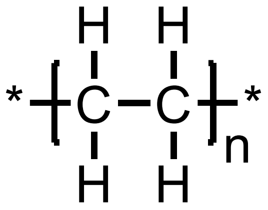
POLYMER PROPERTIES AND APPLICATIONS

The rapid growth and widespread use of polymers are due largely to the versatility of their properties. 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.

POLYETHYLENE



$$*-\left[\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{C}\\ |\\ \mathrm{H}\end{array}-\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{C}\\ |\\ \mathrm{H}\end{array}\right]_n-*$$

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), 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 removed properly 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 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 at100 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-mediumdensity 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.

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.

Properties: 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 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. 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.

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 Mw/Mn 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.

Applications: 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

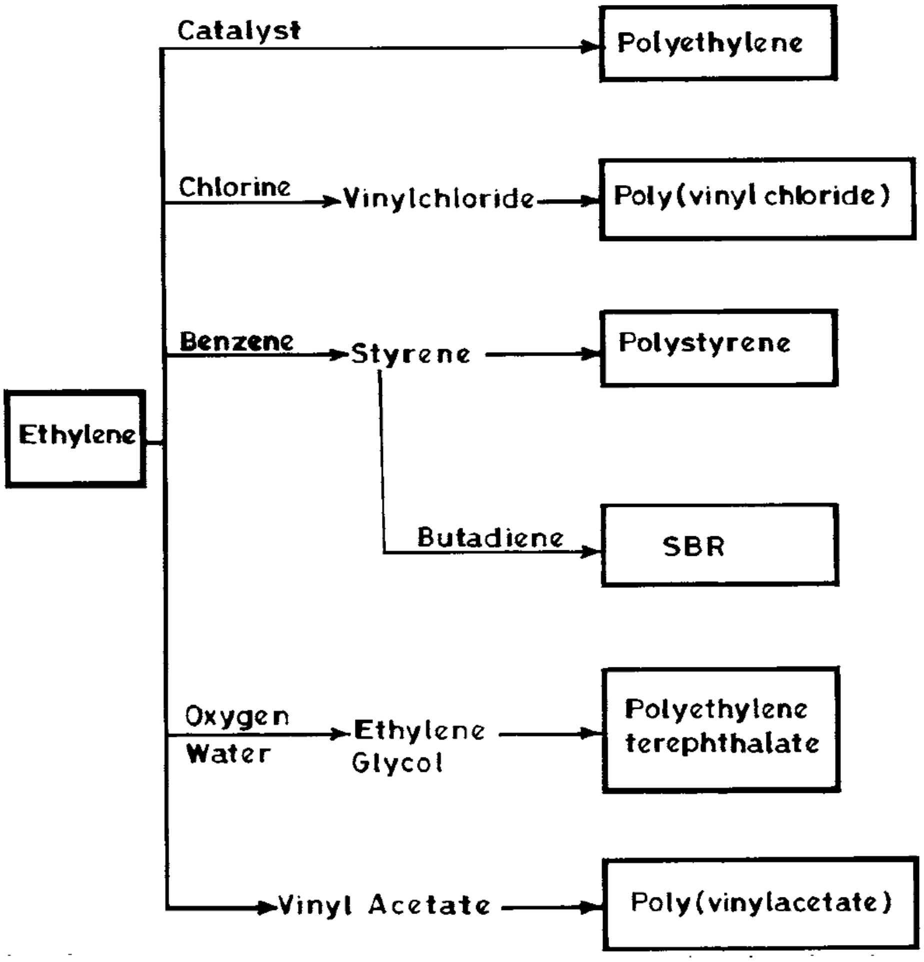
Q1. Why EVA and EEA copolymers are sometimes preferable to conventional LDPE for wire and cable insulation, particularly for outdoor applications?

Ans: LDPE, on exposure to light and O2, 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.

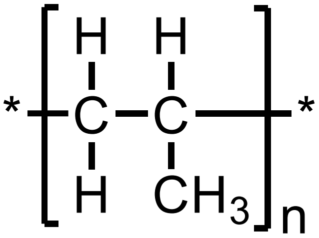
Q2. LDPE is used mainly as thin film for packaging and sheets while HDPE is used predominantly in injection molding of crates, pails, tubs, and automobile gas tanks. EVA copolymer containing a high percentage of the ester comonomer is used in film applications such as disposable protective gloves. Explain.

Ans: 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.



