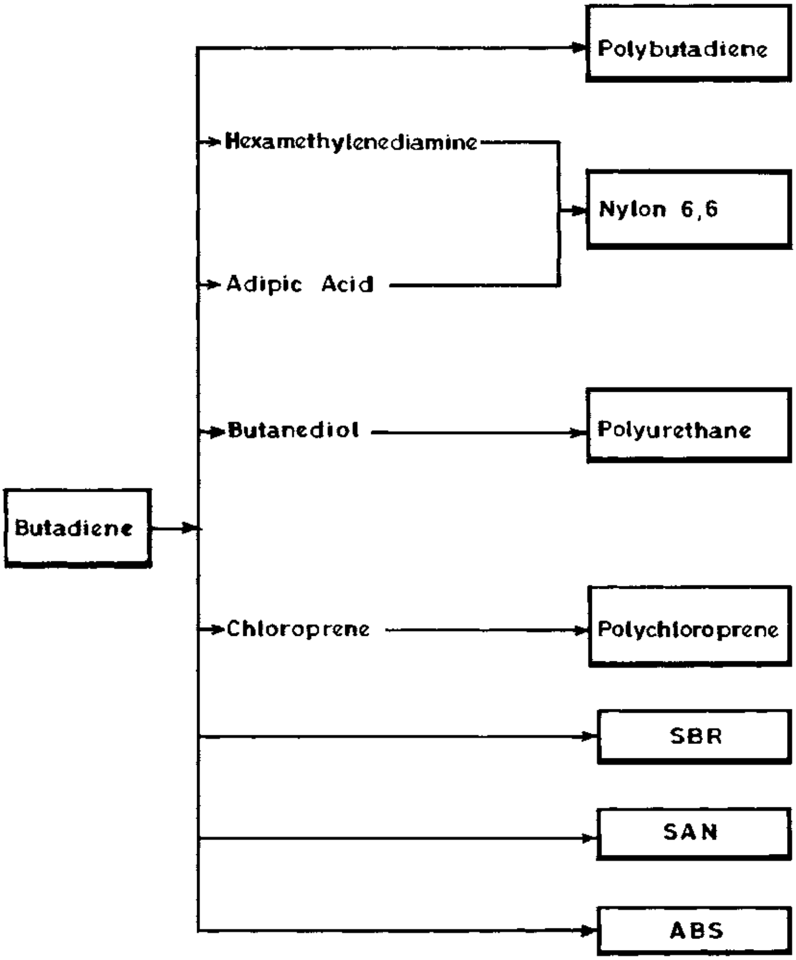


Figure 15.4 *Some polymers from butadiene.*

The molecular weight of LDPE is typically in the range of 6000 to 40,000. Melt index (MI) is used as a convenient measure of average molecular weight. Melt index designates the weight (in grams) of polymer extruded through a standard capillary at 190°C in 10 min (ASTM D 1238). Consequently, melt index is inversely related to molecular weight. Typical melt index values for LDPE are in the range of 0.1 to 109. As molecular weight increases, tensile and tear strength, softening temperatures, and stress cracking and chemical resistance increase, while processibility becomes more difficult and coefficient of friction (film) decreases.

The ratio $\overline{M}_w/\overline{M}_n$ is a measure of molecular weight distribution (MWD). The breadth of MWD is used to evaluate the influence of long-chain branching on the properties of polyethylene. Polyethylene with a narrow MWD has high impact strength, reduced shrinkage and warpage, enhanced toughness and environmental stress cracking resistance, but shows a decrease in the ease of processing.

Polyethylene and its copolymers find applications in major industries such as packaging, housewares, appliances, transportation, communications, electric power, agriculture, and construction. The majority of LDPE is used as thin film for packaging. Other uses include wire and cable insulation, coatings, and injection-molded products (Table 15.2).

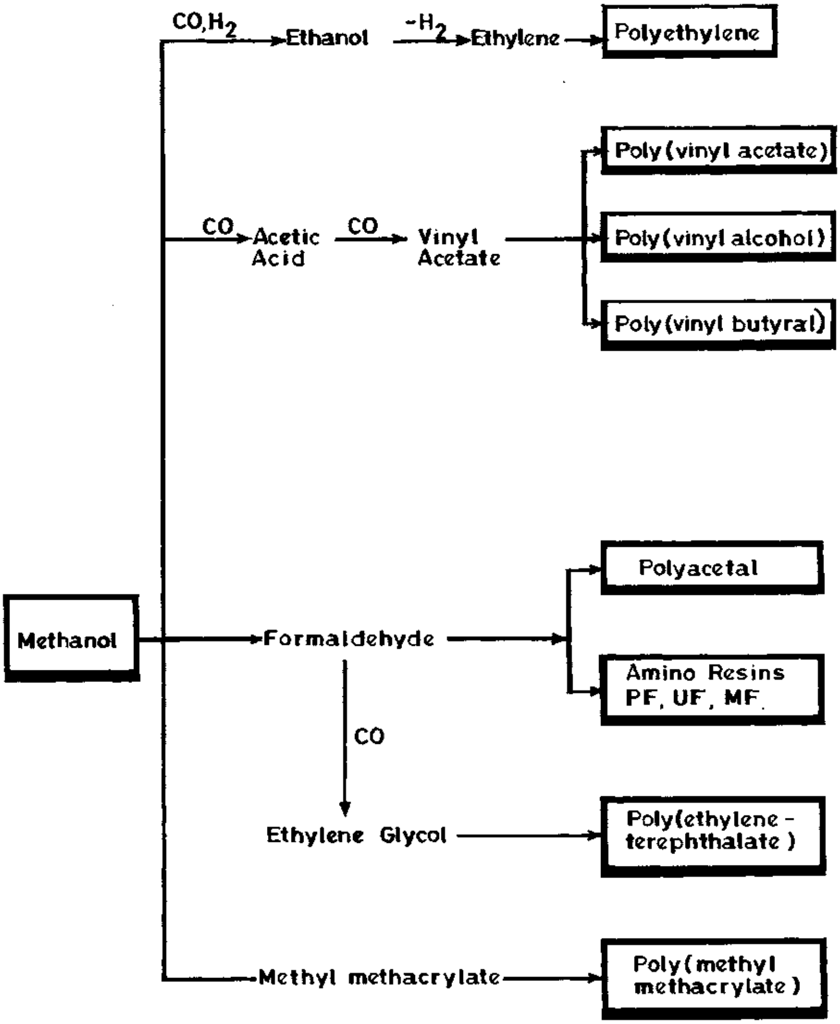


Figure 15.5 *Some polymers from methanol.*

Example 15.1: Explain the following observations.

a. LDPE is used mainly as thin film for packaging and sheets while HDPE is used predominantly in injection molding of crates, pails, tubs, and automobile gas tanks. EVA copolymer containing a high percentage of the ester comonomer is used in film applications such as disposable protective gloves.
b. EVA and EEA copolymers are sometimes preferable to conventional LDPE for wire and cable insulation, particularly for outdoor applications.

Solution:

a. LDPE is used when clarity, flexibility, and toughness are desired. LDPE possesses the desired combination of low density, flexibility, resilience, high tear strength, and moisture and chemical resistance, which are characteristics of a good film material. HDPE is used where hardness, rigidity, high strength, and high chemical resistance are required. EVA copolymers are used in articles requiring extreme flexibility and toughness and rubbery properties.

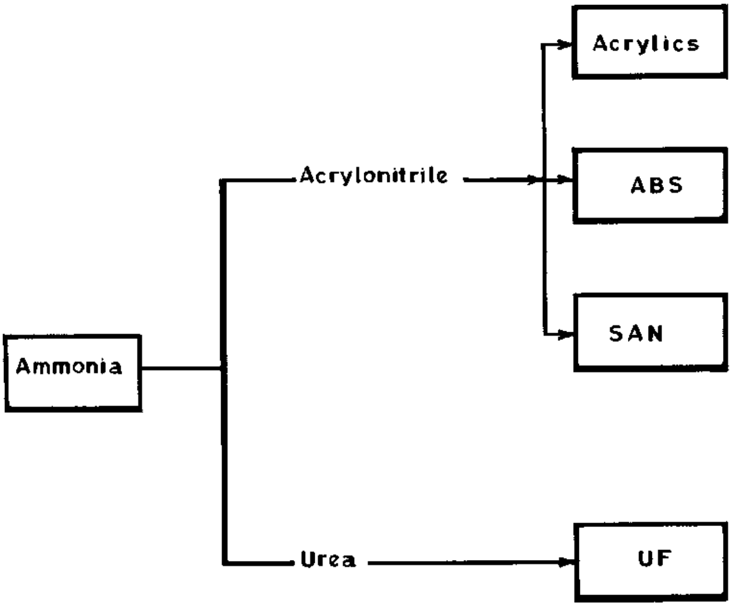
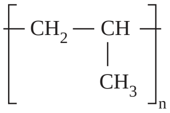


Figure 15.6 *Some polymers from ammonia.*

b. LDPE, on exposure to light and O_2, ages with a consequent loss of strength and a reduction in some other physical properties. It is therefore usual to protect LDPE from the effects of environmental degradation by the addition of carbon black and fillers/stabilizers. Cross-linking of the polyethylene insulating jacket either through chemical or radiation means can also prevent environmental aging. For example, incorporation of relatively stable peroxides provides a chemical means of cross-linking polyethylene. The peroxides, which are stable at normal processing temperatures, decompose and initiate cross-linking in post-processing reactions.

EVA and EEA copolymers as insulating materials show relatively easier acceptance of carbon black and other stabilizers than does conventional LDPE. They are also easier to cross-link presumably because of the greater preponderance of tertiary hydrogens (on the chain at branch points), which are regarded as the probable points of attack during cross-linking. In addition, the low melting points of the copolymers permit a greater ease of incorporation of peroxides by minimizing the risk of premature cross-linking during compounding.

B. POLYPROPYLENE (PP)



$$\left[-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}- \right]_n$$

(Str. 2)

Polypropylene is the third-largest volume polyolefin and one of the major plastics worldwide (Table 15.3). The commercial plastic was first introduced in 1957.

Polypropylene is made by polymerizing high-purity propylene gas recovered from cracked gas streams in olefin plants and oil refineries. The polymerization reaction is a low-pressure process that utilizes Ziegler–Natta catalysts (aluminum alkyls and titanium halides). The catalyst may be slurried in a hydrocarbon mixture to facilitate heat transfer. The reaction is carried out in batch or continuous reactors operating at temperatures between 50 and 80°C and pressure in the range of 5 to 25 atm.

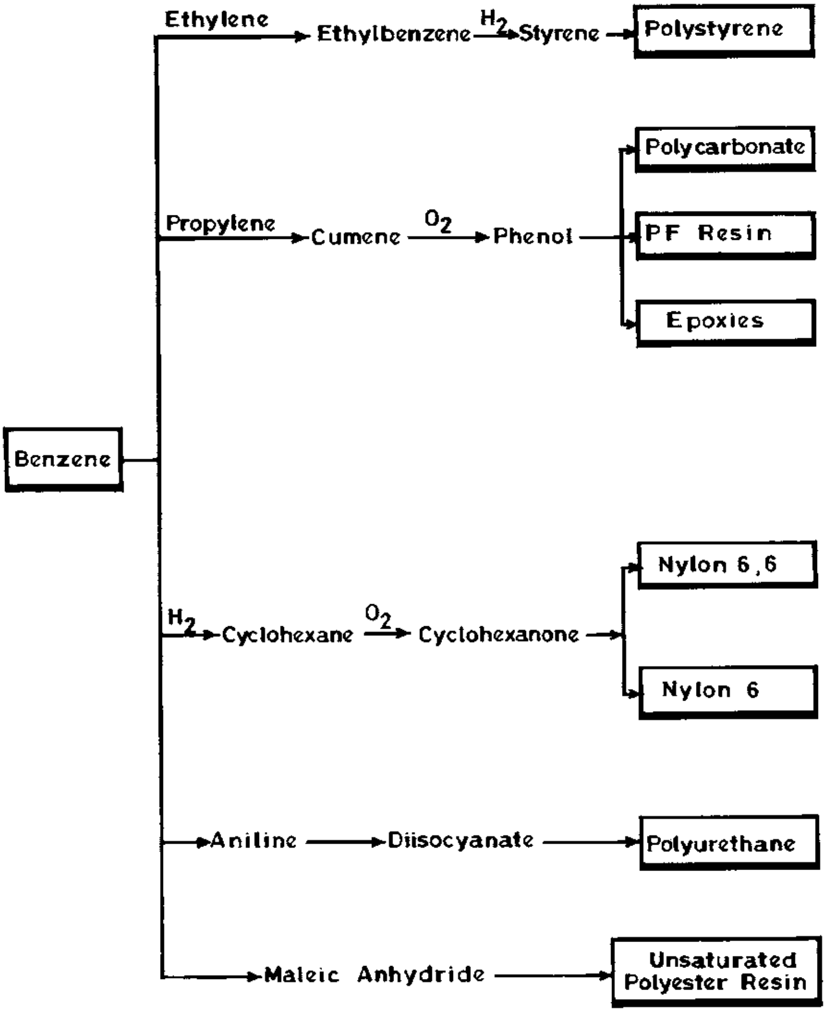


Figure 15.7 *Some polymers from benzene.*

Polypropylene can be made in isotactic (*i*-PP), syndiotactic (*s*-PP), and atactic (*a*-PP) forms. Ziegler–Natta-type catalysts are used to produce stereoregular polypropylene. Usually 90% or more of the polymer is in the isotactic form, which is the form with properties of commercial interest. Isotactic polypropylene is essentially linear, with an ordered arrangement of propylene molecules in the polymer chain. Unlike polyethylene, isotactic polyethylene does not crystallize in a planar zigzag conformation due to steric hindrance from the relatively bulky methyl groups. Instead *i*-PP crystallizes in a helical form with three monomer units per turn of the helix. Isotactic polyethylene is highly crystalline with a melting point of 165 to 171°C (Table 15.1). With a density in the range of 0.90 to 0.91 g/cc, polypropylene is one of the lightest of the widely used commercial thermoplastics.

Polypropylene has excellent electrical and insulating properties, chemical inertness, and moisture resistance typical of nonpolar hydrocarbon polymers. It is resistant to a variety of chemicals at relatively high temperatures and insoluble in practically all organic solvents at room temperature. Absorption of solvents by polypropylene increases with increasing temperature and decreasing polarity. The high crystallinity of polypropylene confers on the polymer high tensile strength, stiffness, and hardness. Polypropylene is practically free from environmental stress cracking. However, it is intrinsically less stable than polyethylene to thermal, light, and oxidative degradation. Consequently, for satisfactory

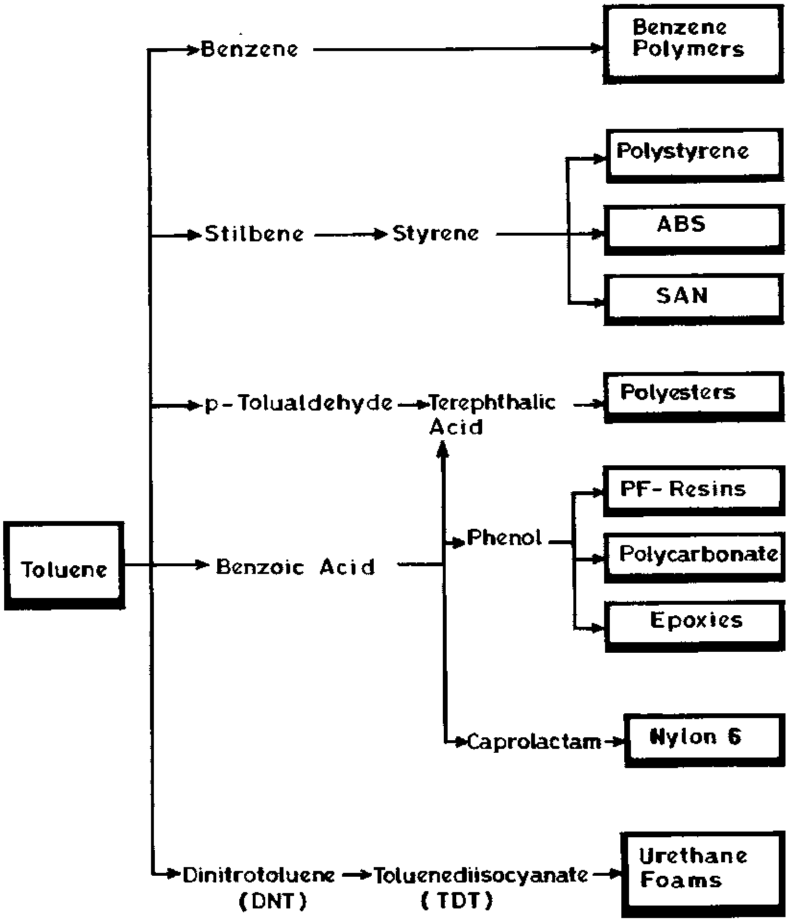
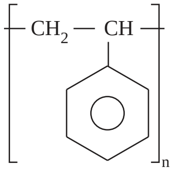


Figure 15.8 *Some polymers from toluene.*

processing and weathering, polypropylene must be stabilized by the incorporation of thermal stabilizers, UV absorbers, and antioxidants.

Polypropylene is used in applications ranging from injection-molded and blow-molded products and fibers and filaments to films and extrusion coatings. Injection molding uses, which account for about half of polypropylene produced, include applications in the automotive and appliance fields. Polypropylene can be designed with an integral hinge fabricated into products ranging from pillboxes to cabinet doors. Extruded polypropylene fibers are used in products such as yarn for carpets, woven and knitted fabrics, and upholstery fabrics. Nonwoven polypropylene fabrics are used in applications such as carpet backing, liners for disposable diapers, disposable hospital fabrics, reusable towels, and furniture dust covers. Polypropylene filaments are employed in rope and cordage applications. Nonwoven polypropylene soft film is suited for overwrap of such products as shirts and hose, while oriented polypropylene film is used as overwrap of such items as cigarettes, snacks, and phonograph records.