Some polymers from ethylene

B. POLYPROPYLENE (PP)



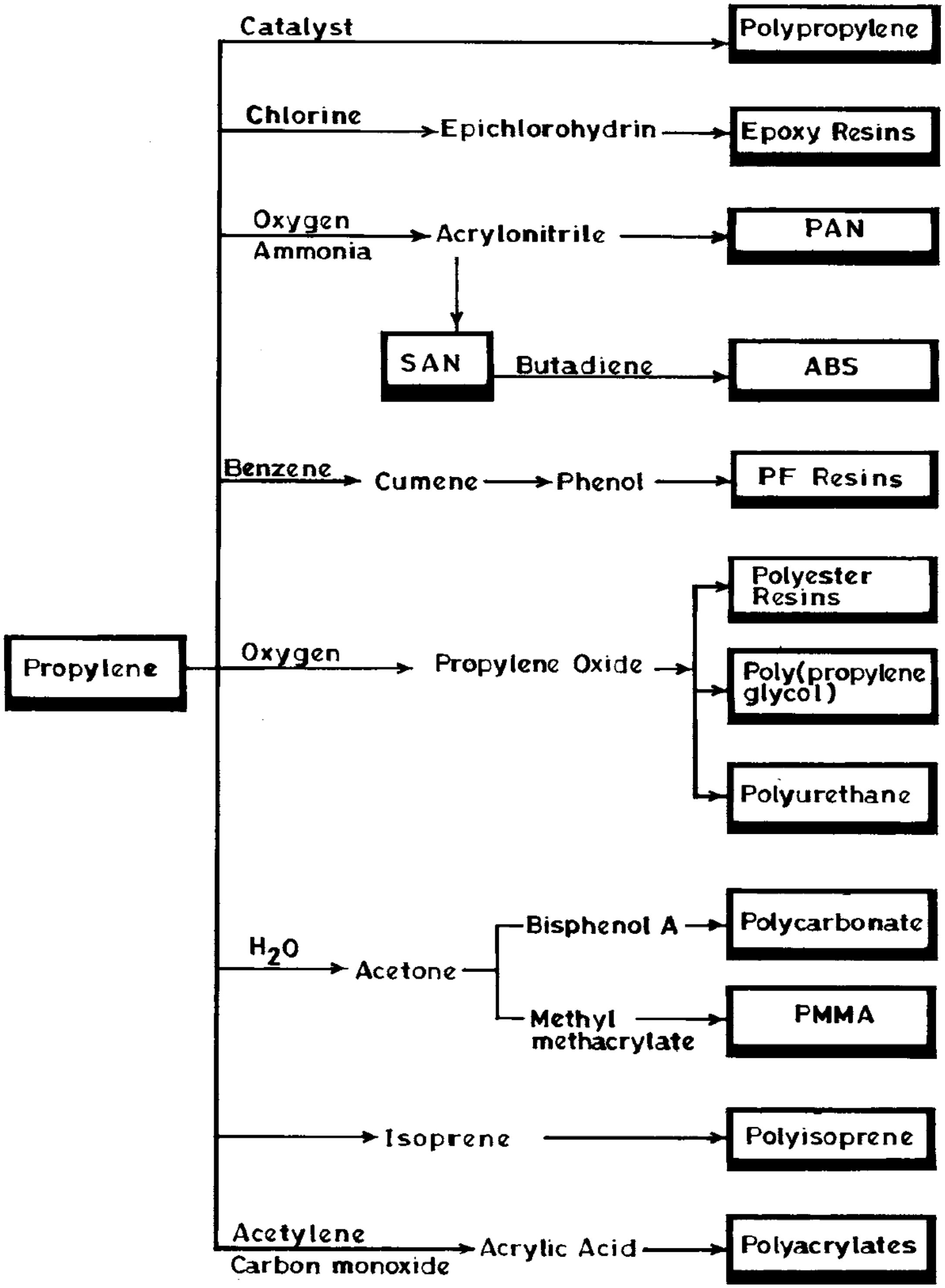
$$*\!-\!\left[\begin{array}{cc} H & H \\ | & | \\ C\!-\! & C \\ | & | \\ H & CH_3 \end{array}\right]_n\!-\!*$$

Polypropylene is the third-largest volume polyolefin and one of the major plastics world-wide. 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.

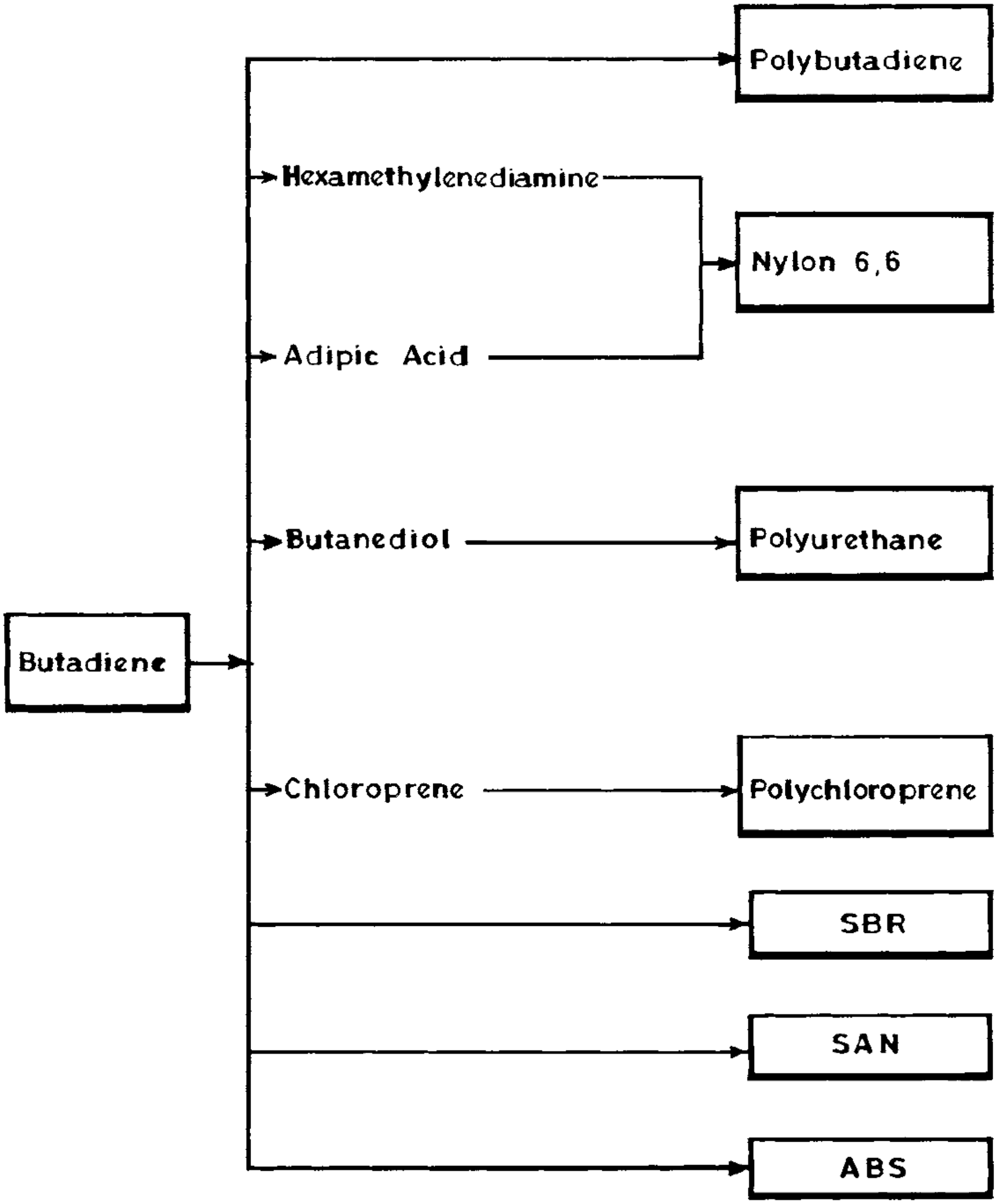
Polypropylene can be made in isotactic (*i*-PP), syndiotactic (*s*-PP), and atactic (*a*-PP) forms. Ziegler–Natta-type catalysts are used to produce stereoregular polypropylene. Usually 90% or more of the polymer is in the isotactic form, which is the form with properties of commercial interest. Isotactic 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. 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.

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

Applications: 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.

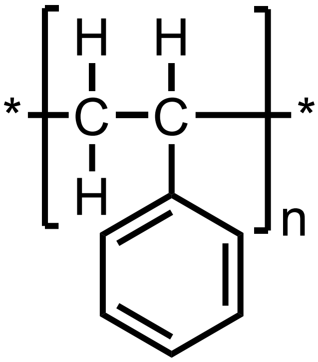


Some polymer from propylene



Some polymers from butadiene

Polystyrene:



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. 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.

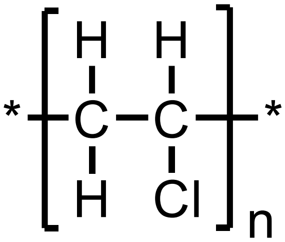
GP-PS is a clear, rigid polymer that is relatively chemically inert. Polystyrene, as produced, has outstanding flow characteristics and consequently is very easy to process. Its excellent optical properties, including high refractive index, make it useful in optical applications. However, GP-PS has a number of limitations, including its brittleness, low heat-deflection temperature, 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 (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 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.

POLY(VINYL CHLORIDE) (PVC)



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 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 Tg (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.

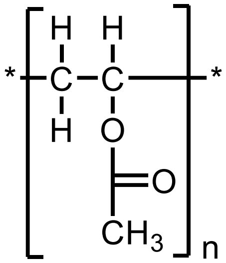
The properties of PVC can be modified through chemical modification, copolymerization, and blending. PVC homopolymer contains about 57% chlorine. Chlorinated PVC with the chlorine content increased to 67% has a higher heat deflection temperature than the homopolymer. This extends the temperature range 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.

Q1. PVC has an advantage over other thermoplastic polyolefins in applications such as insulation for electrical circuitry in household electronic appliances. Explain.

Ans: 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.

POLY(VINYL ACETATE) (PVAC)

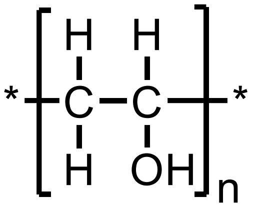


Poly(vinyl acetate) is the most widely used vinyl ester polymer. It is also the precursor or starting material for the production of two other polymers that cannot be prepared by direct polymerization because the starting monomer is unstable. These are poly(vinyl alcohol) and poly(vinyl acetal). The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

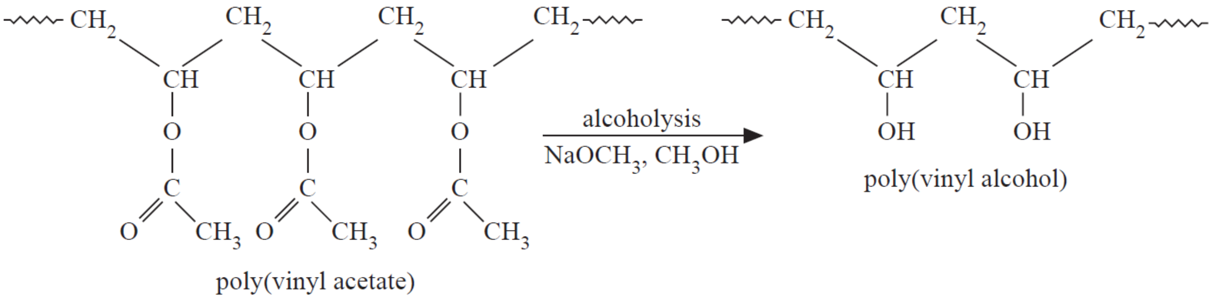
As a result of its highly exothermic nature, bulk polymerization of vinyl acetate poses problems at high conversions. The properties of the resulting polymer are susceptible to deterioration due to chain branching. Therefore, bulk polymerization of vinyl acetate is usually stopped at 20 to 50% conversion. 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, Tg, 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.