C. POLYSTYRENE



(Str. 3)

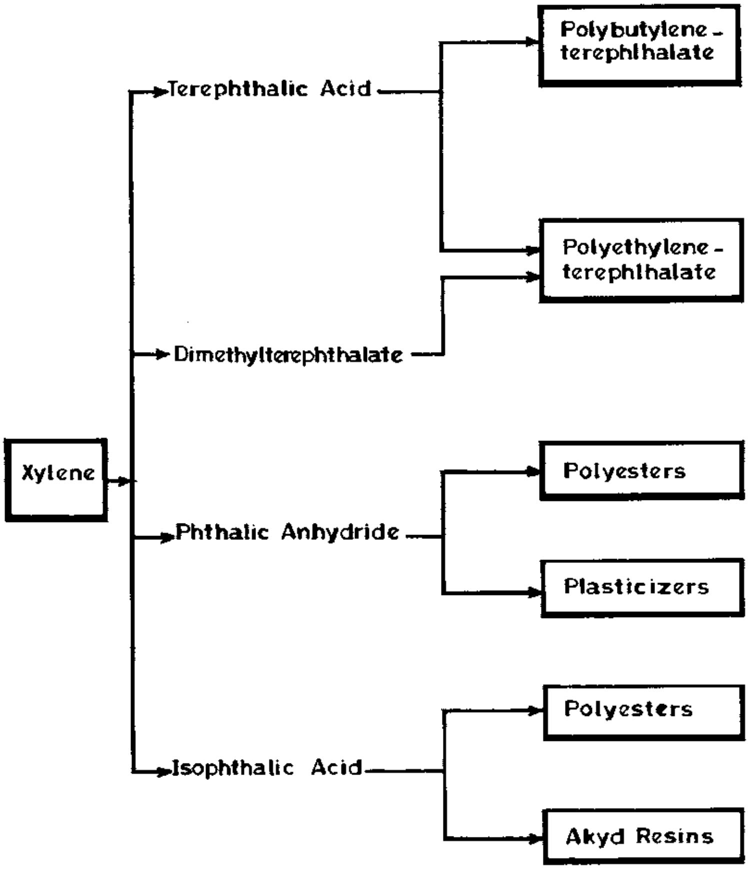


Figure 15.9 *Some polymers from xylene.*

Table 15.1 *Properties of Commodity Polymer*

	Polyethylene		Polystyrene				PVC	
Property	**LDPE**	**HDPE**	**Polypropylene**	**GP-PS**	**HIPS**	**SAN**	**Rigid**	**Flexible**
Specific gravity	0.912–0.94	0.941–0.965	0.902–905	1.04–1.065	1.03–1.06	1.07–1.08	1.30–158	1.16–135
Crystallinity (%)	50–70	80–95	40–68	—	—	—	—	—
Melting temperature (°C)	98–120	127–135	165–174	—	—	—	—	—
Tensile strength (MPa)	15.2–78.6	17.9–33.1	29.3–38.6	36.5–54.5	22.1–33.8	62.0–82.7	41.4–51.7	10.3–24.1
Tensile modulus (MPa)	55.1–172	413–1034	1032–1720	24.3–3378	1792–3240	2758–3861	2413–4136	—
Elongation at break (%)	150–600	20–130	500–900	1–2	13–50	1–4	40–80	200–450
Impact strength (Izod) (ft-lb/in. notch)	716	0.8–14	0.4–6.0	0.25–0.40	0.5–11	0.35–0.50	0.4–20	—
Heat deflection temperature (°C at 66 psi)	38–49	60–88	107–121	75–100	77–93	—	57–82	—

Table 15.2 *Typical Applications of Polyethylene*

Product Type	Typical Applications
Film extrusion	LDPE films used in packaging (bags and wrappings for frozen and perishable foods, produce and textile products); construction cover (moisture barriers and utility covering material); agriculture (greenhouse; ground cover; tank, pond, and canal liners); garment and stripping bags. HDPE film used for floral wrapping, grocery bags, snack and food packaging; EVA film used as produce bags, heavy-duty shipping bags, disposable protective gloves
Extrusion coating	Laminates of foil, paper and used in milk-type cartons (LDPE) for a variety of foods and drinks. Some HDPE used in extrusion coatings over flexible foil packages either as a glue layer between paper on plastics film and aluminum foil or as a heat-seal layer
Wire and cable insulation	LDPE used as insulation of high-frequency electrical cables, insulation materials for television, radar, and multicircuit long-distance telephones
Blow molding	Squeeze bottles, toys, housewares, lids, containers made from LDPE. Blow-molded HDPE used as containers for bleaches, liquid detergents, milk and other beverages, automobile and truck gas tanks, crates and pails
Injection molding	Packaging containers, pails and lids, houseware dishpans, and waste baskets, molded furniture seats, medical labware. HDPE is used in molded structural foam pallets, and crates, underground conduits and housings

Table 15.3 *Typical Applications of Polypropylene*

Product Type	Typical Applications
Injection molded	Automotive and appliance fields: distributor caps, radiator fans, accelerator pedals, battery casings, pillboxes, cabinet doors, bottle crates, jerry cans, cups, plates, file jackets, toys, food and drug containers
Extruded	Yarn for carpets, woven sacks and upholstery fabrics, hoses, drinking straws, hypodermic syringes, reusable towels, overwrap for cigarettes and phonograph records, liners for disposable diapers, furniture dust covers, geotextiles for road stabilization and erosion control

Polystyrene is one of the largest volume thermoplastics. It is a versatile polymer whose principal characteristics include transparency, ease of coloring and processing, and low cost. It is usually available in general-purpose or crystal (GP-PS), high impact (HIPS), and expanded grades. Some members of this family of styrene polymers are copolymers of styrene with other vinyl monomers.

Commercial atactic polystyrene is made by free-radical bulk or suspension polymerization of styrene with peroxide initiators. The reaction exotherm in bulk or mass polymerization of styrene is controlled by using a two-stage polymerization process. In the first stage, inhibitor-free styrene is subjected to low conversion in a stirred tank reactor (prepolymerizer). This is then followed by high conversion in a cylindrical tower (about 40 ft long by 15 ft diameter) with increasing temperature gradient (Chapter 9). The pure molten polymer that emerges from the reactor goes through spinnerets or an extruder to provide the desired finished product.

Polystyrene is a linear polymer that, in principle, can be produced in isotactic, syndiotactic, and atactic forms. The commercial product or general-purpose polystyrene is atactic and as such amorphous: isotactic polystyrene is more brittle and more difficult to process than atactic polystyrene. It is therefore not of commercial interest.

GP-PS is a clear, rigid polymer that is relatively chemically inert. Polystyrene, as produced, has outstanding flow characteristics and consequently is very easy to process. Its excellent optical properties, including high refractive index, make it useful in optical applications. However, GP-PS has a number of limitations, including its brittleness, low heat-deflection temperature (Table 15.1), poor UV resistance, and susceptibility to attack by a variety of solvents. Polystyrene is sensitive to foodstuffs with high fat or oil content; it crazes and turns yellow during outdoor exposure.

Many of the problems associated with GP-PS can be alleviated, or at least minimized, through copolymerization, blending, or proper formulation. For example, polystyrene with enhanced impact resistance and toughness is produced by the incorporation of butadiene rubber. High-impact polystyrene

Table 15.4 *Some Applications of Different Grades of Polystyrene*

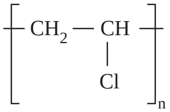
Processing Method	Typical Products
Extrusion	Containers, tubs and trays for food packaging, mirror and picture frames, refrigerator breaker strips, room dividers, shower doors, glazings, lighting
Thermoforming	Refrigerator door liners, signs, horticultural trays, luggage; furniture panels, glove compartment boxes; meat, poultry, and egg containers; fast-food containers, blister packs, container lids; cookie, candy, pastry and other food packages
Injection molding	Packaging and nonpackaging disposables; air conditioner grilles; refrigerator and freezer components; small appliance housings
Others	Consumer electronics such as cassettes, reels, radio, television; and stereo dust covers; business machine housings, smoke detectors, display racks, toys, disposable tumblers, cutlery, bottles, combs, brush blocks

(HIPS) is produced commercially by the emulsion polymerization of styrene monomer containing dispersed particles of polybutadiene or styrene–butadiene (SBR) latex. The resulting product consists of a glassy polystyrene matrix in which small domains of polybutadiene are dispersed. The impact strength of HIPS depends on the size, concentration, and distribution of the polybutadiene particles. It is influenced by the stereochemistry of polybutadiene, with low vinyl contents and 36% *cis*-1,4-polybutadiene providing optimal properties. Copolymers of styrene and maleic anhydride exhibit improved heat distortion temperature, while its copolymer with acrylonitrile, SAN — typically 76% styrene, 24% acrylonitrile — shows enhanced strength and chemical resistance. The improvement in the properties of polystyrene in the form of acrylonitrile–butadiene–styrene terpolymer (ABS) is discussed in Section VII.A.

The expandable grade of styrene homopolymer is used to make foamed products that are beads generally foamed in place during application. Expandable polystyrene beads may be prepared by the suspension polymerization of styrene monomer in the presence of a volatile organic blowing or foaming agent. The foaming agent, such as pentane or hexane, is normally a liquid under polymerization conditions, but volatilizes during subsequent heating to soften the polymer thus forming a foamed product. Requirements for various types of products are satisfied by varying bead size, foaming agent level and composition, polymer molecular weight, and molecular weight distribution. The larger beads, which generally have the lowest density, find uses in thermal insulation, ceiling tiles, and loose-fill applications. On the other hand, the smaller beads, which provide better mechanical properties and surface finish, are employed in custom packaging, insulated drinking cups, and structural and semistructural applications.

The applications for all grades of polystyrene include packaging, housewares, toys and recreational products, electronics, appliances, furniture, and building and construction insulation (Table 15.4).

D. POLY(VINYL CHLORIDE) (PVC)



$$\left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}- \right]_n$$

(Str. 4)

Poly(vinyl chloride) is one of the largest volume thermoplastics in the world. It is chemically inert and versatile, ranging from soft to rigid products that are available at economic costs. PVC is available in essentially two grades — rigid and flexible.

Commercial grade PVC is produced primarily by free-radical-initiated suspension and emulsion polymerization of vinyl chloride. Suspension polymerization accounts for over 80% of PVC produced. Solution and bulk polymerization are also employed to some extent. However, there are difficulties with bulk polymerization because PVC is insoluble in its monomer and therefore precipitates. In suspension polymerization, vinyl chloride droplets are suspended in water by means of protective colloids such as poly(vinyl alcohol), gelatin, or methyl cellulose in pressure vessels equipped with agitators and heat

Table 15.5 *Typical Applications of Poly(vinyl chloride)*

Area	Typical Application
Piping systems	Pressure pipes — water supply and distribution, agricultural irrigation, chemical processing; nonpressure pipes — drain, waste and vent pipes, sewer systems, conduits for electrical and telephone cables
Building construction	Siding, window frames, gutters, interior molding and trim, flooring, wire and cable insulation, wall coverings, upholstery, shower curtains, refrigerator gaskets
Transportation	Upholstery, floor mats, auto tops, automotive wire, interior and exterior trim
Consumer products	Footwear, outerwear, phonograph records, sporting goods, toys

removal systems. Polymerization is conducted at temperatures of 40 to 70°C, typically around 60°C. Higher temperatures can result in minor branching and excessive formation of HCl through dehydrochlorination. Lower temperatures produce a high content of syndiotactic polymers. At a predetermined end point, unreacted vinyl chloride monomer is stripped from the slurry under vacuum. As a result of environmental and health concerns, stringent control of the escape of vinyl chloride monomer into the atmosphere is becoming an important issue.

Poly(vinyl chloride) is partially syndiotactic; it has a low degree of crystallinity due to the presence of structural irregularities. PVC is relatively unstable to heat and light. Unstabilized PVC undergoes dehydrochlorination when heated above its T_g (about 87°C) — for example, during melt processing. This leads to the production of hydrochloric acid, formation of intense color, and deterioration of polymer properties. Consequently, in practice, a number of ingredients must be added to PVC to enhance thermal stability and hence improve processing and product performance. Heat stabilizers are the most important additive. These are generally organometallic salts of tin, lead, barium–cadmium, calcium, and zinc. Other additives include lubricants, plasticizers, impact modifiers, fillers, and pigments.

The properties of PVC can be modified through chemical modification, copolymerization, and blending. PVC homopolymer contains about 57% chlorine. Chlorinated PVC with the chlorine content increased to 67% has a higher heat deflection temperature than the homopolymer. This extends the temperature range over which products can be used, allowing use in residential hot water pipes, for example. Over 90% of PVC produced is in the form of a homopolymer with the rest as copolymers and, to a small extent, terpolymers. Flexible film products are obtained by copolymerizing vinyl chloride with flexible chain monomers such as vinyl acetate and vinylidene chloride. Advantages of copolymers with small amounts of vinyl acetate over the homopolymer include lower softening point and higher solubility and, hence, improved processability, enhanced stability, and better color and clarity. The most commercially important copolymers contain about 13% vinyl acetate and are used for phonograph records and vinyl floor tiles. Copolymers with vinylidene chloride have better tensile properties than the homopolymer. They are used in coating applications because of their improved solubility. Copolymers of vinyl chloride and diethyl fumarate or diethyl maleate (10 to 20% content), while retaining the high softening temperature of poly(vinyl chloride) homopolymer, have enhanced workability and toughness. The toughness of PVC can also be improved by blending with high-impact resins like ABS.

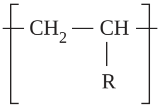
As indicated earlier, PVC is available as rigid or flexible resins. Flexible PVC is obtained by incorporating internal or external plasticizers into PVC. Rigid PVC accounts for about 55% of PVC used while plasticized or flexible PVC accounts for the remainder. The largest single use of PVC is for piping systems. The major areas of use and typical applications of PVC are listed in Table 15.5.

Example 15.2: PVC has an advantage over other thermoplastic polyolefins in applications such as insulation for electrical circuitry in household electronic appliances. Explain.

Solution: Though polar, PVC-like nonpolar thermoplastics can be used as insulation for electrical wires in low-frequency applications. Prolonged use of household electronic appliances has a tendency to generate heat. Therefore, these appliances can be a potential source of fire hazard. Unlike other thermoplastic polyolefins, PVC has inherent (built-in) fire retardancy because of its 57% chlorine content. This reduces the susceptibility to fire outbreak arising from prolonged use of household electronic appliances.

V. OTHER VINYL POLYMERS

As discussed in Chapter 1, olefin polymers are represented by the generalized formula

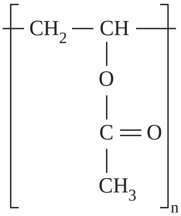


$$\left[\!-\mathrm{CH_2}-\underset{\displaystyle\mathrm{R}}{\underset{|}{\mathrm{CH}}}-\!\right]$$

(Str. 5)

where R may be hydrogen alkyl or aryl, etc. In addition to poly(vinyl chloride) or other halogen-containing polymers, other vinyl polymers are essentially polyolefins in which the R substituents are bonded to the olefin monomers through an oxygen atom [poly(vinyl esters), poly(vinyl ethers)] or a nitrogen atom [poly(vinyl amides)]. In this discussion we focus attention on the commercially important poly(vinyl esters).

A. POLY(VINYL ACETATE) (PVAC)



$$\left[\!-\mathrm{CH_2}-\underset{\underset{\underset{\displaystyle\mathrm{CH_3}}{|}}{\underset{\displaystyle\mathrm{C{=}O}}{\underset{|}{\underset{\displaystyle\mathrm{O}}{|}}}}}{\mathrm{CH}}-\!\right]_n$$

(Str. 6)

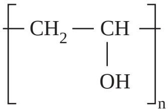
Poly(vinyl acetate) is the most widely used vinyl ester polymer. It is also the precursor or starting material for the production of two other polymers that cannot be prepared by direct polymerization because the starting monomer is unstable. These are poly(vinyl alcohol) and poly(vinyl acetal). The most important of the latter are poly(vinyl butyral) and poly(vinyl formal).

As a result of its highly exothermic nature, bulk polymerization of vinyl acetate poses problems at high conversions. The properties of the resulting polymer are susceptible to deterioration due to chain branching. Therefore, bulk polymerization of vinyl acetate is usually stopped at 20 to 50% conversion. Thereafter, the unreacted monomer is either distilled off or the polymer precipitated with a suitable solvent (methanol, ethanol). Poly(vinyl acetate) is manufactured primarily by free-radical-initiated emulsion and, sometimes, solution polymerization.

Only atactic or amorphous poly(vinyl acetate) is currently commercially available. It has a glass transition temperature, T_g, of 29°C. Consequently, the polymer becomes sticky at temperatures slightly above ambient. The low-molecular polymers, which are normally brittle, become gumlike when masticated (used in chewing gums). Its adhesive strength is dictated by its water sensitivity.

Poly(vinyl acetate) latex is used in the production of water-based emulsion paints, adhesives, and textile and paper treatments. Emulsion paints are stable, dry quickly, and are relatively low cost. PVAC emulsion adhesives are used in labeling and packaging, and as the popular consumer white glue. Copolymers with dibutyl fumarate, vinyl stearate, 2-ethylhexyl acrylate, or ethyl acrylate are used to obtain compositions that are softer for emulsion use. As indicated above, a major use of poly(vinyl acetate) is in the production of poly(vinyl alcohol), which is itself the starting material for poly(vinyl butyral) and poly(vinyl formal).

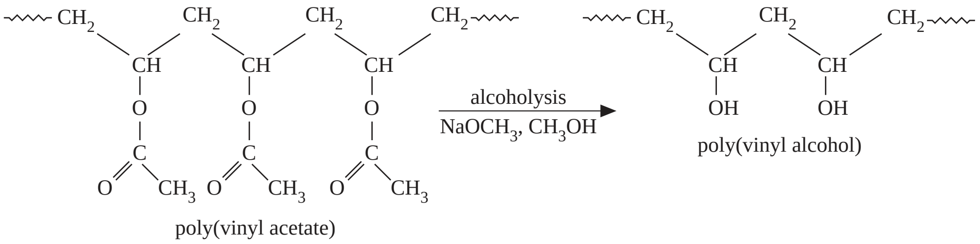
B. POLY(VINYL ALCOHOL) (PVAL)



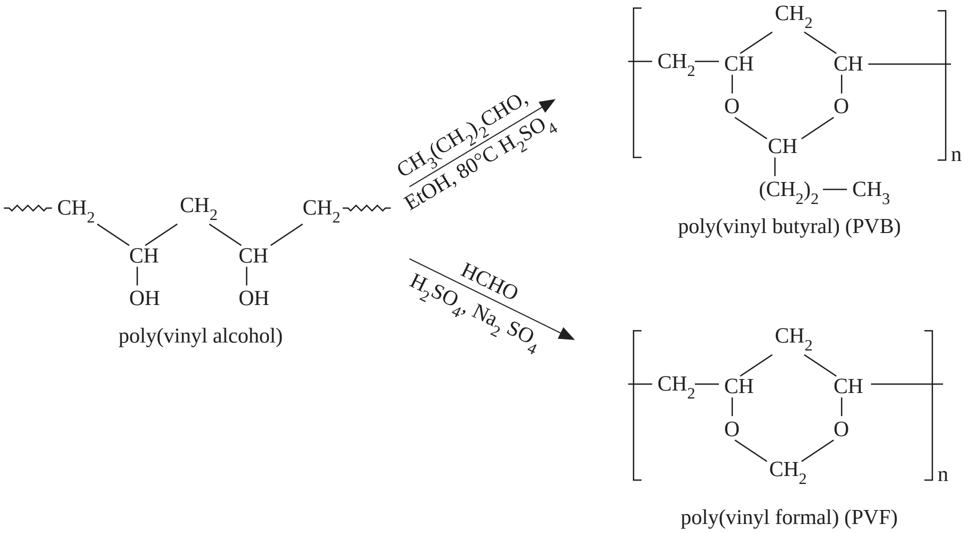
$$\left[\!-\mathrm{CH_2}-\underset{\displaystyle\mathrm{OH}}{\underset{|}{\mathrm{CH}}}-\!\right]_n$$

(Str. 7)

Vinyl alcohol is unstable; it is isomeric with acetaldehyde. Therefore, poly(vinyl alcohol) is obtained indirectly by the alcoholysis of poly(vinyl acetate) in concentrated methanol or ethanol. The reaction is carried out in the presence of acid or base catalyst; base catalysis is usually faster:



(Str. 8)



(Str. 9)

Poly(vinyl alcohol) has an atactic chain structure, and it is consequently amorphous. However, it can be stretched into a crystalline fiber. The small size of the OH groups permits them to fit into a crystal lattice. Poly(vinyl alcohol) is available in various grades defined by the molecular weight and by the degree of hydrolysis, which determines polymer water solubility.

The end uses of PVAL include textile and paper treatment and wet-strength adhesives. It is also used as a polymerization aid such as a thickening and stabilizing agent in emulsion polymerization in cosmetics and as packaging film requiring water solubility. With their much higher water absorption capacity and cottonlike feel, formaldehyde-modified poly(vinyl alcohol) fibers, vinal or vinylon fibers, can replace cotton in applications requiring body contact. These PVAL fibers have good dimensional stability and abrasion resistance, wash easily, and dry quickly.

Poly(vinyl alcohol) is also used in the manufacture of poly(vinyl butyral) (PVB) and poly (vinyl formal) (PVF). By far the largest single application of PVB is as an adhesive or plastic interlayer in the manufacture of laminated safety glass for automotive and aircraft uses. Compared with earlier cellulose acetate-based laminates, safety glass made from PVB has superior adhesion to glass; it is tough, stable on exposure to sunlight, clear, and insensitive to moisture. Poly(vinyl formal) is utilized in the manufacture of enamels for heat-resistant electrical wire insulation and in self-sealing gasoline tanks.

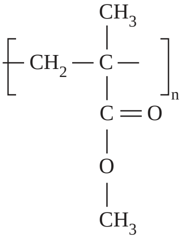
Example 15.3: Poly(vinyl butyral) is made by adding butyraldehyde and an acid catalyst, usually sulfuric acid, to an aqueous solution of poly(vinyl alcohol). For the poly(vinyl butyral) required for safety glass manufacture, the reaction is stopped at about 75% conversion of the hydroxyl groups. Explain.

Solution: For adequate performance of safety glass in end-use situations, a good bond between the components of the laminate is imperative. The residual or unreacted hydroxyl groups provide the required strength and adhesion to glass.

VI. ACRYLICS

Acrylics comprise a broad array of plastics derived from olefin monomers of the type CH_2› CHR in which the R substituent is a cyamide, carboxylic acid, carboxylic acid ester, or carboxylic acid amide group. Two ester families, acrylates and methacrylates, constitute the major component of acrylic polymers. Used singly or as copolymers with monomers containing reactive functional groups, these monomers provide an array of products ranging from soft, flexible elastomers to hard, stiff plastics and thermosets, and from highly polar to oleophic resins. Acrylics generally exhibit crystal clarity and excellent chemical and environmental resistance.

A. POLY(METHYL METHACRYLATE) (PMMA)



$$\left[-\mathrm{CH_2}-\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{C(=O)-O-CH_3}}{\mathrm{C}}}- \right]_n$$

(Str. 10)

The most important member of the acrylic polymers is poly(methyl methacrylate). It is a hard, clear, colorless, transparent plastic that is usually available as molding and extrusion pellets, reactive syrups, cast sheets, rods, and tubes.

Poly(methyl methacrylate) for molding or extrusion is produced commercially by free-radical-initiated suspension or bulk polymerization of methyl methacrylate. To minimize polymerization reaction exotherm and shrinkage, bulk polymerization, which is used in the production of sheets, rods and tubes, is carried out with a reactive syrup of partially polymerized methyl methacrylate, which has a viscosity convenient for handling.

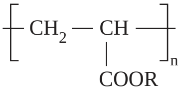
Poly(methyl methacrylate) is an amorphous polymer composed of linear chains. The bulky nature of the pendant group (–O–CO–Me), and the absence of complete stereoregularity makes PMMA an amorphous polymer. Isotactic and syndiotactic PMMA may be produced by anionic polymerization of methyl methacrylate at low temperatures. However, these forms of PMMA are not available commercially. Modified PMMA can be obtained by copolymerizing methyl methacrylate with monomers such as acrylates, acrylonitrile, and butadiene.

Poly(methyl methacrylate) is characterized by crystal-clear light transparency, unexcelled weatherability, and good chemical resistance and electrical and thermal properties. It has a useful combination of stiffness, density, and moderate toughness. PMMA has a moderate T_g of 105°C, a heat deflection temperature in the range of 74 to 100°C, and a service temperature of about 93°C. However, on pyrolysis, it is almost completely depolymerized to its monomer. The outstanding optical properties of PMMA combined with its excellent environmental resistance recommend it for applications requiring light transmission and outdoor exposure. Poly(methyl methacrylate) is used for specialized applications such as hard contact lenses. The hydroxyethyl ester of methacrylic acid is the monomer of choice for the manufacture of soft contact lenses. Typical applications of poly(methyl methacrylate are shown in Table 15.6.

Table 15.6 *Typical Applications of Poly(methyl methacrylate)*

Area	Typical Applications
Construction	Enclosures for swimming pools, shopping malls and restaurants, tinted sunscreens to reduce air-conditioning and glare, domed skylights
Lighting	Lighted signs, luminous ceilings, diffusers, lenses and shields
Automotive	Lenses, instrument panels, signals and nameplates
Aviation	Windows, instrument panels, lighting fixture covers, radar plotting boards, canopies
Household	Housings, room dividers, decorating of appliances, furniture, vanities, tubs, counters
Others	Display cabinets and transparent demonstration models in museums, exhibits, and departments stores

B. POLYACRYLATES



$$\left[CH_2 - \underset{COOR}{\underset{|}{CH}} \right]_n$$

(Str. 11)

Polyacrylates are produced commercially by free-radical-initiated solution and emulsion polymerization of the appropriate monomer. Unlike for methacrylates, suspension and casting procedures are not feasible because of the rubber and adhesive nature of higher acrylates.

As shown in Table 15.7, the glass transition temperatures of acrylate polymers are generally below room temperature. This means that these polymers are usually soft and rubbery.

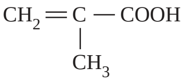
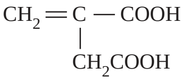
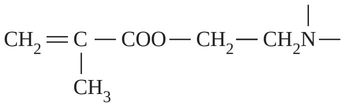
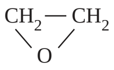
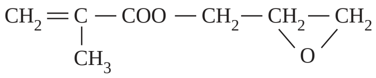
Solubility in oils and hydrocarbons increases with increasing length of the side group, while polymers become harder, tougher, and more rigid as the size of the ester group decreases. Polyacrylates have been used in finishes and textile sizing and in the production of pressure-sensitive adhesives. Poly(methyl acrylate) is used in fiber modification, poly(ethyl acrylate) in fiber modification and in coatings, and poly(butyl acrylate) and poly(2-ethylhexyl acrylate) are used in paints and adhesive formulation.

Table 15.7 *Glass Transition Temperatures of Sample Polyacrylates*

R	T_g (°C)
Methyl	3
Ethyl	–20
n-Propyl	–44
n-Butyl	–56

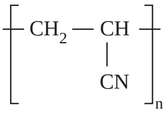
Quite frequently, copolymerization is used to optimize the properties of polyacrylates. For example, copolymers of ethyl acrylate with methyl acrylate provide the required hardness and strength, while small amounts of comonomers with hydroxyl, carboxyl, amine, and amide functionalities are used to produce high-quality latex paints for wood, wallboard, and masonry in homes. These functionalities provide the adhesion and thermosetting capabilities required in these applications. Monomers with the desired functional groups most often used in copolymerization with acrylates are shown in Table 15.8.

Table 15.8 *Functional Comonomers Used with Acrylates*

Monomer	Functional Group	Structure
Acrylic acid	$-COOH$	$CH_2{=}CH-COOH$
Methacrylic acid		 $CH_2{=}\underset{CH_3}{\underset{\vert}{C}}-COOH$
Itaconic acid		 $CH_2{=}\underset{CH_2COOH}{\underset{\vert}{C}}-COOH$
Dimethylaminoethyl methacrylate	$-NH_2$	 $CH_2{=}\underset{CH_3}{\underset{\vert}{C}}-COO-CH_2-CH_2\overset{\vert}{N}-$
2-Hydroxyethyl acrylate	$-OH$	$CH_2{=}CH-COO-CH_2-CH_2-OH$
N-Hydroxyethyl acrylamide		$CH_2{=}CHCONH-CH_2-CH_2-OH$
Glycidyl methacrylate		

From Ulrich, H., *Introduction to Industrial Polymers,* Oxford Press, Oxford, 1982. .

C. POLYACRYLONITRILE (PAN) — ACRYLIC FIBERS



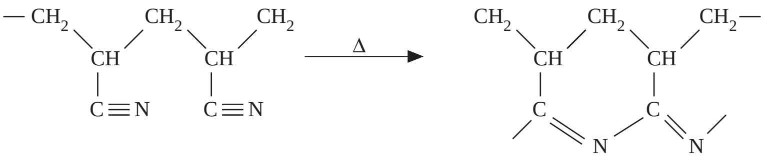
$$\left[CH_2 - \underset{\displaystyle CN}{\underset{|}{CH}} \right]_n$$

(Str. 12)

Polyacrylonitrile, like PVC, is insoluble in its own monomer. Consequently, the polymer precipitates from the system during bulk polymerization. Acrylonitrile can be polymerized in solution in water or dimethyl formamide (DMF) with ammonium persulfate as the initiator (redox initiation). The polyacrylonitrile homopolymer can be dry spun from DMF directly from the polymerization reactor or wet spun from DMF into water.

Acrylic fibers are polymers with greater than 85% acrylonitrile content, while those containing 35 to 85% acrylonitrile are known as modacrylic. Acrylic fibers contain minor amounts of other comonomers, usually methyl acrylate, but also methyl methacrylate and vinyl acetate. These comonomers along with ionic monomers such as sodium styrene sulfonate are incorporated to enhance dyeability with conventional textile dyes. Modacrylics usually contain 20% or more vinyl chloride (or vinylidene chloride) to improve fire retardancy.

Polyacrylonitrile softens only slightly below its decomposition temperature. It cannot, therefore, be used alone for thermoplastic applications. In addition, it undergoes cyclization at processing temperatures.



(Str. 13)

The resulting polymer, on further heat treatment at elevated temperatures, is a source of graphite filaments. However, acrylonitrile copolymerized with other monomers finds extensive use in thermoplastic and elastomeric applications. Examples of such copolymers include styrene–acrylonitrile (SAN), acrylonitrile–butadiene–styrene terpolymer (ABS) and nitrile–butadiene rubber (NBR).

The presence of the highly polar nitrile group (–C;N) in acrylic fibers results in strong intermolecular hydrogen bonding. This generates stiff, rodlike structures with high fiber strength from which acrylic fibers derive their properties. Acrylic fibers are used primarily in apparel and home furnishings. They are more durable than cotton and are suitable alternatives for wool. Typical applications of acrylic fibers include craft yarns, simulated fur, shirts, blouses, blankets, draperies, and carpets and rugs.

VII. ENGINEERING POLYMERS

Engineering plastics are high-performance polymers used in engineering applications because of their outstanding balance of properties. They generally attract a premium price due to their relatively low production volume and are replacing traditional materials in many engineering applications. For example, engineering plastics may be used as replacements for metals in automotive and home appliance applications where a high strength-to-weight ratio is an important requirement. As engineering polymers continue to replace traditional materials in many applications, they are being developed with more specialized properties so as to be distinctly superior to the displaced material in all significant respects.

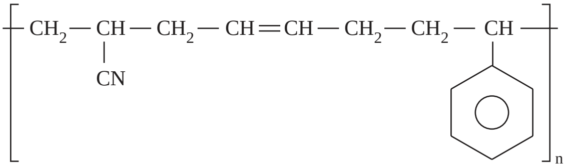
Engineering polymers are strong, stiff, tough materials with high thermal stability, excellent chemical resistance, and good weatherability. They have relatively high tensile, flexural, and impact strengths and are capable of withstanding a wide range of temperatures. Engineering plastics derive their outstanding properties mainly from their inherently strong intermolecular forces. The superior properties of engineering polymers can be enhanced by the addition of various types of reinforcements, by blending and alloy formation, and through chemical modification such as cross-linking. Typical properties of some engineering polymers are shown in Table 15.9.

Table 15.9 *Typical Properties of Some Engineering Polymers*

Property	ABS[a]	Acetal	Nylon 6	Nylon 6,6	PC	PPO	PSF	PPS	Polyamide
Specific gravity	1.01–1.04	1.42	1.12–1.14	1.13–1.15	1.2	1.06	1.24	1.3	1.36–1.43
Tensile strength (MPa)	33.1–43.4	65.5–82.7	68.9	75.8	65.5	66.2	70.3	65.5	72.4–117.9
Tensile modulus (MPa)	1586–2275	3585	689	—	2378	2447	2482	3309	2068
Flexural strength (MPa)	55.2–75.8	96.5	34.5	42.1	93.1	93.1	106.2	96.5	131–199
Flexural modulus (MPa)	1724–2413	2620–2964	965	1275	2344	2482–2758	2689	3792	3102–3447
Impact strength, Izod (ft-lb/in notch)	3.0–12	1.3–2.3	3.9	2.1	16	1.8–5.0	1.2	1.8–5.0	1.5
Elongation at break	5–70	25–75	300	300	110	20–60	50–100	20–60	8–10
Heat deflection temperature (°C at 455 kPa)	102–107	124	150–185	180–240	138	137	181	135	—

[a] High impact grade

A. ACRYLONITRILE–BUTADIENE–STYRENE (ABS)



(Str. 14)

Acrylonitrile–butadiene–styrene resins are terpolymers composed, as the name suggests, of acrylonitrile, butadiene, and styrene. Each component contributes special characteristics to the ultimate properties of products derived from the resins. Acrylonitrile provides heat and chemical resistance and high strength. Butadiene acts as the reinforcing agent providing impact strength and toughness even at low temperatures, while styrene contributes rigidity, easy processability, and gloss. By varying the ratio of the three components, the designer is provided with ABS resins with a wide range of properties to develop a variety of products with a well-balanced combination of properties. For example, general-purpose ABS includes both medium-impact-strength and high-impact-strength grades as well as the low-temperature, high-impact-strength variety. In addition, there are flame-retardant, structural foam, heat-resistant, low-gloss, and transparent grades.

ABS resins are produced primarily by grafting styrene and acrylonitrile onto polybutadiene latex in a batch or continuous polymerization process. They may also be made by blending emulsion latexes of styrene–acrylonitrile (SAN) and nitrile rubber (NBR).

ABS resins consist of two phases: a continuous glassy matrix of styrene–acrylonitrile copolymer and a dispersed phase of butadiene rubber or styrene–butadiene copolymer. The styrene–acrylonitrile matrix is ordinarily brittle; however, the reinforcing influence of the rubbery phase results in a product with greatly improved (high) load-bearing capacity. To optimize properties, it is usually necessary to graft the glassy and rubbery phases. A variety of ABS resins are produced by varying the ratio of components and the degree of bonding between the rubbery and glassy phases (graft level).

ABS resins have relatively good electrical insulating properties. They are resistant to weak acids and weak and strong bases. However, they have poor resistance to esters, ketones, aldehydes, and some chlorinated hydrocarbons. ABS resins are easily decorated by painting, vacuum metallizing, and electroplating. They are readily processed by all techniques commonly employed with thermoplastics and, like metals, can be cold-formed. ABS is hygroscopic and therefore requires drying prior to processing.

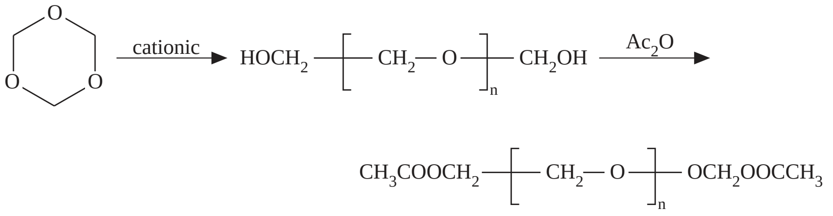
ABS resins are true engineering plastics particularly suited for high-abuse applications. Injection-molded ABS is used for housewares, small tools, telephones, and pipe fittings, which are applications requiring prolonged use under severe conditions. Extruded ABS sheet is used in one-piece camper tops and canoes. Applications of ABS in automobile and truck machinery include headliners, kick panel, wheel wells, fender extensions, wind deflectors, and engine covers. Profile-extruded ABS resins are used in pipes, sewer, well casing, and conduits. Specialty products from ABS include electroplating grades (automotive grilles and exterior decorative trim); high-temperature-resistant grades (automotive instrument panels, power tool housings); and structural foam grades, which are used in molded parts where high strength-to-weight ratio is required.

B. POLYACETAL (POLYOXYMETHYLENE — POM)

$$\left[CH_2 - O \right]_n \qquad \text{(Str. 15)}$$

Polyoxymethylene (polyacetal) — sometimes known as polyformaldehyde — is the polymer of formaldehyde. It is obtained either by anionic or cationic solution polymerization of formaldehyde or cationic ring-opening bulk polymerization of trioxane. Highly purified formaldehyde is polymerized in the presence of an inert solvent such as hexane at atmospheric pressure and a temperature usually in the range of –50 to 70°C. The cationic bulk polymerization of trioxane is the preferred method of production of polyoxymethylene.

Polyoxymethylene is susceptible to depolymerization, or unzipping, under molding conditions. To improve thermal stability, end capping is essential. The capping of the hydroxyl end groups is achieved by etherification or, preferably, by esterification using acetic anhydride:



(Str. 16)

Polyacetal can also be stabilized against degradative conditions by copolymerizing trioxane with small amounts of ethylene oxide. This introduces a random distribution of –C–C– bonds in the polymer chain. Hydrolysis of the copolymer with aqueous alkali gives a product with stable hydroxyethyl end groups. The presence of these stable end groups coupled with the randomly distributed C–C bonds prevents polymer depolymerization at high temperature.

Polyacetal is a linear, high-molecular-weight polymer with a highly ordered chain structure that permits an ordered arrangement of chain molecules in a crystalline structure. It is about 80% crystalline, with a melting point of 180°C. Polyacetal has excellent chemical resistance, has good dimensional stability due to negligible water absorption, and is insoluble in common solvents at room temperature. The stiffness, strength, toughness, and creep and fatigue resistance of polyacetals are higher than those of other unreinforced crystalline thermoplastics. It has good frictional and electrical properties. Products from polyacetal retain most of these engineering properties over a wide range of useful temperatures and other end-use conditions. Polyacetals can be processed by the usual molding and extrusion methods.

The relatively advantageous properties of polyacetals have led to applications in a variety of markets, particularly as a replacement for metals, where it provides enhanced properties and lower costs. Table 15.10 shows areas and typical applications of polyacetals.

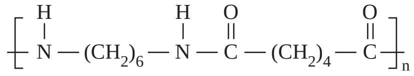
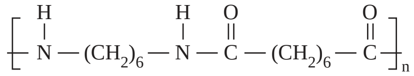
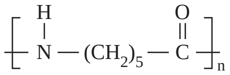
C. POLYAMIDES (NYLONS)

The word *nylon* is a generic term used to describe a family of synthetic polyamides. Nylons are characterized by the amide group (–CONH–), which forms part of the polymer main chain (interunit

Table 15.10 *Typical Applications of Polyacetals*

Area	Typical Applications
Automotive	Filler necks for gasoline tanks, instrument panels, seat belts, steering columns, window support brackets, door handles, bearing and gear components, dashboard components, controls, wheel covers, gas caps
Plumbing	Shower heads, shower mixing valves, faucet cartridges, ball cocks
Consumer	Handles and other hardware items, the bodies of lighters, replaceable cartridges in showers, telephone components, lawn sprinklers, garden sprayers, stereo cassette cases, spools for video cassettes, zippers
Machinery	Machinery couplings, small engine starters, pump impellers and housings, fire extinguisher handles, gears

Table 15.11 *Nomenclature of Nylons*

Monomer(s)		Polymer
$H_2N-(CH_2)_6-NH_2$ Hexamethylenediamine	$HOOC-(CH_2)_4-COOH$ Adipic acid	 $\left[-\overset{\overset{H}{\mid}}{N}-(CH_2)_6-\overset{\overset{H}{\mid}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\right]_n$ Poly(hexamethylene adipamide), nylon 6,6
$H_2N-(CH_2)_6-NH_2$ Hexamethylenediamine	$HOOC-(CH_2)_6-COOH$ Sebacic acid	 $\left[-\overset{\overset{H}{\mid}}{N}-(CH_2)_6-\overset{\overset{H}{\mid}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_6-\overset{\overset{O}{\|}}{C}-\right]_n$ Poly(hexamethylene sebacamide), nylon 6,10
$H_2N-(CH_2)_5-COOH$ ω-amino caproic acid		 $\left[-\overset{\overset{H}{\mid}}{N}-(CH_2)_5-\overset{\overset{O}{\|}}{C}-\right]_n$ Polycaprolactam, nylon 6

linkage). In terms of chemical structure, nylons may be divided into two basic types: those based on diamines and dibasic acids (A–A/B–B type); and those based on amino acids or lactams (A–B type). Nylons are described by a numbering system that reflects the number of carbon atoms in the structural units. A–B type nylons are designated by a single number. For example, nylon 6 represents polycaprolactam [poly(ω-amino caproic acid)]. A–A/B–B nylons are designated by two numbers, with the first representing the number of carbon atoms in the diamine and the second referring to the total number of carbon atoms in the acid (Table 15.11).