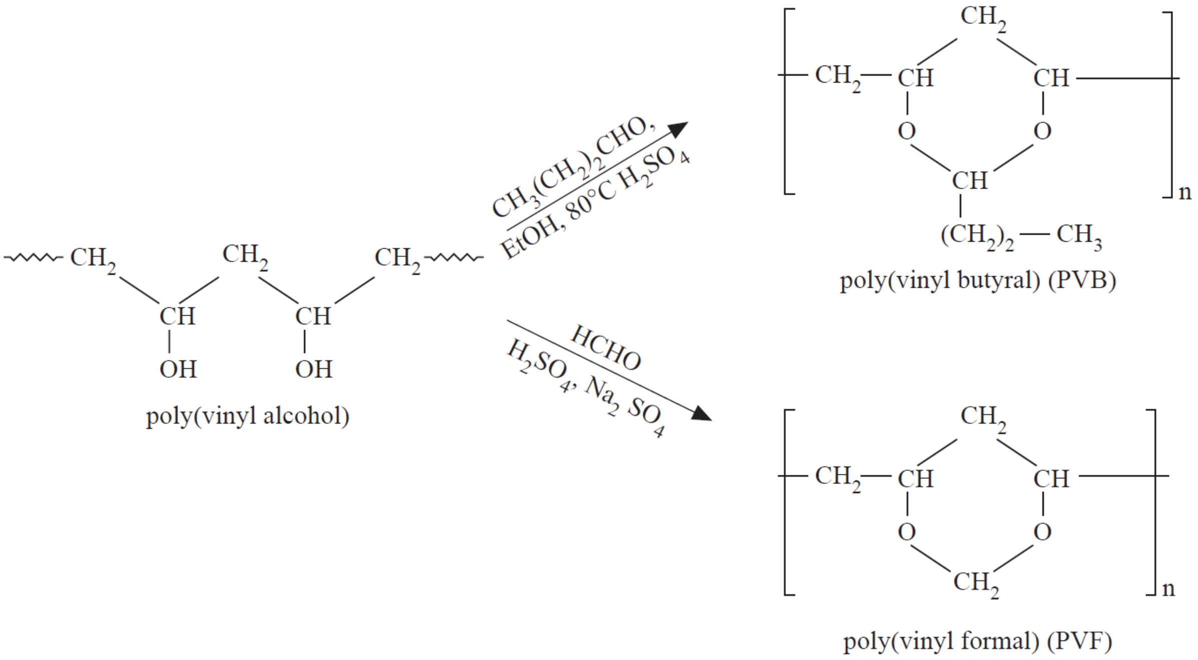
Poly(vinyl acetate) latex is used in the production of water-based emulsion paints, adhesives, and textile and paper treatments. Emulsion paints are stable, dry quickly, and are relatively low cost. PVAC emulsion adhesives are used in labeling and packaging, and as the popular consumer white glue. Copolymers 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).

POLY(VINYL ALCOHOL) (PVAL)



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:



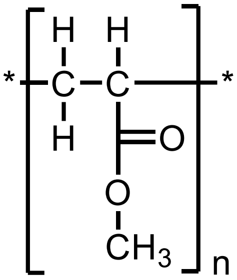


Poly(vinyl alcohol) has an atactic chain structure, and it is consequently amorphous. However, it can be stretched into a crystalline fiber. The small size of the OH groups permits them to fit into a crystal lattice. Poly(vinyl alcohol) is available in various grades defined by the molecular weight and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

POLY(METHYL METHACRYLATE) (PMMA)



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.

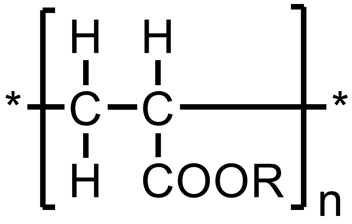
Poly(methyl methacrylate) for molding or extrusion is produced commercially by free-radical-initiated suspension or bulk polymerization of methyl methacrylate. To minimize polymerization reaction exotherm and shrinkage, bulk polymerization, which is used in the production of sheets, rods and tubes, is 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 Tg 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.

POLYACRYLATES



$*\!-\!\left[CH_2-CH(COOR)\right]_n\!-\!*$

R=	T_g (^oC)
Methyl	3
Ethyl	-20
n-Propyl	-44
n-Butyl	-56

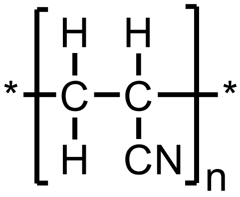
Polyacrylates are produced commercially by free-radical-initiated solution and emulsion polymerization of the appropriate monomer. Unlike for methacrylates, suspension and casting procedures are not feasible because of the rubber and adhesive nature of higher acrylates.

As shown above, 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.

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.

POLYACRYLONITRILE (PAN) — ACRYLIC FIBERS

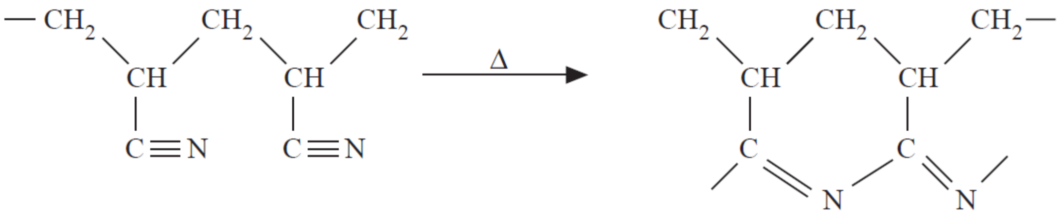


$$*\!-\!\left[\mathrm{CH_2-CH(CN)}\right]_n\!-\!*$$

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.



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.

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.

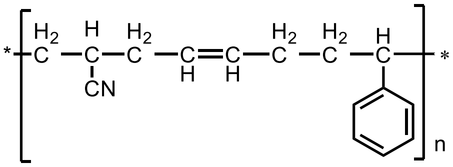
In addition to polytetrafluoroethylene, several other partially fluorinated polymers are available commercially. These include poly(chlorotrifluoroethylene), which is also available as a copolymer with ethylene or vinylidene fluoride, poly(vinyl fluoride), and poly(vinylidene fluoride).

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.

ACRYLONITRILE–BUTADIENE–STYRENE (ABS)



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, lowgloss, 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).