Among the nylons, nylon 6,6 and nylon 6 are of the greatest commercial importance and most widely used. Other commercially useful materials are the higher analogs such as nylon 6,9; 6,10; 6,12; 11; and 12. Nylon 6,6 and nylon 6 are widely used because they offer a good balance of properties at an economic price. Other nylons command relatively higher prices.

Nylon 6,6 is formed by the step-growth polymerization of hexamethylenediamine and adipic acid. The exact stoichiometric equivalence of functional groups needed to obtain a high-molecular-weight polymer is achieved by the tendency of hexamethylenediamine and adipic acid to form a 1:1 salt. This intermediate hexamethylene diammonium adipate is dissolved in water and then charged into an autoclave. Monofunctional acids such as aluric or acetic acid (0.5 to 1 mol%) may be added to the polymerization mixture for molecular-weight control. As the temperature is raised, the steam generated is purged by air. The temperature is raised initially to 220°C, and subsequently to 270 to 280°C when monomer conversion is about 80 to 90%, while maintaining the pressure of the steam generated at 250 psi. Pressure is then reduced to atmospheric, and heating is continued until polymerization is totally completed.

A–B type nylons are usually prepared by ring-opening polymerization of a cyclic lactam. Water is added in a catalytic amount to effect the ring-opening and then removed at higher temperature to encourage high polymer formation. High-molecular-weight nylon 6 is obtained from the anionic polymerization of ε-caprolactam with a strong base such as sodium hydride. Commercially, nylon 6 is produced by the hydrolytic polymerization of ε-caprolactam.

As a class, aliphatic polyamides exhibit excellent resistance to wear and abrasion, low coefficient of friction, good resilience, and high impact strength. Nylons are generally characterized by a good balance of high strength, elasticity, toughness, and abrasion resistance. They maintain good mechanical properties

Table 15.12 *Melting Points and Moisture Absorption of Some Nylons*

Nylon	Tm °C	Water Absorption (ASTM) D-570)
6,6	265	1.0–1.3
6,8	240	—
6,9	226	0.5
6,10	225	—
6,12	212	0.4
4	265	—
6	226	1.3–1.9
7	223	—
11	188	—
12	180	0.25–0.30

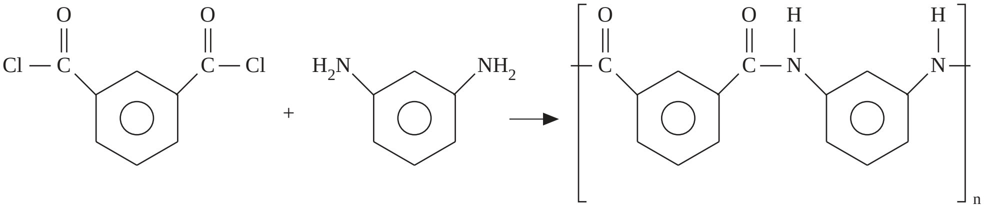
at elevated temperatures — sometimes as high as 150°C — while also retaining low-temperature flexibility and toughness.

Nylons are sensitive to water due to the hydrogen-bond-forming ability of the amide groups. Water essentially replaces amide–amide–hydrogen bond with amide–water–hydrogen bond. Consequently, water absorption decreases with decreasing concentration of amide groups in the polymer backbone (Table 15.12). Water acts as a plasticizer, which increases toughness and flexibility while reducing tensile strength and modulus. The absorption of moisture results in a deterioration of electrical properties and poor dimensional stability in environments of changing relative humidity. Therefore, care must be taken to reduce the water content of nylon resins to acceptable levels before melt processing to avoid surface imperfections and embrittlement due to hydrolytic degradation.

The markets for nylon products have been broadened considerably because of the apparent ease with which polyamides can be modified to produce improved properties for special applications. Modified nylons of various grades are produced by copolymerization and the incorporation of various additives (usually in small amounts) such as heat stabilizers; nucleating agents; mold-release agents; plasticizers; mineral reinforcements (glass fiber/beads, particulate minerals); and impact modifiers. For example, in applications involving long exposure to temperatures above 75 to 85°C such as automotive under-hood parts, polyamides have limited use due to their susceptibility to surface oxidation in air at elevated temperatures and the attendant loss of mechanical properties. Addition of less than 1% copper salt heat stabilizer permits use of nylons at elevated temperatures. The mechanical properties of nylons depend largely on their crystallization. Consequently, control of these properties can be achieved partly by controlling the degree of crystallinity and spherulite size by the use of nucleating agents.

Nylons are used in applications requiring durability, toughness, chemical inertness, electrical insulating properties, abrasion and low frictional resistance, and self-lubricating properties. Table 15.13 lists markets and typical applications of nylons. In many of these applications, nylons are used as small parts or elements in subassemblies of the finished commercial article.

The term *aramid* is used to describe aromatic polyamides, which were developed to improve the heat and flammability resistance of nylon. Nomex is a highly heat-resistance nylon introduced in 1961 by DuPont. It is produced by the solution or interfacial polymerization of isophthaloyl chloride and *m*-phenylenediamine:



poly(*m*-phenyleneisophthalamide) (Nomex)

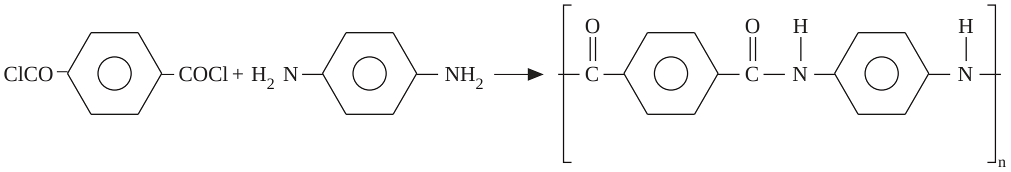
(Str. 17)

Table 15.13 *Markets and Typical Applications of Nylons*

Market	Typical Applications
Automotive/truck	Speedometer gears, door lock wedges, distributor point blocks; automotive electrical system such as connectors, fuse blocks, generator parts, spark wire separators, wire insulation; monofilament thread for upholstery, license plate bolts and nuts, fuel vapor canisters, fender extensions, mirrors and grilles; pneumatic tubing and lubrication lines, fuel and fuel-vent lines
Electrical/electronics	Connector, tie straps, wire coil, bobbins, tuner gears
Industrial/machinery	Lawn mower carburetor components, window and furniture guides, pump parts, power tools, fans, housings, gears, pulleys, bearings, bushings, cams, sprockets, conveyor rollers, screws, nuts, bolts, washers
Monofilament/film coatings	Fishing lines, fish nets, brush bristles, food and medical packaging, coatings for wire and cable
Appliances	Refrigerators, dishwashers, ranges, hair dryers and curlers, corn poppers, smoke detectors
Consumer items	Combs, brushes, housewares, buttons, rollers, slides, racquetball racquets

Nomex has a melting point of about 365°C and is virtually nonflammable. It is used in many applications such as protective clothing and hot gas filtration equipment as a substitute for asbestos.

Another aramid, Kevlar, is the corresponding linear aromatic polyamide obtained from terephthaloyl chloride and phenylenediamine.



poly(*p*-phenylene terephthalamide) (Kevlar) (Str. 18)

Kevlar, which decomposes only above 500°C, provides a fiber material which is as strong as steel at one-fifth its weight. It is a good substitute for steel in belted radial tires and is used in the manufacture of mooring lines as well as bulletproof vests and other protective clothing. Fiber-reinforced plastic composites are also produced from Kevlar fiber. Typical applications of these composites include fishing rods, golf club shafts, tennis rackets, skis, and ship masts. Significant quantities of Kevlar composites are used in Boeing 757 and 767 planes.

Example 15.4: Explain the following observations.

a. Major uses of polyacetals are as direct replacements for metals such as brass, cast iron, aluminum, and zinc in many applications. For example, in the plumbing industry, shower heads, shower mixing valves, and faucet cartridges molded of acetal homopolymer are replacing brass and zinc parts.
b. Nylons have good resistance to solvents. However, good solvents for nylon 6,6 and nylon 6 are strong acids (such as H_2SO_4, HBr, trichloracetic acid) formic acid, phenols, cresols and perfluoro compounds.

Solution:

a. The use of polyacetals has a number of property advantages over the use of metals. These include a good balance of stiffness; light weight; resistance to corrosion, wear, and abrasion; and dimensional stability. In addition, cost savings result from elimination of metal assemblies, the reduced number of parts, and the use of low-cost plastic assembly techniques such as welding, snap fits, and self-threading screws. In other words, the provision of improved properties at reduced cost permits the use of polyacetals as replacements for metals.

b. The hydrogen bonding capability of nylons is the primary factor controlling their solvent resistance. The hydrogen bond must be broken or replaced during dissolution. Consequently, only strong acids, which can protonate the amide nitrogen atom and preclude formation of hydrogen bonds or other compounds (formic acid, phenols, etc.) that can form hydrogen bonds, are solvents for nylon 6,6 and nylon 6. These nylons are polyamides with a high content of amide groups.

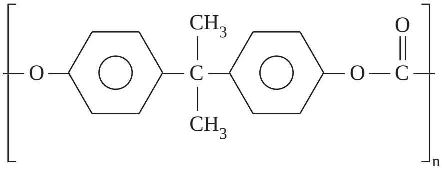
Example 15.5: Indicate the polymer property/properties required for the following applications of nylons:

a. Gears, bearings, bushings, cams
b. Screws, nuts, bolts
c. Food packaging
d. Coatings for wire and cable insulation.

Solution:

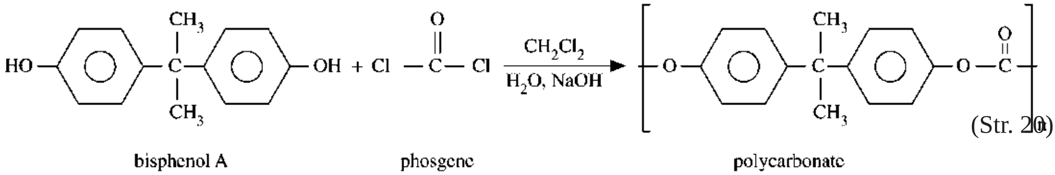
Applications	Responsible Nylon Properties
a. Gears, bearings, bushings, cams	High tensile and impact strength; toughness; lubricity; low coefficient of friction
b. Screws, nuts, bolts	High strength; corrosion resistance
c. Food packaging	Low permeability to water and air to preserve freshness; high strength; puncture resistance
d. Coatings for wire and cable	Resistance to stress cracking, abrasion, and corrosion; low moisture absorption

D. POLYCARBONATE (PC)

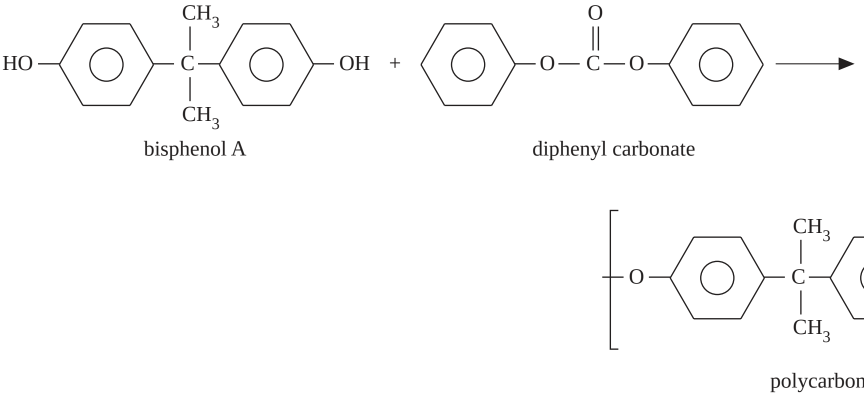


(Str. 19)

Polycarbonates are characterized by the carbonate (–O–COO–) interunit linkage. They may be prepared by interfacial polycondensation of bisphenol A and phosgene in methylene chloride–water mixture. The resulting hydrogen chloride is removed with sodium hydroxide or, in the case of solution polymerization, pyridine is used as the hydrogen chloride scavenger. Polycarbonate may also be made by ester interchange between bisphenol A and diphenyl carbonate.



(Str. 20)

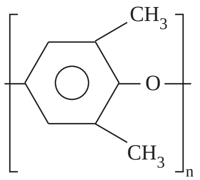


(Str. 21)

Polycarbonate is an amorphous polymer with a unique combination of attractive engineering properties. These include exceptionally high-impact strength even at low temperatures, low moisture absorption, good heat resistance, good rigidity and electrical properties, and high light transmission. It possesses good dimensional stability (high creep resistance) over a broad temperature range. The transparency of polycarbonate has led to its use as an impact-resistant substitute for window glass. Polycarbonate, however, has a limited scratch and chemical resistance. It also has a tendency to yellow under long-term exposure to UV light. Copolymerization and/or incorporation of additives are used to modify the base resin for greater creep resistance, UV light performance, flame retardance, and thermal stability. For example, fire-retardant grades of polycarbonates are made by copolymerizing bisphenol A with tetrabromobisphenol A comonomer, while addition of glass fiber reinforcements greatly extends the level and range of creep resistance of polycarbonates.

Polycarbonates are processed by all the conventional techniques for processing thermoplastics. The balanced combination of properties permits polycarbonates to be used in a variety of applications. Markets for polycarbonates include automotive, construction, electronics, appliances, and lighting, while typical applications are automobile taillight lenses, lamp housings, bumpers, door and window components, drapery fixtures, furniture and plumbing, business machine housings, machinery housings, telephone parts, glazing signs, and returnable bottles.

E. POLY(PHENYLENE OXIDE) (PPO)



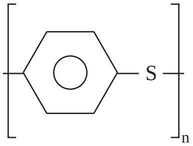
(Str. 22)

Polyphenylene oxide is a large-volume engineering thermoplastic developed in 1956 by General Electric. It is made by free-radical step-growth oxidative coupling polymerization of 2,6-xylenol, with copper salts and pyridene as catalysts. Poly(phenylene oxide) homopolymer is difficult to process. Therefore, the commercial resins, marketed under the trade name Noryl, are modified poly(phenylene oxides) containing high-impact polystyrene (HIPS). The styrene component of HIPS forms homogeneous phase with PPO.

Poly(phenylene oxide) is an amorphous thermoplastic material with a low specific gravity, high impact strength, chemical resistance to mineral and organic acids, good electrical properties, and excellent dimensional stability at high temperatures. It has exceptionally low water absorption and complete hydrolytic stability.

Poly(phenylene oxide) resins are available in general-purpose, flame-retardant, glass-reinforced extrudable, foamable, and specialty grades. In addition to their applications as appliance, electrical, and business machine housings, PPO resins find use in a variety of pumps, showerheads, and components for underwater equipment. Platable grades are used for automotive grilles and wheel covers and plumbing fixtures.

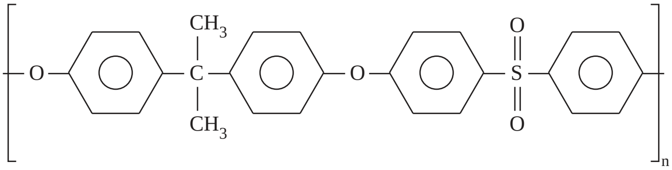
F. POLY(PHENYLENE SULFIDE) (PPS)


(Str. 23)

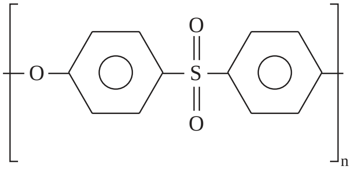
Poly(phenylene sulfide), sold by Phillips Chemical Company under the trade name Rylon, is a highly crystalline aromatic polymer (mp 285°C). It is obtained by the polycondensation of *p*-dichlorobenzene and sodium sulfide. The symmetrical arrangement of *p*-substituted benzene rings and sulfur atoms on the polymer backbone permits a high degree of crystallization. This, in addition to the extreme resistance of the benzene ring–sulfur bonds to thermal degradation, confers thermal stability, inherent nonflammability, and chemical resistance on PPS resin.

Even though concentrated oxidizing acids, some amines, and halogenated compounds can affect PPS, it has no known solvents below 200°C. Poly(phenylene sulfide) is characterized by high stiffness and good retention of mechanical properties at elevated temperatures. It has high tensile and flexural strengths, which can be increased substantially by addition of fillers such as glass fibers. PPS has good electrical properties, low coefficient of friction, and high transparency to microwave radiation. Poly(phenylene sulfide) is available in grades suitable for injection and compression molding and coating. Principal applications are in electrical and electronic components and industrial-mechanical uses such as parts for chemical processing equipment that require high temperature stability, mechanical strength, and chemical resistance.

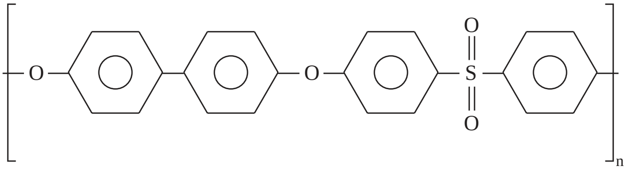
G. POLYSULFONES


Polysulfone (Bisphenol A)

(Str. 24)

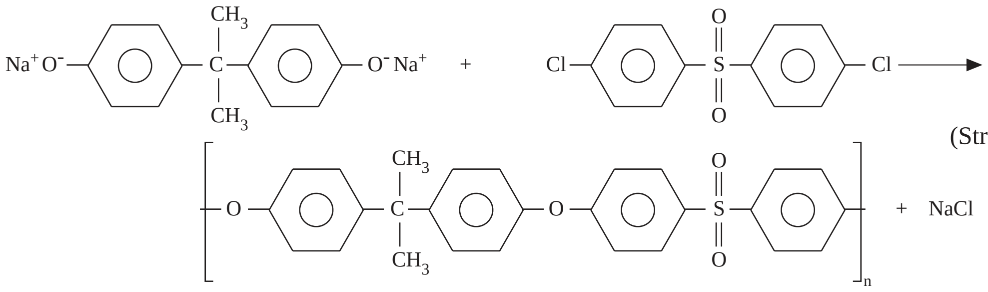

Polyethersulfone

(Str. 25)


Polyphenylsulfone

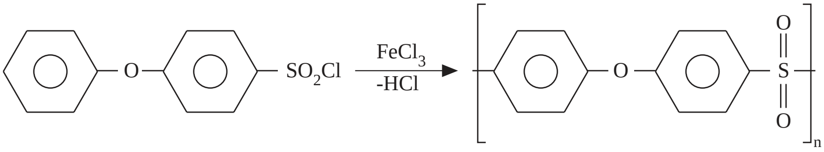
(Str. 26)

Polysulfones constitute a family of high-performance transparent engineering thermoplastics with high oxidative and hydrolytic stability and excellent high-temperature properties. They may be prepared by condensation polymerization of 4,4′-dichlorophenyl sulfone with alkali salt of bisphenol A in polar solvents like dimethylsulfoxide (DMF) or sulfolane.



(Str. 27)

Alternatively, polysulfones may also be synthesized by a Friedel–Crafts reaction of aromatic sulfonyl chlorides using Lewis acid catalyst:



(Str. 28)

The presence of the diaryl sulfone group with a *para* oxygen atom confers oxidation resistance, good thermal stability, and rigidity at high temperatures. The ether linkages provide chain flexibility and, consequently, impart good impact strength. Polysulfones have good resistance to aqueous mineral acids, alkali, salt solutions, and oils and greases. They are strong, rigid, tough, amorphous polymers that can be extruded and injection molded on conventional equipment. Typical properties on some polysulfones are shown in Table 15.14.

Polysulfones have been used satisfactorily in a wide range of products, including consumer, medical, automotive, aircraft, aerospace, industrial, electrical, and electronic applications. Like other engineering thermoplastics, they are replacing metals in a variety of applications because they can be injection molded into complex shapes at reduced cost since costly machining and finishing operations can be avoided. Table 15.15 lists some of the applications of polysulfones.

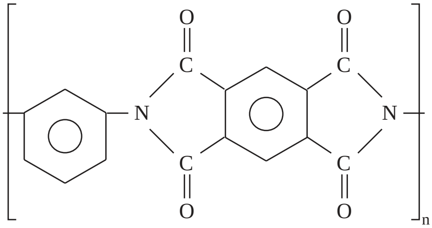
Table 15.14 *Typical Properties of Polysulfones*

Property	Polysulfone (Bisphenol A)	Polyether Sulfone	Polyphenyl Sulfone
Specific gravity	1.24	1.37	1.29
Tensile strength (MPa)	70.3	84.1	71.7
Tensile modulus (MPa)	2482	2696	2137
Flexural strength (MPa)	106.2	128.6	85.5
Flexural modulus (MPa)	2689	2585	2275
Notched Izod impact strength (ft-lb/in)	1.2	1.6	12.

Table 15.15 *Some Applications of Polysulfones*

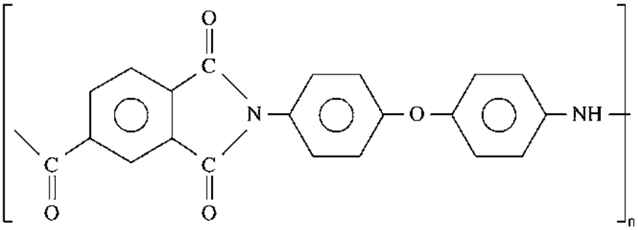
Polysulfone	Typical Applications
Polysulfone (bisphenol A)	Medical instrumentation; food processing and handling, including microwave ware, coffeemakers, beverage-dispensing tanks; electrical/electronic applications such as connectors, automotive fuses, switch housings, television components, structural circuit boards; chemical processing and other applications, including corrosion-resistant piping, tower packing, pumps, membranes, camera and watch cases, battery cell frames and housing
Polyether sulfone	High-temperature electrical parts such as connectors, motor components, lamp housings and alternator insulators; sterilizable medical components; oven windows; aerospace, aircraft and automobile composite structures
Polyphenyl sulfone	High-temperature coil bobbins, aircraft window reveals, automatic transmission housing, firemen's helmets, gas compressor valves, carbon fiber composites, flexible printed circuit boards

H. POLYIMIDES



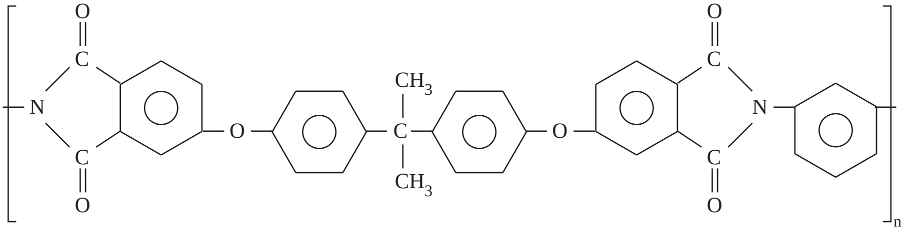
Polyimide

(Str. 29)



Polyamide-imide (Torlon)

(Str. 30)



(Str. 31)

Polyetherimide (Ulterm)

Polyimides are made by a two-stage process involving an initial polycondensation of aromatic dianhydrides and aromatic diamines to produce a soluble intermediate, polyamic acid, which is then dehydrated at elevated temperatures to form the polyimide. While the intermediate, polyamic acid, is soluble, the cured or fully imidized polyimide is insoluble and infusible, with essentially the characteristics of a thermoset.

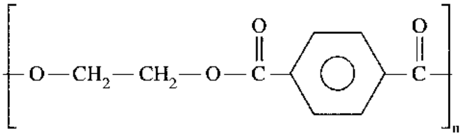
Polyimide molded parts and laminates display high heat, chemical, and wear resistance, with virtually no creep even at high temperatures. It has high oxidative stability, good electrical insulation properties, low coefficient of friction, and good cryogenic properties. However, polyimide has inherent structural weakness arising from imperfections and void formation due to water release in the curing process.

Typical uses of polyimide include electronic applications, sleeve bearings, valve seatings, and compressor vanes in jet engines. Other uses include aircraft and aerospace applications with high performance requirements. They are used for printed circuit boards in computers and electronic watches for both military and commercial uses. Polyimides are used in the insulation of automotive parts that require thermal and electrical insulation, such as wires used in electric motors, wheels, pistons, and bearings.

The thermoplastic variety of polyimides with enhanced melt processability is obtained by combining the basic imide structure with more flexible aromatic groups such as aromatic ethers or amides. Polyamide-imides are produced by condensing trimellitic anhydrides with aromatic diamines, while polyetherimides are made by the reaction between bisphenol A, 4,4′-methylene dianiline, and 3-nitrophthalic anhydride.

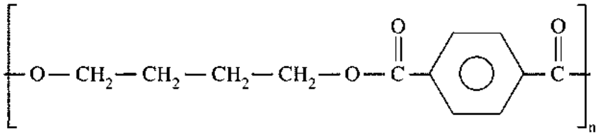
Both polyamide-imide and polyetherimide have high heat distortion temperature, tensile strength, and modulus. Polyamide-imide is useful from cryogenic temperatures up to 260°C. It is virtually unaffected by aliphatic and aromatic chlorinated and fluorinated hydrocarbons and by most acid and alkali solutions. These polymers are used in high-performance electrical and electronic parts, microwave appliances, and under-the-hood automotive parts. Typical automotive applications include timing gears, rocker arms, electrical connectors, switches, and insulators.

I. ENGINEERING POLYESTERS



Poly(ethylene terephthalate) (Mylar, Dacron, Torelene)

(Str. 32)

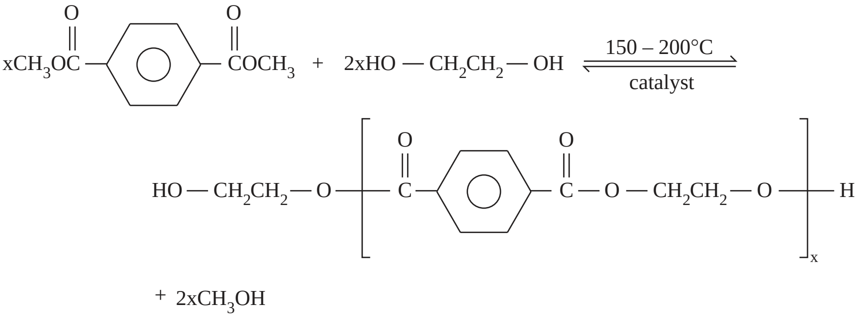


Poly(butylene terephthalate) (PBT)

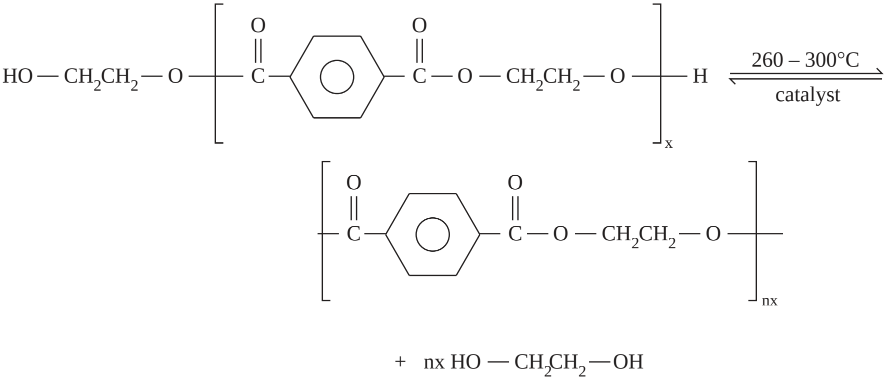
(Str. 33)

Commercially important polyesters are based on polymers with the *p*-phenylene group in the polymer chain. In contrast to the low melting, linear aliphatic polyesters, the stiffening action of this group coupled with the high degree of symmetry results in a high melting point and other important engineering properties. For example, all commercial polyester fibers are based on terephthalic acid as the primary building block. Different products are obtained by varying the difunctional alcohols used in polycondensation reaction with this acid. However, the major engineering polyesters are poly(ethylene terephthalate) and poly(butylene terephthalate).

Polyesters are produced commercially by melt polymerization, ester interchanges, and interfacial polymerization. Commercial poly(ethylene terephthalate) is produced traditionally by two successive ester interchange reactions. In the first step, dimethyl terephthalate is heated with ethylene glycol at temperatures near 200°C. This yields an oligomeric dihydroxyethyl terephthalate (x = 1 to 4) and methanol, which is removed. In the second step, the temperature is increased, leading to polymer formation, while ethylene glycol is distilled off.



(Str. 34)



(Str. 35)

Poly(butylene terephthalate) is a highly crystalline thermoplastic polyester that is manufactured by condensation polymerization of 1,4-butanediol and dimethyl terephthalate in the presence of tetrabutyl titanate.

PET and PBT are characterized by high strength, rigidity, and toughness; low creep at elevated temperatures; excellent dimensional stability; low coefficient of friction; good chemical, grease, oil, and solvent resistance; minimal moisture absorption; and excellent electrical properties. Reinforcement of these polymers with glass fibers enhances many of their properties (Table 15.16).

PET has been used for a long time in fiber applications, including apparel, home furnishings, and tire cord. The fiber applications of PET depend on its outstanding crease resistance, work recovery, and low moisture absorption. Clothing made from PET fibers exhibit good wrinkle resistance. As a plastic, PET has been used in the production of films and, more recently, as blow-molded bottles for carbonated soft drinks. Biaxially oriented PET film is used industrially in magnetic tape, X-ray and photographic films, and electrical insulation. Both oriented and unoriented PET films are also used in food packaging

Table 15.16 *Properties of Engineering Polyesters*

	Poly(ethylene terephthalate)		**Poly(butylene terephthalate)**	
Property	**Unfilled**	**30% Glass Fiber Reinforced**	**Unfilled**	**30% Glass Fiber Reinforced**
Specific gravity	1.34–1.39	1.27	1.31–1.38	1.52
Melting temperature (°C)	265	265	224	224
Tensile strength (MPa)	58.6–72.4	158.6	56.5	117.2–131.0
Tensile modulus (MPa)	2758–4136	9927	1930	8962
Flexural strength (MPa)	96.5–124.1	230.9	82.7–115.1	179.2–200.0
Flexural modulus (MPa)	2413–3102	8962	2275–2758	7583–8273
Impact strength (Izod) (ft-lb/in)	0.25–0.65	1.9	0.8–1.0	1.3–1.6
Water absorption (24 hr)	0.1–0.2	0.05	0.08–0.09	0.06–0.08

applications such as boil-in-bag food pouches. Applications of 30% glass-fiber-reinforced PET resins include pump and power-tool housings, sporting goods, and automotive exterior components such as rearview mirror housings, hinges, and windshield-wiper components.

Automobile applications of PBT include window and door hardware, speedometer frames and gears, servo pistons, and automobile ignition system components (distributor caps, coil bobbins, and rotors). In addition, it is used as bases, handles, and housings for small appliances (toasters, cookers, fryers and irons) as well as small industrial pump housing, impellers, and support brackets, gears, showerhead and faucet components, and consumer products like buckles, clips, buttons, and zippers.

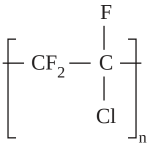
Example 15.6: Comment on the relative melting points as well as the impact strength and water absorption of unfilled PET and PBT.

Solution: PBT has four methylene groups compared with two in PET. This confers a greater chain flexibility on PBT. Consequently, PBT has a lower melting (due to greater susceptibility to thermal agitation) and a higher impact strength than PET. On the other hand, the hydrocarbon nature of PBT is greater than that of PET, making PBT more hydrophobic.

$$\left[CF_2 - CF_2 \right]_n$$

Polytetrafluorethylene (Teflon)

(Str. 36)



$$\left[CF_2 - \underset{Cl}{\overset{F}{C}} \right]_n$$

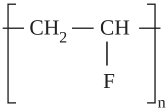
Polychlorotrifluoroethylene (CTFE)

(Str. 37)

$$\left[CH_2 - CF_2 \right]_n$$

Poly (vinylidene fluoride) PVDF)

(Str. 38)



$$\left[CH_2 - \underset{F}{CH} \right]_n$$

Poly (vinyl fluoride) (PVF)

(Str. 39)

J. FLUOROPOLYMERS

Fluoropolymers constitute a class of polyolefins in which some or all of the hydrogens are replaced by fluorine. The structures of some of these polymers are shown above. Fluoropolymers have a broad range of properties, offering unique performance characteristics. Within this family of polymers are those with high thermal stability and useful mechanical properties both at high temperatures and at cryogenic temperatures. Most fluoropolymers are chemically inert and totally insoluble in common organic solvents. The family of fluoropolymers has extremely low dielectric constants and high dielectric strength. Most fluoropolymers have unique nonadhesive and low friction properties.

Polytetrafluoroethylene, the most widely used fluoropolymer, is produced by emulsion free-radical polymerization of tetrafluoroethylene using redox initiators. As a result of its highly regular chain structure, PTFE is a highly crystalline polymer with high density and melting temperature (mp 327°C). It is a high-temperature-stable material characterized by low-temperature flexibility and extremely low coefficient of friction, dielectric constant, and dissipation factor. PTFE exhibits outstanding chemical inertness, is resistant to attack even by corrosive solvents, and is practically unaffected by water. While PTFE has a high impact strength, its tensile strength and wear and creep resistance are low relative to other engineering polymers.

Given its extremely high crystallinity and the associated high melting point, its melt viscosity, and its low melt flow rates, PTFE cannot be processed by conventional fabrication techniques used for polymers. Instead, unusual techniques have been developed for shaping polytetrafluoroethylene. Molding PTFE powders are processed by the two-staged press and sinter methods used in powder metallurgy. Granular PTFE is first pressed into the desired shape at room temperature and pressure (in the range 2000 to 10,000 psi). The resulting preform is then sintered at a temperature above the crystalline melting point (360 to 380°C) to obtain a dense, strong, homogeneous product. Better melt processing is achieved by reducing the crystallinity of PTFE through incorporation of a small concentration of a comonomer such as hexafluoropropylene. The resulting copolymer retains most of the desirable properties of polytetrafluoroethylene but has a reduced melt viscosity that permits processing by traditional techniques.

Polytetrafluoroethylene is used primarily in applications that require extreme toughness, outstanding chemical and heat resistance, good electrical properties, low friction, or a combination of these properties. Principal applications or PTFE are as components or linings for chemical process equipment, high-temperature cable insulation, molded electrical components, tape, and nonstick coatings. Chemical process equipment applications include linings for pipe, pipe fittings, valves, pumps, gaskets, and reaction vessels. PTFE is used as insulation for wire and cable, motors, generators, transformers, coils and capacitors, high-frequency electronic uses, and molded electrical components such as insulators and tube sockets. Nonstick low friction uses include home cookware, tools, and food-processing equipment.

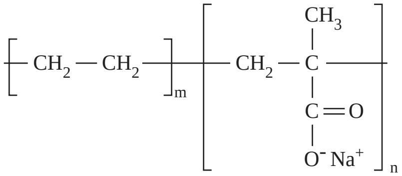
In addition to polytetrafluoroethylene, several other partially fluorinated polymers are available commercially. These include poly(chlorotrifluoroethylene), which is also available as a copolymer with ethylene or vinylidene fluoride, poly(vinyl fluoride), and poly(vinylidene fluoride). Poly(chlorotrifluoroethylene) is a chemically inert and thermally stable polymer, soluble in a number of solvents above 100°C, tough at temperatures as low as –100°C while retaining its useful properties at temperatures as high as 150°C. Its melt viscosity, though relatively high, is sufficiently low to permit the use of conventional molding and extrusion processing methods. It is used for electrical insulators, gaskets and seals, and pump parts.

Poly(vinyl fluoride) is a highly crystalline polymer available commercially as a tough, flexible film sold under the trade name Tedlar by DuPont. It has excellent chemical resistance like other fluoropolymers, excellent outdoor weatherability, and good thermal stability, abrasion, and stain resistance. It maintains useful properties between –180°C to 150°C. It is used as protective coatings for materials like plywood, vinyl, hardboard, metals, and reinforced polyesters. These laminated materials find applications in aircraft interior panels, in wall covering, and in the building industry.

Poly(vinylidene chloride) is a crystalline polymer (mp 170°C), with significantly greater strength and creep and wear resistance than PTFE. Poly(vinylidene chloride), which is also available as a copolymer with hexafluoroethylene, has very good weatherability and chemical and solvent resistance. It is used primarily in coatings; as a gasket material; in wire and cable insulation; in piping, tanks, pumps and other chemical process equipment; and in extrusion of vinyl siding for houses.

K. IONOMERS

Ionomers are a family of polymers containing ionizable carboxyl groups, which can create ionic intermolecular cross-links. They are generally copolymers of α-olefins with carboxylic acid monomers that are partially neutralized by monovalent or divalent cations. A typical ionomer is DuPont Surlyn, which is a copolymer of ethylene and methacrylic acid partially neutralized with sodium or zinc cations.



$$\left[-CH_2-CH_2-\right]_m\left[-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle \underset{\displaystyle O^- Na^+}{C=O}}{C}}-\right]_n$$

(Str. 40)

Table 15.17 *Some Commercial Ionomers*

Polymer System	Trade Name	Manufacturer	Uses
Poly(ethylene-*co*-methacrylic acid)	Surlyn	DuPont	Modified thermoplastic
Poly(butadiene-*co*-acrylic acid)	Hycar	BF Goodrich	High green strength elastomer
Perfluorosulfonate ionomers	Nafion	DuPont	Multiple membrane uses
Perfluorocarboxylate ionomer	Flemion	Asahi Glass	Chloralkali membrane
Telechelic polybutadiene	Hycar	BF Goodrich	Specialty Uses
Sulfonated ethylene–propylene–diene terpolymer	Ionic elastomer	Uniroyal	Thermoplastic elastomer

From Lundberg, R.D., in *Encyclopedia of Chemical Technology*, 3rd ed., Mark, H.F., Othmer, D.F., Overberger, C.G., and Seaborg, G.T., Eds., Interscience, New York, 1984. With permission.

For ionomers, the ratio n/m typically does not exceed 10 mol%. The metal ions act as the cross-links between chains. The ionic interchain forces confer solid-state properties normally associated with a cross-linked structure on ionomers, but the cross-links are labile at processing temperatures. Consequently, ionomers, like other thermoplastic materials, can be processed on conventional molding and extrusion equipment.

The preparation of ionomers involves either the copolymerization of a functionalized monomer with an olefinic unsaturated monomer or direct functionalization of a preformed polymer. Typically, free-radical copolymerization of ethylene, styrene, or other α-olefins with acrylic acid or methacrylic acid results in carboxyl-containing ionomers. The copolymer, available as a free acid, is then neutralized partially to a desired degree with metal hydroxides, acetates, or similar salts. The second route for the preparation of ionomers involves modification of a preformed polymer. For example, sulfonated polystyrene is obtained by direct sulfonation of polystyrene in a homogeneous solution followed by neutralization of the acid to the desired level. Some commercially available ionomers are listed in Table 15.17.

In contrast to homogeneous polymer systems, the pendant ionic groups in ionomers interact or associate, forming ion-rich aggregates immersed in the nonpolar matrix of polymer backbone (Figure 15.10). The extent of ionic interactions and, hence, the properties of ionomers, are dictated by the ionic content, degree of neutralization, type of polymer backbone, and cation.