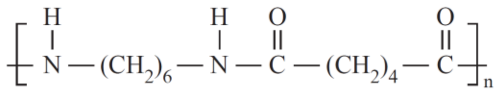
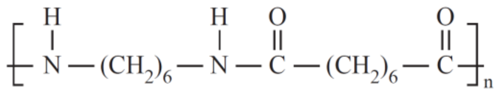
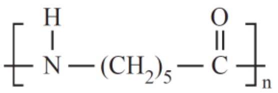
ABS resins have relatively good electrical insulating properties. They are resistant to weak acids and weak and strong bases. However, they have poor resistance to esters, ketones, aldehydes, and some chlorinated hydrocarbons. ABS resins are easily decorated by painting, vacuum metallizing, and electroplating. 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. Injectionmolded 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.

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 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).

Table 15.11 *Nomenclature of Nylons*

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

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 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.

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

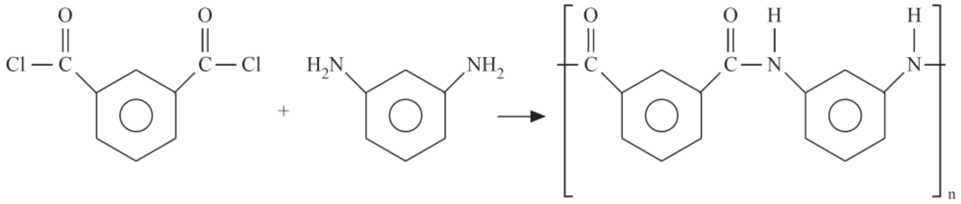
The markets for nylon products have been broadened considerably because of the apparent ease with which polyamides can be modified to produce improved properties for special applications. Modified nylons of various grades are produced by copolymerization and the incorporation of various additives (usually 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.

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

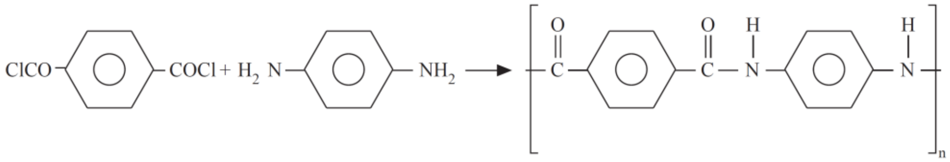
The term aramid is used to describe aromatic polyamides, which were developed to improve the heat and flammability resistance of nylon. Nomex (str. 17) is a highly heat-resistance nylon introduced in 1961 by DuPont. It is produced by the solution or interfacial polymerization of isophthaloyl chloride and m-phenylenediamine:



poly(*m*-phenyleneisophthalamide) (Nomex) (Str. 17)

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 (str. 18), is the corresponding linear aromatic polyamide obtained from terephthaloyl chloride and phenylenediamine.



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

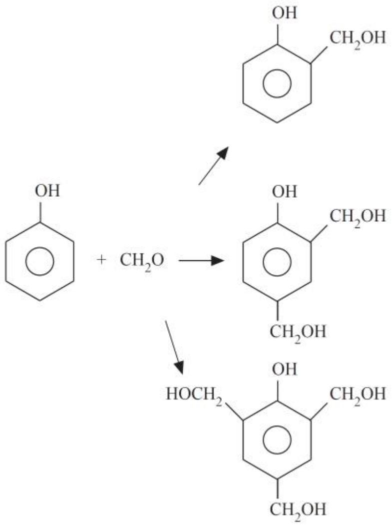
Kevlar, which decomposes only above 500°C, provides a fiber material which is as strong as steel at one-fifth its weight. It is a good substitute for steel in belted radial tires and is used in the manufacture of mooring lines as well as bulletproof vests and other protective clothing. Fiber-reinforced 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.

Q. 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 – explain.

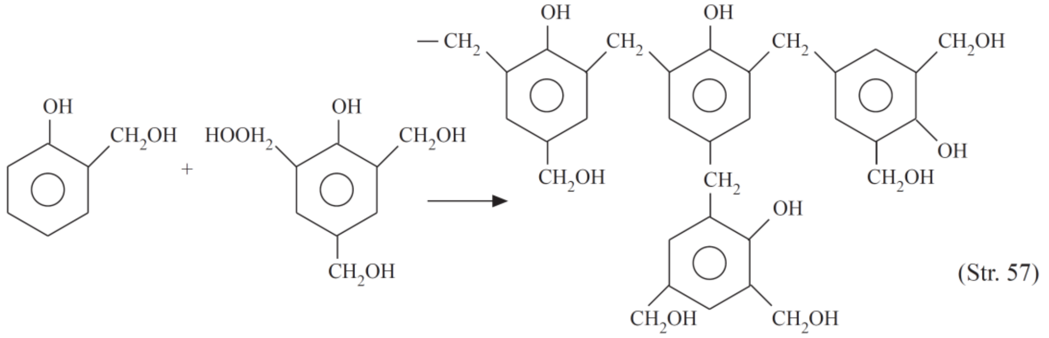
Ans. The hydrogen bonding capability of nylons is the primary factor controlling their solvent resistance. The hydrogen bond must be broken or replaced during dissolution. Consequently, only strong acids, which can protonate the amide nitrogen atom and preclude formation of hydrogen bonds or other compounds (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.