Ionomers are characterized by outstanding abrasion and oil resistance, toughness, flexibility, good adhesion, and high transparency. These properties dictate the uses of these polymers. For example, the high melt viscosity of Surlyn provides good extrusion performance for paper and foil coatings of multiwall bags for food and drug packaging. Its toughness and abrasion resistance have resulted in extensive use for covering of golf balls (as a replacement of gutta-percha) and roller-skate wheels. The high impact strength coupled with its printability has led to the use of Surlyn in the manufacture of automotive bumper strips and guards. Nafion, with its selective permeability to ions, is used in the production of chlorine and caustic by electrolysis of salt solutions.

VIII. ELASTOMERS

As we saw in Chapter 1 elastomers are polymers that are amorphous in the unstretched state and are above their glass transition temperatures at normal ambient temperatures. They have low glass transition temperatures, usually in the range –50 to –70°C. Elastomers are composed of irregularly shaped chain molecules that are held together by a network of cross-links to prevent gross mobility of chains while permitting local mobility of chain segments. The network of cross-links may be formed by covalent bonds or may be due to physical links between chain molecules. The process of introducing covalent cross-links into an elastomer is referred to as vulcanization. Elastomers possess the unique ability to stretch usually to several times their initial dimensions without rupturing, but retract rapidly with full recovery on the release of the imposed stress. In the stretched state, elastomers exhibit high strength and modulus.

A. DIENE-BASED ELASTOMERS

Polymerization of conjugated dienes like butadiene, isoprene, and chloroprenes involves activation of either or both of the double bonds to give 1,2; 3,4; or 1,4 polymers (Figure 15.11). The residual unsaturation in the polymer chains provides convenient sites for the introduction of elastomeric network

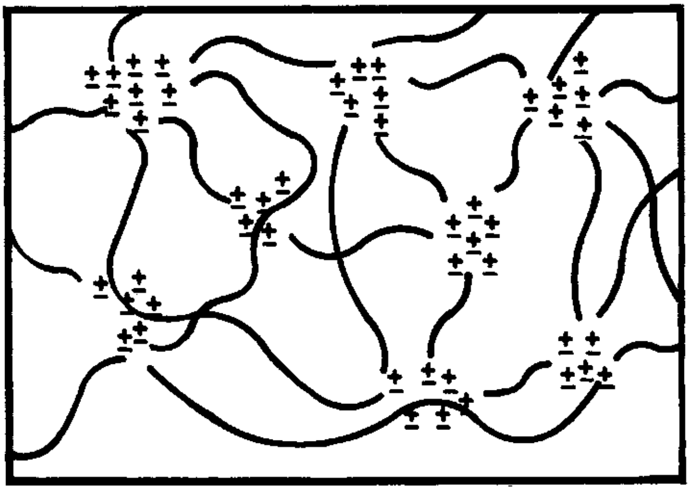
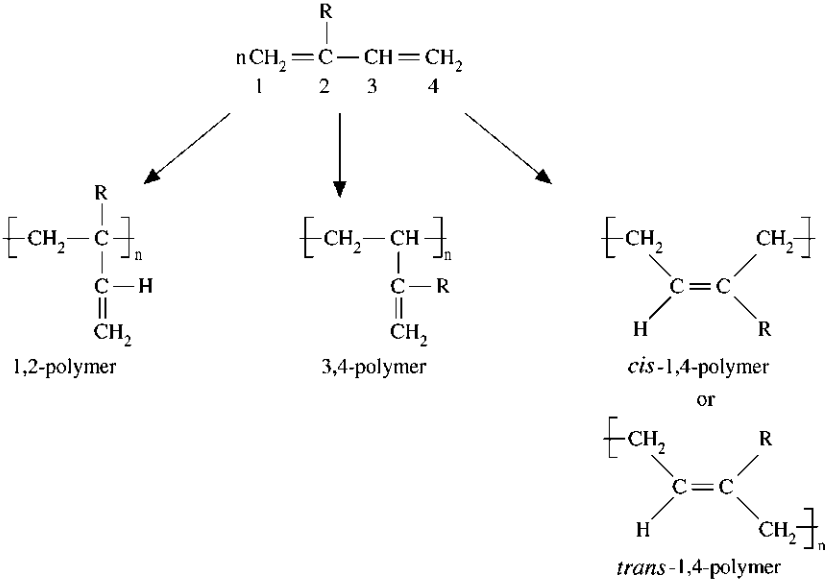


Figure 15.10 *Schematic representation of ionomer. Lines represent nonpolar polymer backbone while + and – represent metal ions and anions, respectively.*



R	Monomer	Elastomer (common name)
H	1,3-butadiene	Polybutadiene
Cl	2-chloro-1,3-butadiene	Polychloroprene
CH_3	2-methyl-1,3-butadiene	Polyisoprene

Figure 15.11 *Possible polymer structures from the polymerization of conjugated dienes.*

of cross-links (vulcanization). Therefore, conjugated dienes are the source of some of the most important commercially available synthetic rubbers or elastomers. For isoprene and chloroprene, eight arrangements are theoretically possible: the 1,2 and 3,4 polymers (vinyl polymers) can be isotactic, syndiotactic, or atactic, while in the 1,4 polymer both *cis* and *trans* configurations are possible. In the case of 1,3 butadiene, the 1,2 and 3,4 structures are identical because of the absence of the asymmetrical substituent group. Both the thermal and physical properties of these polymers are influenced by the relative amounts of the various structures in the polymer chains. The proportion of each type of structure depends on the method and conditions of polymerization.

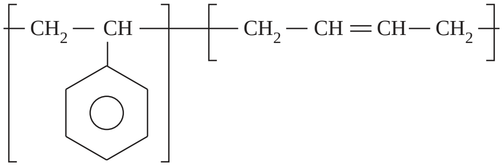
1. Polybutadiene (Butadiene Rubber, BR)

$$\left[\mathrm{CH_2-CH=CH-CH_2}\right]_n \qquad \text{(Str. 41)}$$

Polybutadiene is second-largest-volume synthetic elastomer, next only to SBR. Polybutadiene can be produced by free-radical addition polymerization of butadiene. The resulting polymer has predominantly *trans*-1,4 units, with only about 20% 1,2 units. As the polymerization temperature is increased, the proportion of *cis*-1,4 units increases, while that of 1,2 structure remains essentially unchanged. Butadiene can also undergo anionic polymerization with lithium or organolithium initiators like *n*-butyllithium in nonpolar solvent, such as pentane or hexane. The resulting polymer has a high content of *cis*-1,4 structure, which decreases as either higher alkali-metal initiators or more polar solvents are used. High-molecular-weight polybutadiene with a high content of *trans*-1,4 polymers is prepared by solution polymerization of butadiene using stereo-selective coordination Ziegler–Natta catalysts. Slight changes in catalyst composition can produce drastic changes in polymer composition.

Like SBR, the principal use of BR is in the production of tires and tire products. BR exhibits good resilience and abrasion resistance and low heat buildup, which are important requirements for tire applications. However, in general, BR processes with more difficulty than SBR. Consequently, BR is blended with SBR and natural rubber in tire manufacturing for improved milling, traction, and wet skid resistance of tire treads, while BR contributes good resistance to wear and groove cracking, lowered rolling resistance, and low heat buildup.

2. Styrene–Butadiene Rubber (SBR)



(Str. 42)

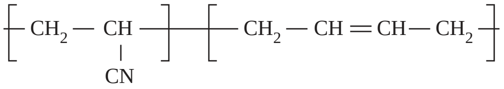
Styrene–butadiene rubber is the largest volume synthetic elastomer commercially available. It can be produced by free-radical emulsion polymerization of styrene and butadiene either at 50 to 60°C (hot emulsion SBR) or at about 5°C (cold emulsion SBR). The two kinds of SBR have significantly different properties. The hot emulsion SBR process, which was developed first, leads to a more branched polymer than the cold emulsion process. Cold SBR has a better abrasion resistance and, consequently, provides better tread wear and dynamic properties.

SBR may also be produced by anionic solution polymerization of styrene and butadiene with alkyllithium initiator (e.g., butyllithium) in a hydrocarbon solvent, usually hexane or cyclohexane. In contrast to emulsion SBR, which may have an emulsifier (soap) content of up to 5% and nonrubber materials sometimes in excess of 10%, solution SBR seldom has more than 2% nonrubber materials in its finished form. Solution SBR has a narrower molecular weight distribution, higher molecular weight, and higher *cis*-1,4-polybutadiene content than emulsion polymerization SBR.

SBR is a random copolymer with a styrene content in the range of 10 to 25%. The presence of styrene contributes to the good wearing and bonding characteristics of SBR and reduces its price. Also, compared with polybutadiene rubber alone, strength, abrasion resistance, and blend compatibility are improved. The butadiene units in SBR are composed approximately of 60 to 70% *trans*-1,4; 15 to 20% *cis*-1,4; and 15 to 20% 1,2 configuration for the polymer at 50°C. Polymers made at lower temperatures have a higher content of *trans*-1,4 polybutadiene units. In diene polymerization, high conversion of monomers or the absence of a chain transfer agent leads to branching due to chain transfer to polymer or reaction of both double bonds.

The major use of SBR is in the production of tires, particularly passenger-car and light-truck tires, and in other automotive applications where SBR is blended with other elastomers. These applications include belts, hoses, seals, and various extruded and molded items. Nontire and nonautomotive uses of SBR are in industries that require hoses, belts, gaskets, or seals. Others include footwear (shoe soles); various kinds of solid wheels; roll covers; coated fabrics; and electrical (wire and cable) insulation.

3. Acrylonitrile–Butadiene Rubber (Nitrile Rubber, NBR)



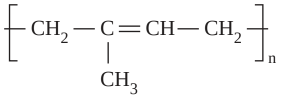
$$\left[CH_2 - \underset{\underset{\displaystyle CN}{|}}{CH} \right]\left[CH_2 - CH = CH - CH_2 \right]$$

(Str. 43)

Nitrile rubber is a unique elastomer that is a copolymer of butadiene and acrylonitrile. As in SBR production, butadiene can be copolymerized with 18 to 40% acrylonitrile in either cold or hot free-radical emulsion polymerization. Unlike SBR, NBR is not suitable for tire production, but it is unique for its excellent oil resistance, which increases with the proportion of acrylonitrile in the copolymer. Elastomers with high acrylonitrile content (40 to 50%) in addition to high hydrocarbon resistance generally are also more resistant to abrasion and have lower permeability to gases. Elastomers with about 20% acrylonitrile content exhibit enhanced resilience that is retained even at low temperatures. NBR retains its good tensile strength and abrasion resistance even after immersion in gasoline, water, alcohols, and aromatic solvents. While it has good heat resistance if properly protected with antioxidants, NBR has poor dielectric properties and ozone resistance.

As result of their excellent oil resistance, nitrile rubbers are used mainly to handle oils, fuels, and similar chemicals in the form of hoses, tubing, gaskets, seals, O-rings, and gasoline hose. These items are used in equipment for transportation of all kinds, food processing, and petroleum production. Nitrile rubbers are also used to enhance the impact strength of polymers such as PVC and ABS. In latex form, nitrile rubber is used to saturate paper for masking tapes, building papers, and labels.

4. Polyisoprene



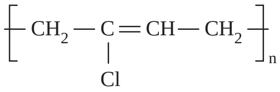
$$\left[CH_2 - \underset{\underset{\displaystyle CH_3}{|}}{C} = CH - CH_2 \right]_n$$

(Str. 44)

Polyisoprene is another widely used commercial synthetic rubber. It is produced by the polymerization of isoprene (2-methyl-1,3-butadiene) in a hydrocarbon solvent such as *n*-pentane using Ziegler–Natta catalyst systems. Out of the eight theoretically possible configurations, only three isomers: *cis*-1,4; *trans*-1,4; and atactic-3,4 forms have been isolated. Depending on the makeup of the catalyst employed in the polymerization reaction, a very high content of *cis*-1,4-polyisoprene can be obtained. The *cis*-1,4-polyisoprene is structurally identical to natural rubber. However, it is cleaner, lighter in color, more uniform and less expensive to process than natural rubber. The *trans*-1,4 isomer has limited commercial use in nonelastomeric applications. It was used originally for covering golf balls, but more recently as a material for orthopedic splints.

Cis-1,4-polyisoprene, like most diene-based elastomers, has poor resistance to attack by ozone, gasoline, oil, and organic solvents. It has, however, many of the good properties of natural rubber, including high resilience, strength, and abrasion resistance. Consequently, it is used mostly in tire making, usually as a replacement for natural rubber in blends with polybutadiene that are used for making heavy-duty truck and bus tires. Other uses of polyisoprene elastomer are in extruded and molded mechanical goods, footwear, sporting goods, and sealants.

5. Polychloroprene (Neoprene)



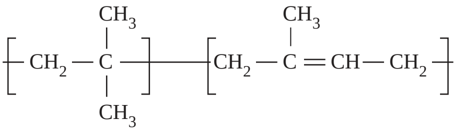
$$\left[CH_2 - \underset{\displaystyle Cl}{\underset{|}{C}} = CH - CH_2 \right]_n$$

(Str. 45)

Polychloroprene, developed and sold under the trade name Neoprene by DuPont, was the first commercially successful synthetic elastomer. It is produced by free-radical emulsion polymerization of chloroprene (2-chloro-1,3-butadiene). The commercial material is mainly *trans*-1,4-polychloroprene, which is crystallizable.

Polychloroprenes are noted generally for their good resistance to abrasion, hydrocarbons, sunlight, oxygen, ozone, gas; weathering characteristics; and toughness. They are more difficult to process than most synthetic elastomers. Polychloroprene elastomer has a wide range of applications, ranging from adhesives to wire coverings. All the applications depend on its overall durability. The largest use of polychloroprene elastomer is in the fabrication of mechanical rubber goods for automotive products; petroleum production; and transportation, construction, and consumer products. The major uses include wire and cable coatings, industrial hoses, conveyor belts, diaphragms, seals, gaskets, O-rings, gasoline tubing, shoe heels, and solid tires. Neoprene latex is used in making gloves, adhesives, and binders.

6. Butyl Rubber



$$\left[CH_2 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} \right] \left[CH_2 - \overset{\displaystyle CH_3}{\overset{|}{C}} = CH - CH_2 \right]$$

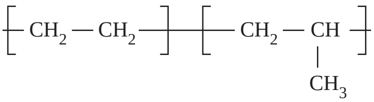
(Str. 46)

Butyl rubber is a copolymer of isobutylene with a small amount (0.5 to 2.5 mol%) of isoprene, which provides the unsaturation sites necessary for vulcanization. Butyl rubber is produced by cationic polymerization of isobutylene and chloroprene in methyl chloride in the presence of Friedel–Crafts catalysts such as aluminum chloride at about –100°C.

Butyl rubber exhibits unusually low permeability to gases and outstanding resistance to attack by oxygen and ozone. It has excellent chemical inertness, due to the very low residual unsaturation, and good electrical properties because of its nonpolar saturated nature. Butyl rubber has good tear resistance. Butyl elastomers can be tailored to have good thermal stability and vibrational damping characteristics.

As a result of its very low gas permeability, butyl rubber is used predominantly in the inner tubes of tires and inner liners for tubeless tires. Some of the other uses of butyl rubber include sealants, adhesives, hoses, gaskets, pads for truck cabs, bridge bearing mounts, and other places where vibration damping is important.

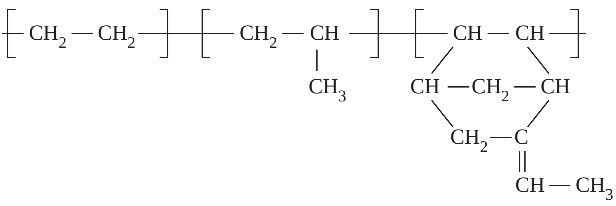
B. ETHYLENE–PROPYLENE RUBBERS



$$\left[CH_2 - CH_2 \right] \left[CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} \right]$$

(Str. 47)

ethylene–propylene copolymer (EPM)



(Str. 48)

ethylene–propylene–diene terpolymer (EPDM)

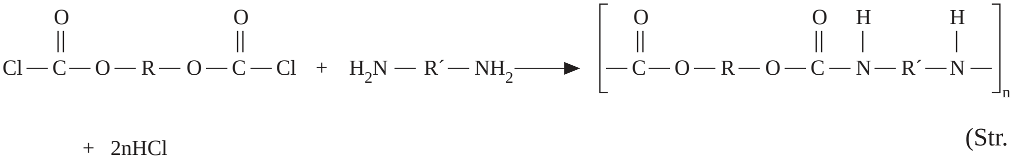
Copolymerization of ethylene with propylene results in a random, noncrystalline copolymer that is a chemically inert and rubbery material. EPM is a saturated copolymer that can be cross-linked through the combination of the free radicals generated by peroxides or radiation. To incorporate sites for vulcanization, an unsaturated terpolymer can be prepared from ethylene, propylene, and a small amount (3 to 9%) of a nonconjugated diene (EPDM). The diene is either dicyclopentadiene, ethylidene norbornene, or 1,4-hexadiene. The resulting unsaturated terpolymer can be vulcanized by traditional techniques. Each of the termonomers confers different characteristics on the final elastomer.

Ethylene–propylene elastomers are made by solution polymerization of ethylene and propylene in a solvent such as hexane using Ziegler–Natta catalysts. EPDM terpolymers can be similarly made by adding 3 to 9% of any of the above dienes to the monoolefin mixture.

Even though tire use is small, automotive applications are still the largest market for ethylene–propylene elastomers. They are used predominantly in radiator and heater hoses, seals, gaskets, grommets, and weather stripping. Blends of polypropylene and EPDM are used as material in the manufacture of car bumpers, fender extensions, and rub strips. Other applications of ethylene–propylene elastomers include appliance parts, wire and cable insulation, and modification of polyolefins for improved impact and stress resistance.

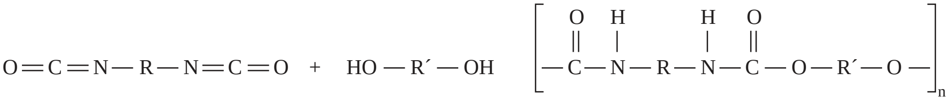
C. POLYURETHANES

Polyurethane is the generic name of polymers with the urethane $(-N-\overset{\overset{O}{\|}}{C}-O-)$ interunit linkage in the chain. There are two main synthetic routes for the preparation of linear urethane homopolymer. These are the condensation reaction between a bischloroformate and a diamine and the addition reaction of a diisocyanate with diol:



$$Cl-\overset{\overset{O}{\|}}{C}-O-R-O-\overset{\overset{O}{\|}}{C}-Cl + H_2N-R'-NH_2 \longrightarrow \left[-\overset{\overset{O}{\|}}{C}-O-R-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R'-\overset{\overset{H}{|}}{N}-\right]_n + 2nHCl$$

(Str. 49)

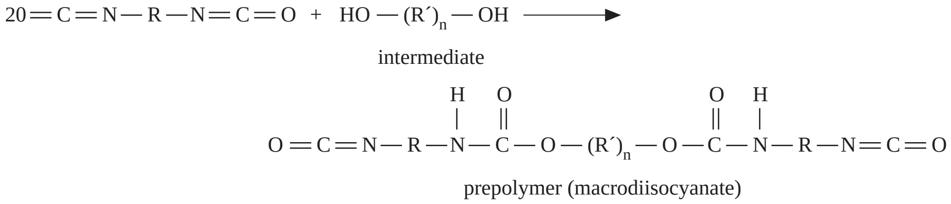


$$O=C=N-R-N=C=O + HO-R'-OH \quad \left[-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-R'-O-\right]_n$$

(Str. 50)

Typical diisocyanates include aromatic diisocyanates such as methylenediphenyl isocyanate (MDI) (or 4,4-diphenylmethane dissocyanate) and toluene diisocyanate (TDI). TDI is generally supplied as an 80:20 mixture of 2,4 and 2,6 isomers. Aliphatic diisocyanates include 1,6-hexamethylene diisocyanate (HMI). Dihydroxyl compounds employed are usually hydroxyl-terminated low-molecular-weight polyesters, polyethers, hydrocarbon polymers, and polydimethylsiloxanes. A typical example is polytetramethylene oxide (PTMO). Cross-linking or chain extension is achieved by using a number of di- and polyfunctional active hydrogen-containing compounds, the most significant of which are diol, diamines, and polydroxyl compounds.