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:

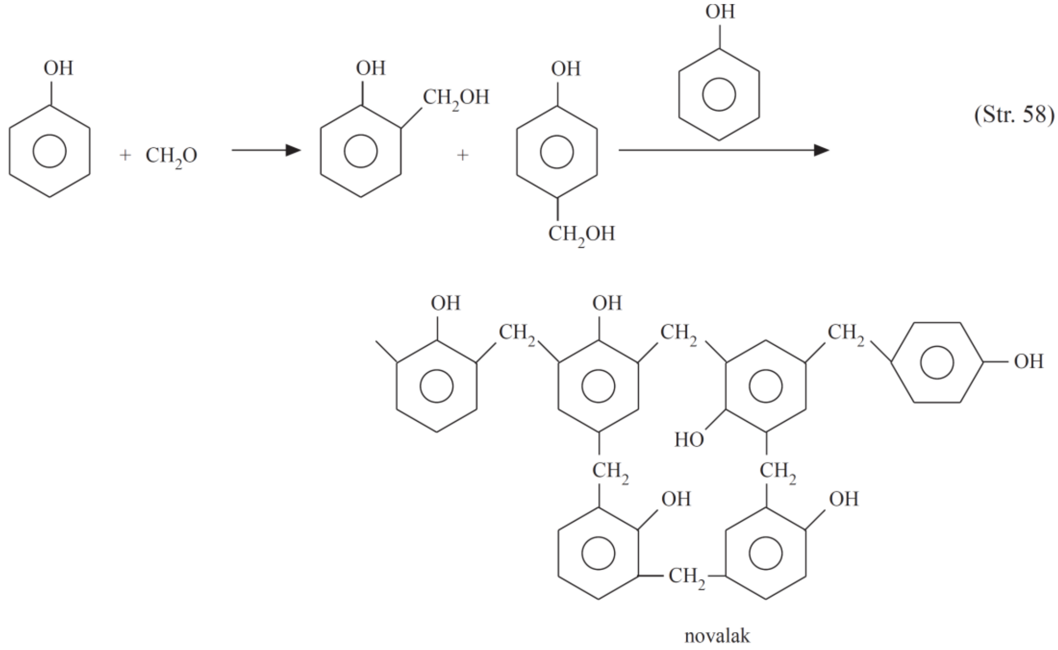


When heated, methylol phenols, condense either through methylene or methylene oxide linkages to give a low-molecular-weight prepolymer called resole, which is soluble and fusible and contains alcohol groups:


(Str. 57)

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 crosslinked 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.

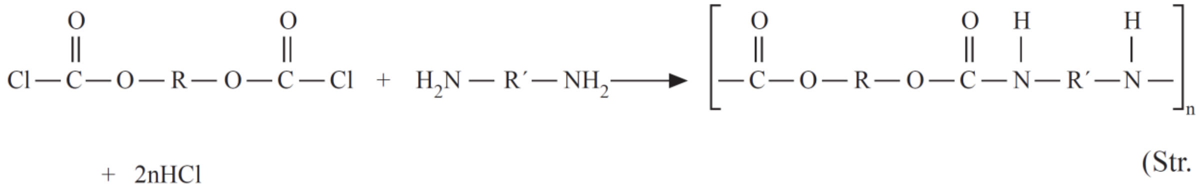

(Str. 58)

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.

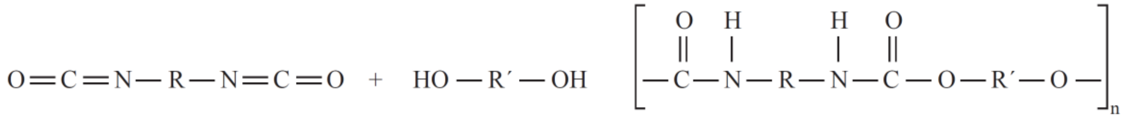
POLYURETHANES

Polyurethane is the generic name of polymers with the urethane (–N– CO–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:



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

(Str. 49)

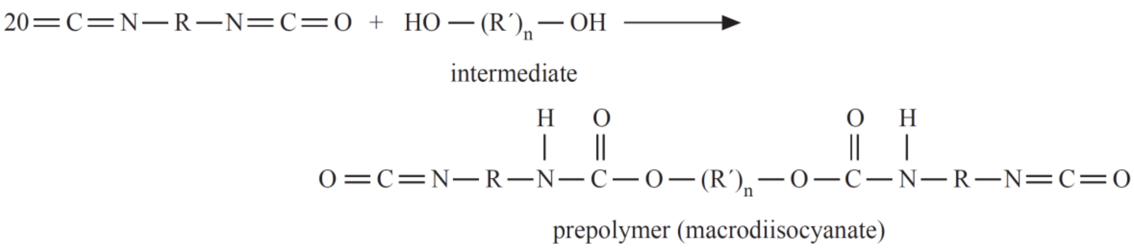


$$\mathrm{O{=}C{=}N{-}R{-}N{=}C{=}O} + \mathrm{HO{-}R'{-}OH} \quad \left[\mathrm{-\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'{-}O{-}}\right]_n$$

(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.

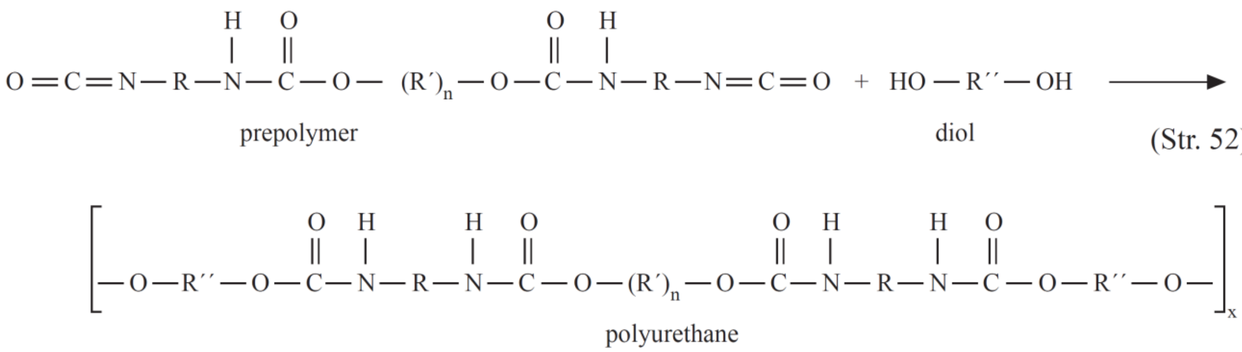
Polyurethanes are used in four principal types of products: foams, elastomers, fibers, and coatings. The majority of polyurethane is used as rigid or flexible foams. However, about 15% is used for elastomer applications. Production of polyurethane elastomers involves a number of steps. As indicated above, 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:



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

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

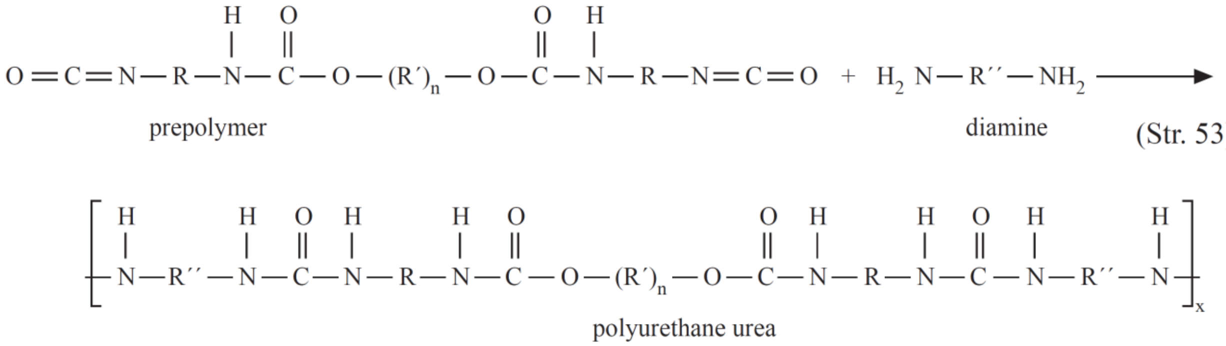
(Str. 51)



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

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

(Str. 52



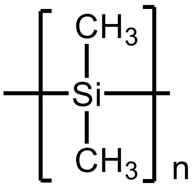
$$O{=}C{=}N{-}R{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}(R')_n{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R{-}N{=}C{=}O + H_2N{-}R''{-}NH_2 \longrightarrow$$

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

(Str. 53

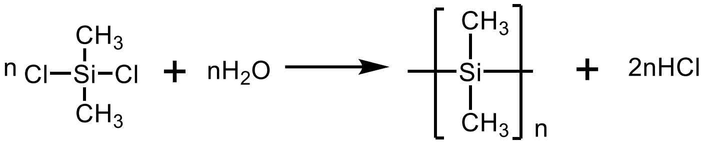
Polyurethane elastomers have high strength; extremely good abrasion resistance; good resistance to gas, greases, oils, and hydrocarbons; and excellent resistance to oxygen and ozone. Applications include solid tires, shoe soles, gaskets, and impellers.

SILICONE ELASTOMERS



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

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



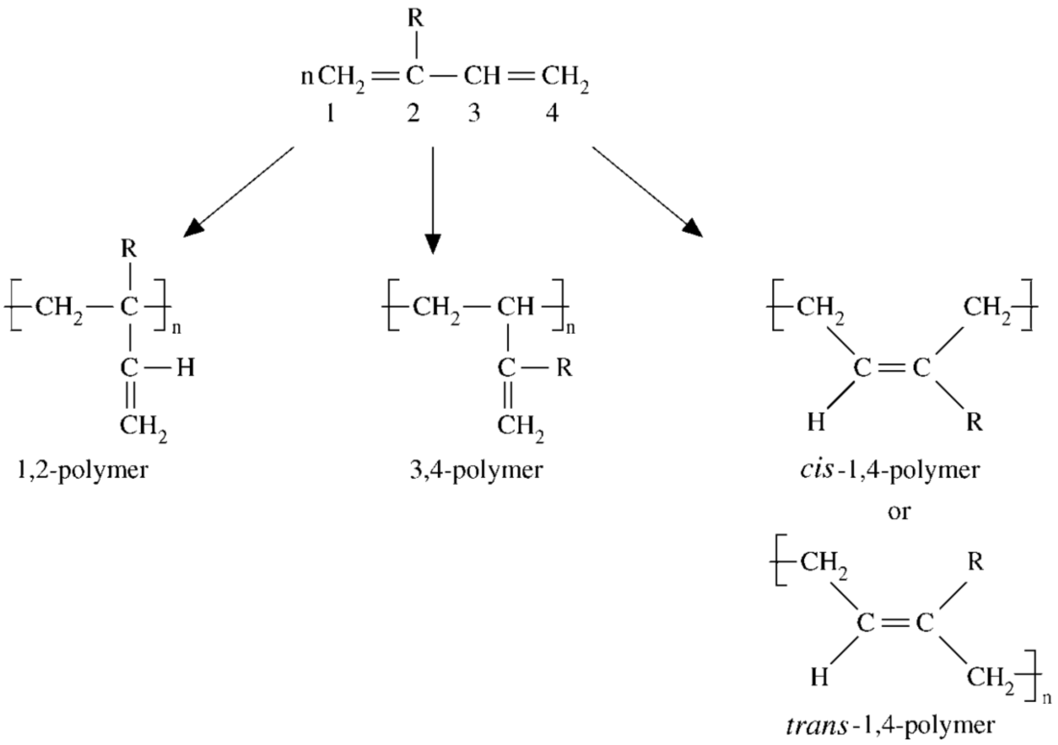
$$n\,\mathrm{Cl{-}Si(CH_3)_2{-}Cl} + n\mathrm{H_2O} \longrightarrow \left[\mathrm{Si(CH_3)_2}\right]_n + 2n\mathrm{HCl}$$

The process tends to result in the formation of cyclic products, typically trimers and tetramers. Highmolecular- 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.