Polyurethanes are used in four principal types of products: foams, elastomers, fibers, and coatings. The majority of polyurethane is used as rigid or flexible foams. However, about 15% is used for elastomer applications. Production of polyurethane elastomers involves a number of steps. As indicated above, an intermediate hydroxyl-terminated low-molecular-weight polyester or polyether is prepared. This intermediate is reacted with an isocyanate to form a prepolymer (macrodiisocyanate). The prepolymers are coupled or vulcanized by adding a diol or diamine:



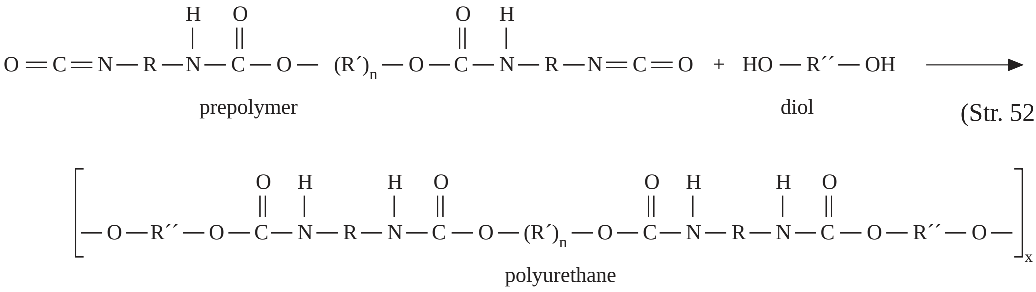
$$2O=C=N-R-N=C=O + HO-(R')_n-OH \longrightarrow$$

intermediate

$$O=C=N-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-(R')_n-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-N=C=O$$

prepolymer (macrodiisocyanate)

(Str. 51)



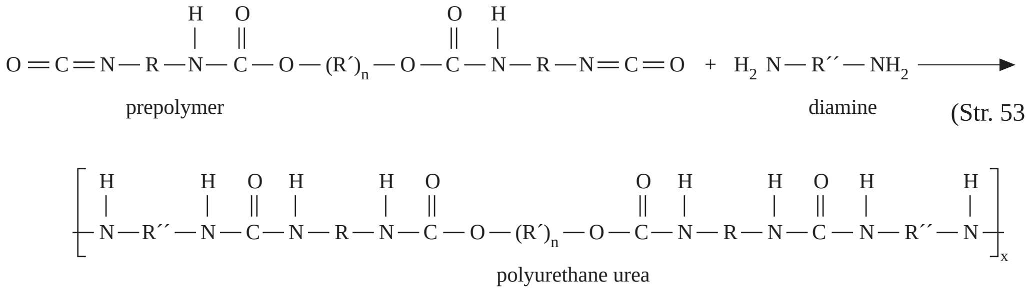
$$O=C=N-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-(R')_n-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-N=C=O + HO-R''-OH \longrightarrow$$

prepolymer diol

$$\left[-O-R''-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-(R')_n-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R''-O-\right]_x$$

polyurethane

(Str. 52)



$$O=C=N-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-(R')_n-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-N=C=O + H_2N-R''-NH_2 \longrightarrow$$

prepolymer diamine

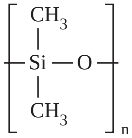
$$\left[-\overset{H}{\overset{|}{N}}-R''-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-(R')_n-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R''-\overset{H}{\overset{|}{N}}-\right]_x$$

polyurethane urea

(Str. 53)

Polyurethane elastomers have high strength; extremely good abrasion resistance; good resistance to gas, greases, oils, and hydrocarbons; and excellent resistance to oxygen and ozone. Applications include solid tires, shoe soles, gaskets, and impellers.

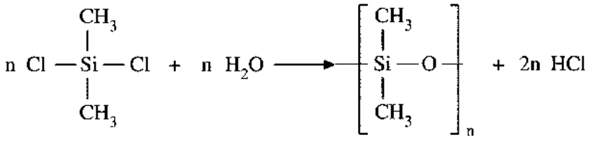
D. SILICONE ELASTOMERS



$$\left[-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O-\right]_n$$

(Str. 54)

Polysiloxanes can be prepared by the hydrolysis of dichlorosilanes such as dimethydichlorosilanes:



$$n\ Cl-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-Cl + n\ H_2O \longrightarrow \left[-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O-\right]_n + 2n\ HCl$$

(Str. 55)

The process tends to result in the formation of cyclic products, typically trimers and tetramers. High-molecular-weight elastomers may be obtained by a subsequent base-catalyzed ring-opening polymerization of these cyclic siloxanes. Cross-linked siloxane elastomers are produced by partially cross-linking these linear polydimethylsiloxanes through the use of peroxide-based free-radical-initiated process. Alternatively, cross-linking may be effected by the incorporation of trifunctional monomers such as trichlorosiloxanes. To improve the efficiency of vulcanization, unsaturation is introduced into the polymer by copolymerizing a vinyl-group-containing siloxane. Typically about 10% of the methyl groups in polydimethylsiloxane are replaced by vinylmethylsilanol.

Silicone elastomers are noted for high temperature and oxidative stability, low temperature flexibility, good electrical properties, and high resistance to weathering and oil. They are used in wire and cable insulation and surgical implants and as material for gaskets and seals.

E. THERMOPLASTIC ELASTOMERS (TPE)

Thermoplastic elastomers are materials with functional properties of conventional thermoset rubbers and the processing characteristics of thermoplastics. They do not have the permanent cross-links present in vulcanized elastomers. Instead, elastomeric properties are the result of rigid-domain structures used to create a network structure. The domain structure is based on a block copolymer; one block consists of relatively long, flexible polymer chains (soft segment), while the other block is composed of stiff polymer molecules (hard segment). The rubber–plastic TPE is a two-phase mixture with a dispersion of the soft rubbery phase in a continuous glassy plastic matrix (Figure 15.12). Each polymer or major polymer segment or block has its softening temperature, T_s. The useful temperature range for TPE lies above the T_s of the elastomeric (soft) phase and below the T_s of the hard phase. Within this temperature range, the polymer molecules in the soft phase can undergo significant segmental motion. However, this motion is restricted by the bonds, such as hydrogen bonding, between chemical groups in the hard and soft phases. The reinforcing action of the hard phase disappears above its softening temperature, and the TPE behaves as a viscous liquid. Upon cooling, the hard phase resolidifies and the TPE becomes rubbery again. Similarly, cooling below the T_s of the soft phase changes the material from a rubbery to a hard, brittle solid. This process is also reversible. It is evident, therefore, that the physical nature of the domain structure of thermoplastic elastomers permits their reversibility. These elastomers are thermoplastic and can therefore be fabricated by conventional molding techniques by heating them above the softening temperature of the hard phase. The advantages and disadvantages of thermoplastic elastomers compared with conventional cross-linked rubbers are shown in Table 15.18.

A number of different classes of thermoplastic elastomers are currently commercially available. These include styrenics, polyurethanes, polyesters, polyolefin, and polyamides.

1. Styrene Block Copolymers (Styrenics)

The first and still most commercially important thermoplastic elastomers are those based on A–B–A block copolymers. A is a high-molecular-weight (50,000 to 100,000) polystyrene hard block, and B is low-molecular-weight (10,000 to 20,000) diene soft (elastomeric) block such as polybutadiene or polyisoprene or, sometimes, poly(ethylene–butylene).

These types of TPE, known as styrenics, e.g., Shell’s kraton, have a useful temperature range of –70°C to 100°C. They are viscous melts above 130°C and can be molded and extruded into various articles. Typical applications include shoe soles, adhesives, and a number of molded products.

2. Thermoplastic Polyurethane Elastomers (TPUs)

Thermoplastic polyurethane elastomers are linear copolymers of the (AB)n type. They are composed of one block of polymer chain consisting of a relatively long, flexible “soft segment” derived from hydroxy-terminated polyester, polyether, or polyalkene. The second copolymer block is composed of a highly polar, rather stiff block (hard block) formed by the reaction of diisocyanates with low-molecular-weight diol or diamine chain extender. Intermolecular hydrogen bonding between the –NH group (proton donor) and the carbonyl group or ether oxygens (proton acceptor) results in a domain structure in which the hard blocks restrict the movement of the soft segments. This provides resistance to deformation when these elastomers are stretched.

Thermoplastic polyurethanes exhibit good abrasion and mar resistance. They are stable to attack by oxygen and hydrocarbons, but are sensitive to moisture and acidic and basic solutions, which can result in hydrolytic chain scission. They are used as coatings and adhesives and in footwear and automotive parts.

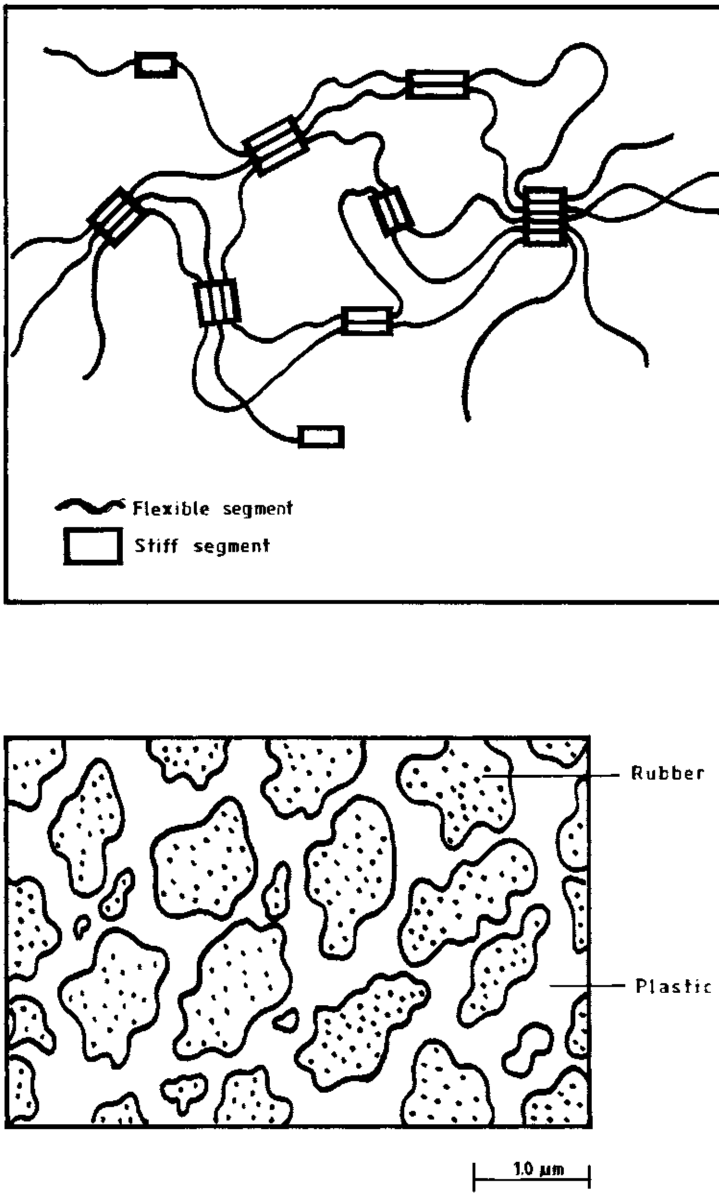


Figure 15.12 *Thermoplastic elastomers are composed of a two-phase system either of a block copolymer (top) or a rubber–plastic mixture (bottom).*

3. Polyolefin Blends

Olefinic thermoplastic elastomers are block copolymers or blends of polyolefins — commonly, polypropylene, which forms the hard crystalline block, and another olefin block, most commonly ethylene or EPDM. Some less common soft segments include natural rubber, nitrile rubber, and EVA. Olefinic thermoplastic elastomers exhibit better processability than neoprene and have excellent resistance to oils. Therefore, they offer attractive replacements for neoprene in oil-resistant wire and cable insulation.

4. Thermoplastic Copolyesters (COPE)

Thermoplastic copolyesters are condensation block copolymers based on a crystalline polyester hard segment and an amorphous long-chain polyether soft segment. The hard segment, for example, formed

Table 15.18 *Advantages and Disadvantages of Thermoplastic Elastomers*

Advantages	Disadvantages
TPEs require little or no compounding since they are fully formulated and are ready for use as received. Offer rapid, efficient, and economical means of fabricating rubber articles.	Most TPEs may require drying before processing
Processing of TPEs is cheaper and simpler requiring fewer steps than does a thermoset rubber. A single step is required to shape TPEs into final article, whereas thermoset rubbers require mixing and vulcanization in addition to the shaping step.	TPEs melt at elevated temperatures; consequently, they are unsuitable for applications requiring even brief exposures to temperatures above their melting points. Many thermoset rubbers can withstand such a short exposure.
Processing times for TPEs are shorter since the long cycle time required for vulcanization is eliminated. Cycle time is typically seconds instead of the minutes required for thermoset rubbers. This enhances productivity and reduces costs.	
Being thermoplastic, TPE scrap generated during processing can be recycled without any loss in functional properties. In contrast, thermoset elastomers are not recyclable.	
As a result of the fewer processing steps and shorter cycle time, lower energy is consumed in TPE processing than processing of thermoset rubbers.	
It is easier to obtain finished parts having closer tolerances with TPEs because of consistent material base and greater ease and control of processing.	
Elastomers are generally purchased on weight basis but used on volume basis. Consequently, TPEs offer cost advantages since they normally have lower specific gravity than thermoset rubbers.	

From Heineck, D.W. and Rader, C.P., *Plast. Eng.*, 45(3), 87, 1987. With permission.

by the reaction of terephthalic acid and butanediol, and the soft segment, such as poly(tetramethylene ether glycol), are joined by an ester linkage. Thermoplastic copolyesters, for example, DuPont Hytrel, are durable, high-performance thermoplastic elastomers that exhibit good resistance to abrasion and hydrocarbons. They are, however, susceptible to attack by moisture, acids, and bases at elevated temperatures. Applications of thermoplastic copolyesters include wire and cable insulation, gaskets, seals, hoses, and automotive parts.

5. Thermoplastic Polyamides

Thermoplastic polyamides are a relatively new class of block-copolymer thermoplastic elastomers. They have amide linkages between the hard and soft segments. This class of thermoplastic elastomers has the highest performance and is the most expensive of the TPEs.

Example 15.7: Currently available thermoplastic elastomers cannot be used in applications with use temperatures above 170°C. Comment on this statement.

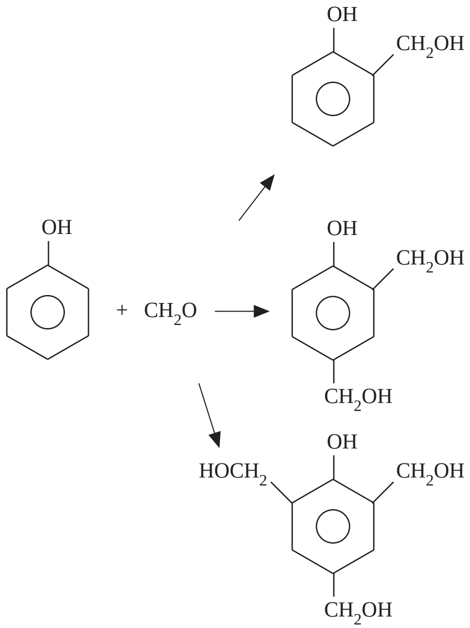
Solution: The thermoplastic elastomers that are currently available are used in numerous applications requiring the elastomeric properties of conventional thermoset rubbers. These include nontire automotive applications (fascia, hoses, gaskets, seals, bushings, protective boots, weather stripping); mechanical rubber goods (components of modern appliances, including dishwashers, power drills, telephone, and electronic equipment); architectural and construction uses (window glazing systems, seals for windows and doors, primary electrical insulation and jacketing for cables, and foamed seals and tapes); and use in rubber articles in contact with food and in medical applications. However, the upper limit of the useful temperature range of thermoplastic elastomers is set by the softening or melting temperature of the hard segment. Above this temperature, the TPE loses its elastomeric properties and becomes a viscous liquid. Thermoplastic elastomers that are currently available have hard segments, with melting or softening temperatures much below 170°C.

IX. THERMOSETS

The principal feature that distinguishes thermosets and conventional elastomers from thermoplastics is the presence of a cross-linked network structure. As we have seen from the above discussion, in the case of elastomers the network structure may be formed by a limited number of covalent bonds (cross-linked rubbers) or may be due to physical links resulting in a domain structure (thermoplastic elastomers). For elastomers, the presence of these cross-links prevents gross mobility of molecules, but local molecular mobility is still possible. Thermosets, on the other hand, have a network structure formed exclusively by covalent bonds. Thermosets have a high density of cross-links and are consequently infusible, insoluble, thermally stable, and dimensionally stable under load. The major commercial thermosets include epoxies, polyesters, and polymers based on formaldehyde. Formaldehyde-based resins, which are the most widely used thermosets, consist essentially of two classes of thermosets. These are the condensation products of formaldehyde with phenol (or resorcinol) (phenoplasts or phenolic resins) or with urea or melamine (aminoplastics or amino resins).

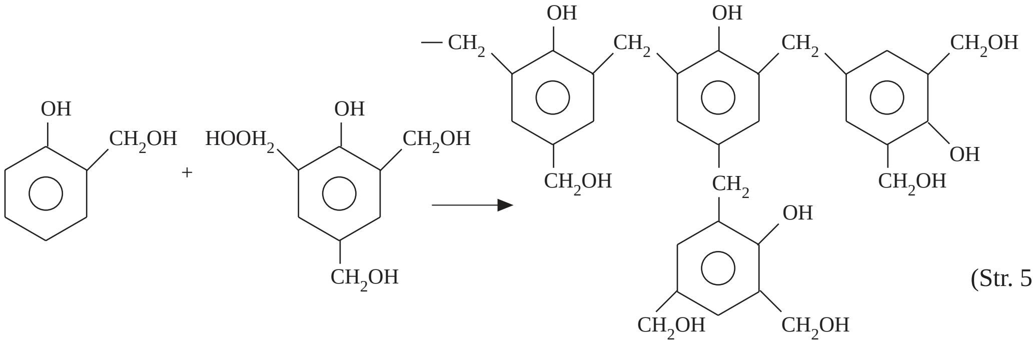
A. PHENOLIC RESINS

Phenolic resins, introduced in 1908, are formed by either base- or acid-catalyzed addition of formaldehyde to phenol to give ortho- and para-substituted products. The nature of these products depends largely on the type of catalyst and the mole ratio of formaldehyde to phenol. In resole formation, excess formaldehyde is reacted with phenol under basic conditions. The initial reaction products are ortho- and para-substituted mono-, di-, and trimethylolphenols:



(Str. 56)

When heated, methylol phenols, condense either through methylene or methylene oxide linkages to give a low-molecular-weight prepolymer called resole, which is soluble and fusible and contains alcohol groups:

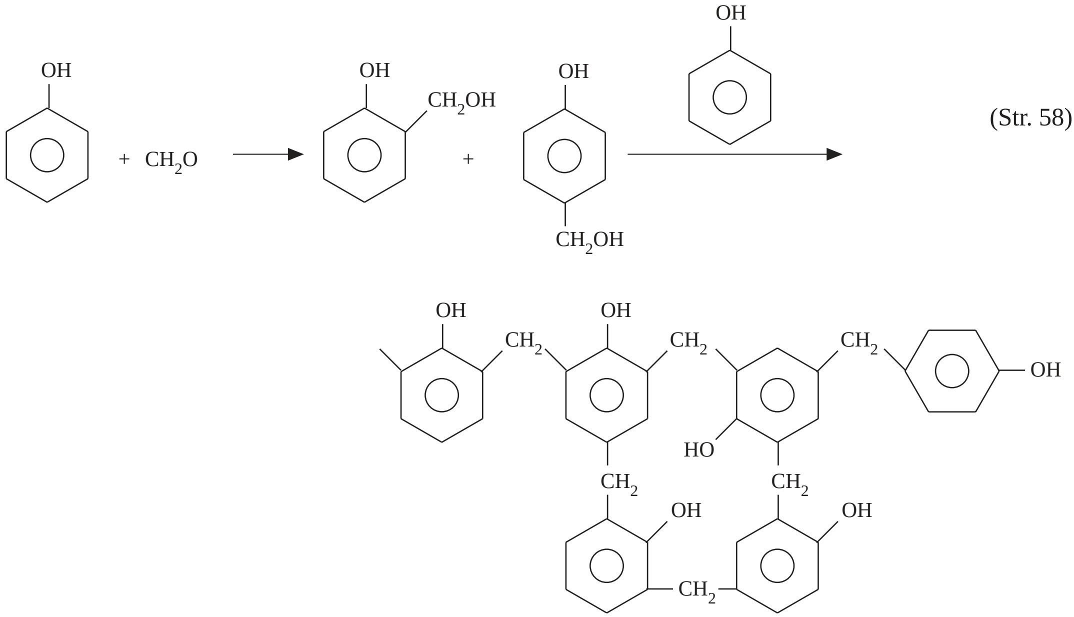


(Str. 57)

resole

When resoles are heated at elevated temperatures, under basic, neutral, or slightly acidic conditions, condensation of large numbers of phenolic nuclei takes place resulting in a high-molecular-weight cross-linked network structure.

Formation of novolak involves an acid-catalyzed reaction of formaldehyde with excess phenol (i.e., formaldehyde-to-phenol mole ratio less than 1). The initial methylol phenols condense with the excess phenol to form dihydroxydiphenyl methane, which undergoes further condensation yielding low-molecular-weight prepolymer or novolak. Unlike resoles, novolaks do not contain residual methylol groups. They are fusible and insoluble.



(Str. 58)

novalak

When novolaks are heated with additional paraformaldehyde or hexamethylene tetramine to raise the formaldehyde-to-phenol ratio above unity, high-molecular-weight cross-linked network structure is formed.

The largest use of phenol–formaldehyde resins is in plywood manufacture. Other applications include lacquers and varnishes, cutlery handles, and toilet seats. Molded parts are used in distributor caps, fuse boxes, and other electrical outlets because of the superior dimensional stability and electrical properties of PF resins. Decorative laminates from PF resins are used for countertops and wall coverings, while industrial laminates are used for electrical parts, including printed circuits. Other industrial applications of phenolics based on their excellent adhesive properties and bond strength include brake linings, abrasive wheels and sandpaper, and foundry molds.

B. AMINO RESINS

Urea–formaldehyde (UF) resins are obtained by a two-staged polymerization process. The first stage involves the reaction of formaldehyde with urea at a formaldehyde-to-urea (F/U) mole ratio equal to or greater than one under slightly alkaline conditions. This results in the formation of mono- and dimethylol urea and, possibly, trimethylol urea, depending on the F/U ratio (Figure 15.13A). The next stage involves condensation of these methylol ureas, usually under acidic conditions. Depending on the extent of reaction, the condensation reactions lead ultimately to a cross-linked product (Figure 15.13B). The production of melamine–formaldehyde resins, like UF resins, involves initial methoylation reaction followed by the formation of a rigid network structure (Figure 15.13C,D).

In contrast to phenolic resins, amino resins are clear and colorless. They are harder and have higher strength but lower moisture and heat resistance than phenolics. Melamine–formaldehyde resins have better moist-heat aging resistance than UF resins, but are more costly. Like phenolics, aminoplasts can be used to improve the shrink and crease properties, fire retardance, and water repellency of textiles and the wet and bursting strength of paper. UF resins are used in molding and in laminating applications. However, a greater part of UF resins are used for adhesive applications, particularly where the darker color of phenolics may be objectionable and the relatively inferior durability of UF resins does not pose

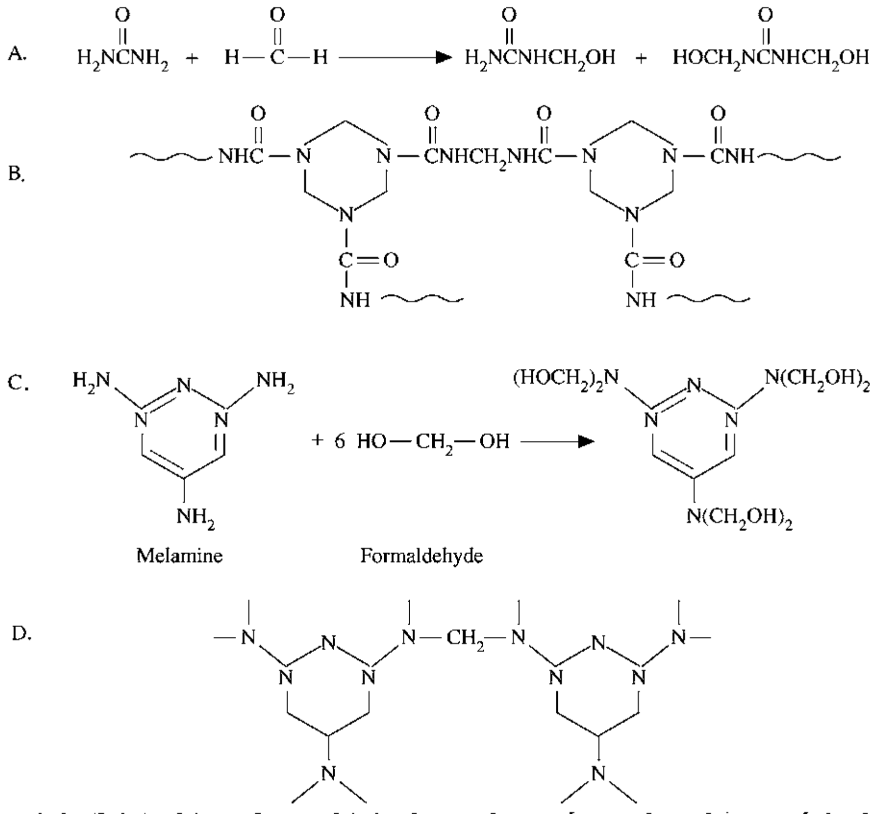
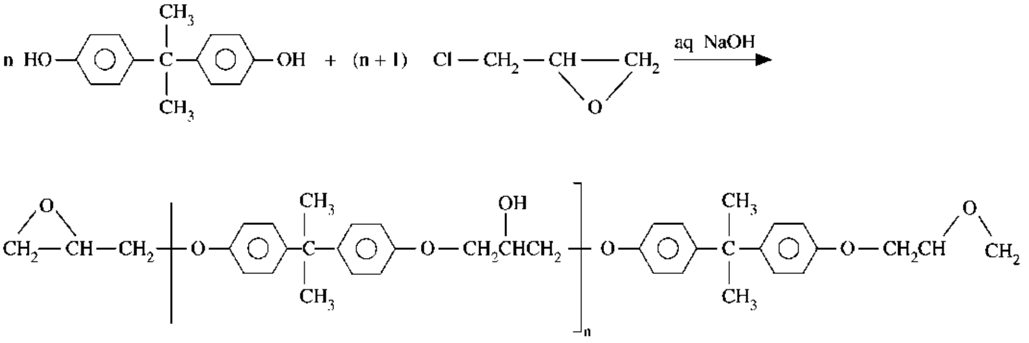


Figure 15.13 *Two-staged process for the formation of network structure by UF resin (A and B) and MF resin (C and D).*

a serious problem. A typical example is in the production of interior grade plywood. UF resins are also used in the manufacture of electrical switches and plugs. Typical applications of MF resins include high-quality decorative dinnerware, laminated counter-, cabinet, and tabletops; and electrical fittings. Formaldehyde-based resins may be used neat or compounded with various additives such as wood flour to improve strength properties and reduce cost.

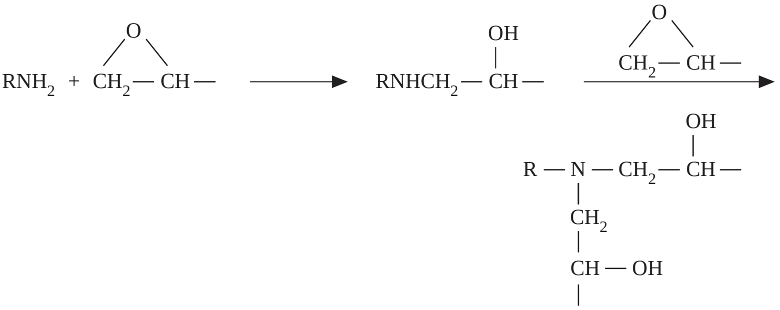
C. EPOXY RESINS

Epoxy resins are complex network polyethers usually formed in a two-staged process. The first stage involves a base-catalyzed step-growth reaction of an excess epoxide, typically epichlorohydrin with a dihydroxy compound such as bisphenol A. This results in the formation of a low-molecular-weight prepolymer terminated on either side by an epoxide group.



(Str. 59)

The prepolymer may be a viscous liquid, generally for commercial epoxies, or a hard and tough solid depending on the value of n. Other hydroxyl-containing compounds such as resorcinol, glycol, and glycerol can also be used but commercial epoxy resins are based on bisphenol A. In the second stage, a cross-linked network structure is formed by curing the prepolymer with active hydrogen-containing compounds. These curing agents include polyamines, polyacids and acid anhydrides, polyamides, and formaldehyde resins. Amines, preferably liquid amines like triethylene diamine, effect cure of the prepolymer by ring-opening of the terminal epoxide groups.

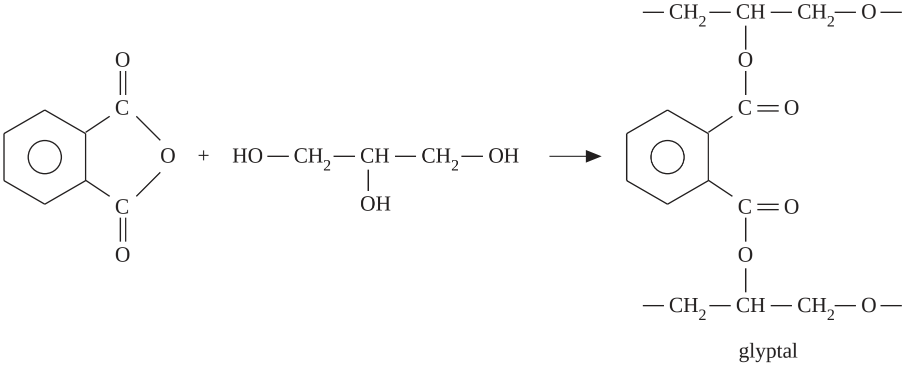


(Str. 60)

Epoxy resins are very versatile materials with a wide range of applications. They are tough and flexible and have high tensile, compressive, and flexural strengths. Epoxy resins have excellent chemical and corrosion resistance and good electrical insulation properties. They can be cured over a wide range of temperatures with very low shrinkage. Epoxy resins have outstanding adhesion to a variety of substrates, including metals and concrete. Consequently, the major uses of epoxy resins are in protective coating applications. Other uses of epoxies include laminates and composites. Potting, encapsulation, and casting with epoxy resins are common procedures in the electrical and tooling industries.

D. NETWORK POLYESTER RESINS

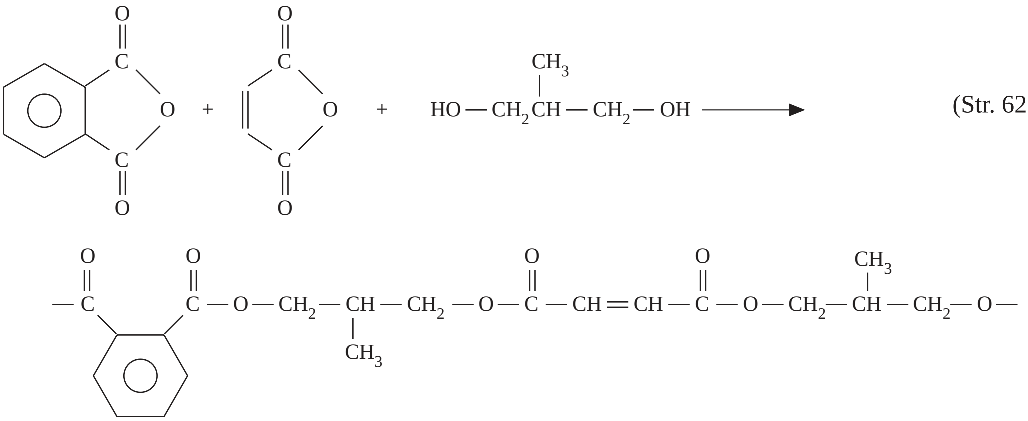
Network polyester resins may be categorized into saturated and unsaturated polyesters. Unlike linear saturated polyesters such as PET, which are made from difunctional monomers, saturated polyesters (glyptal) are formed by the reaction of polyols such as glycerol with dibasic acids such as phthalic anhydride.



(Str. 61)

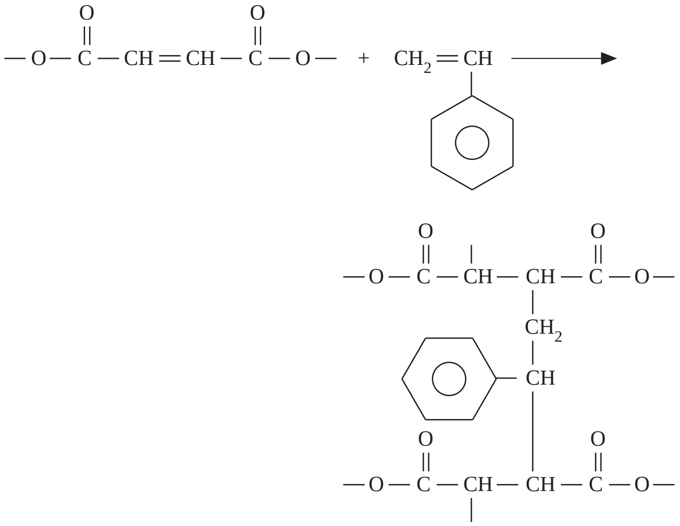
The reaction involves an initial formation of a viscous liquid that is then transferred to a mold for hardening or network formation.

Unsaturated network polyesters may be produced by using an unsaturated dibasic acid or glycol or both. Typically the unsaturated dibasic acid, such as maleic anhydride or fumaric acid, is copolymerized with a saturated acid such as phthalic acid and a glycol (e.g., propylene glycol or diethylene glycol).



(Str. 62)

The acid and glycol components are allowed to react until a low-molecular-weight (1500 to 3000) viscous liquid (usually) is formed. This prepolymer is then dissolved in styrene monomer, which participates in cross-linking with the double bonds in the prepolymer by addition of peroxide or hydroperoxide to form the final network structure.



(Str. 63)

The saturated acid (phthalic anhydride) helps to reduce the cross-link density and, hence, the brittleness of the cured polyester resin. Resin composition can be varied so that product properties can be tailored to meet specific end-use requirements. For example, a resin with enhanced reactivity and improved stiffness at high temperatures is obtained by increasing the proportion of unsaturated acid. On the other hand, a less reactive resin with reduced stiffness is obtained with a higher proportion of the saturated acid.

Unsaturated polyester resins are light in color, easy to handle and cure rapidly without emission of volatiles. They are dimensionally stable and have good physical and electrical properties. The major markets for reinforced polyester resins are in marine applications, transportation, construction, and electrical and consumer products. Fabrication of pleasure boats as well as large commercial vessels from polyester sheet molding compounds (SMC) are typical marine applications of polyester. In transportation, polyester resins are used in passenger-car parts and bodies and truck cabs in an attempt to reduce weight. Polyester resins are used mainly as sheet and paneling and also as tubs, shower stalls, and pipes in the construction industry. Consumer products from polyesters include luggage, chairs, fishing rods, and trays. Other uses of polyester are electrical applications, appliances, business equipment, and corrosion-resistant products.

X. PROBLEMS

15.1. Explain the following observations.

- a. Extremely broad MWD HDPE with polypropylene copolymer is used in the insulation of telephone cables.
- b. Polypropylene is preferred to polyethylene and polystyrene in products that must be heat or steam sterilized.
- c. Polypropylene is inert to ethanol and acetone, while solvents like benzene and carbon tetrachloride will cause swelling.
- d. To retain transparency, random copolymers of propylene and ethylene are used for films applications, while polypropylene homopolymer is used almost exclusively for filaments.
- e. Chlorinated PVC pipes are used in residential hot-water systems.
- f. PVC currently has limited application in food packaging and in such applications it must meet stringent government standards.
- g. General-purpose ABS finds extensive use as refrigerator door and food liners, while fire-retardant grades are used in appliance housing, business machines, and television cabinets and in aircraft for interior applications.
- h. Nylon is used for low- and medium-voltage 60-Hz application, for example, as secondary insulation or jacket for primary electrical wire insulation.

i. Nylons 11, 12, 6,12 are preferred to nylons 6 and 6,6 for automotive wiring harness and pneumatic tubing.
j. Principal applications of poly(phenylene sulfide) include cookware, bearings, and pump parts for service in various corrosive environments.
k. Compared with PTFE, poly(chlorotrifluoroethylene) has a lower melting point (218°C vs. 327°C); has inferior electrical properties, particularly for high frequency applications; and can be quenched to quite clear sheets.
l. Butyl rubber has excellent resistance to ozone attack and is less sensitive to oxidative aging than most other elastomers — for example, natural rubber.

REFERENCES

1. Frados, J., Ed., *The Society of the Plastics Industry,* 13th ed., Society of the Plastics Industry, New York, 1977.
2. Ulrich, H., *Introduction to Industrial Polymers,* Macmillan, New York, 1982.
3. Waddams, A.L., *Chemicals from Petroleum,* Gulf Publishing Co., TX, 1980.
4. Chruma, J.L. and Chapman, R.D., *Chem. Eng. Prog.,* 81(1), 49, 1985.
5. Fried, J.R., *Plast. Eng.,* 38(12), 21, 1982.
6. Fried, J.R., *Plast. Eng.,* 39(5), 35, 1983.
7. Billmeyer, F.W., Jr., *Textbook of Polymer Science,* 3rd ed., Interscience, New York, 1984.
8. Mock, J.A., *Plast. Eng.,* 40(2), 25, 1984.
9. Lundberg, R.D., Ionomers, in *Encyclopedia of Chemical Technology,* 3rd ed., Mark, H.F., Othmer, D.F., Overberger, C.G., and Seaborg, G.T., Eds., Interscience, New York, 1984.
10. *1979/80 Modern Plastics Encyclopedia,* McGraw-Hill, New York, 1980.
11. MacKnight, W.J. and Earnest, T.R., Jr., *J. Polym. Sci. Macromol. Rev.,* 16, 41, 1981.
12. Fried, J.R., *Plast. Eng.,* 39(3), 67, 1983.
13. Greek, B.F., *Chem. Eng. News,* 25, March 21, 1988.
14. Gogolewski, S., *Colloid Polym. Sci.,* 267, 757, 1989.
15. Heineck, D.W. and Rader, C.P., *Plast. Eng.,* 45(3), 87, 1987.