DIENE-BASED ELASTOMERS

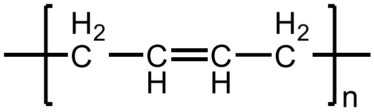
Polymerization of conjugated dienes like butadiene, isoprene, and chloroprenes involves activation of either or both of the double bonds to give 1,2; 3,4; or 1,4 polymers (Figure 15.11). The residual unsaturation in the polymer chains provides convenient sites for the introduction of elastomeric network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



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.*

Polybutadiene (Butadiene Rubber, BR)

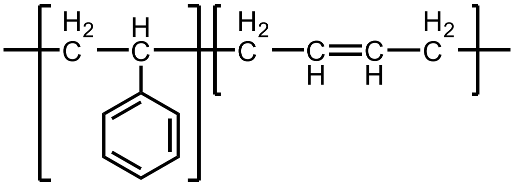


$$\left[-CH_2-CH=CH-CH_2-\right]_n$$

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-molecularweight 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.

Styrene–Butadiene Rubber (SBR)



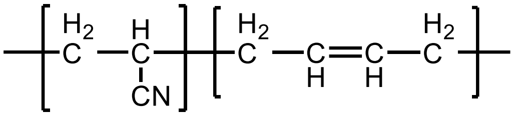
Styrene–butadiene rubber is the largest volume synthetic elastomer commercially available. It can be produced by free-radical emulsion polymerization of styrene and butadiene either at 50 to 60°C (hot emulsion SBR) or at about 5°C (cold emulsion SBR). The two kinds of SBR have significantly different 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.

Acrylonitrile–Butadiene Rubber (Nitrile Rubber, NBR)

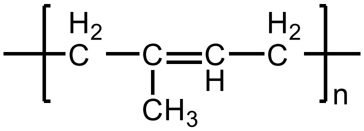


$$-[CH_2-CH(CN)]-[CH_2-CH=CH-CH_2]-$$

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 freeradical 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.

Polyisoprene

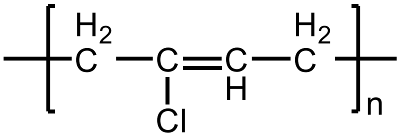


$$-[CH_2-C(CH_3)=CH-CH_2]_n-$$

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 non-elastomeric 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.

Polychloroprene (Neoprene)

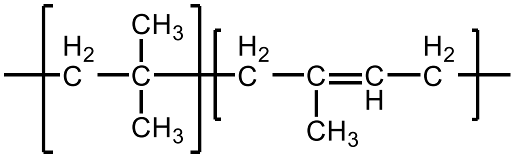


$$\left[-CH_2-C(Cl)=CH-CH_2- \right]_n$$

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.

Butyl Rubber



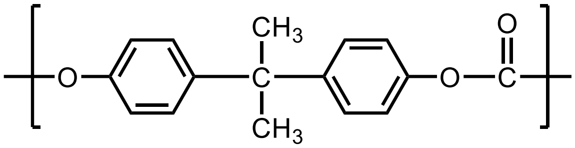
$$-\left[CH_2-C(CH_3)_2 \right]-\left[CH_2-C(CH_3)=CH-CH_2 \right]-$$

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.

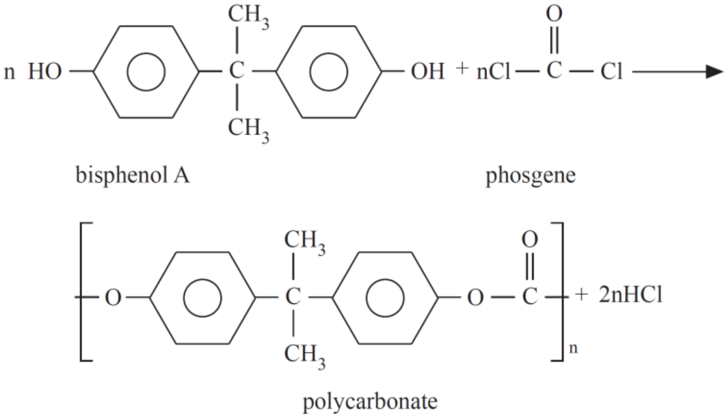
Butyl rubber exhibits unusually low permeability to gases and outstanding resistance to attack by oxygen and ozone. It has excellent chemical inertness, due to the very low residual unsaturation, and good electrical properties because of its nonpolar saturated nature. Butyl rubber has good tear resistance.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

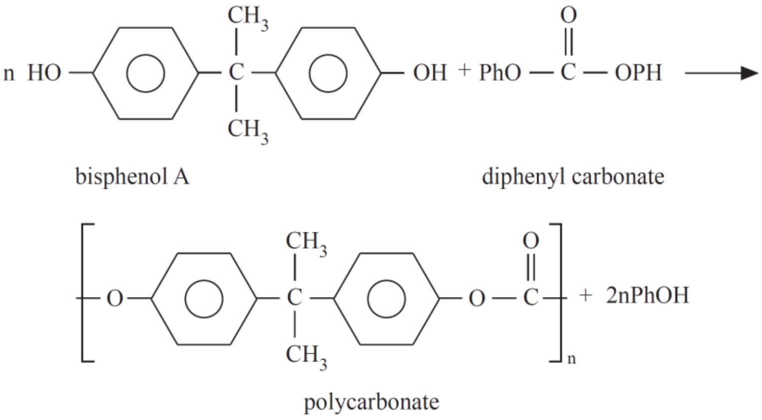
As a result of its very low gas permeability, butyl rubber is used predominantly in the inner tubes of tires and inner liners for tubeless tires. Some of the other uses of butyl rubber include sealants, adhesives, hoses, gaskets, pads for truck cabs, bridge bearing mounts, and other places where vibration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

Polycarbonates



Polycarbonates are characterized by the carbonate (–O–COO–) interunit linkage. Polycarbonates are the second largest by volume engineering thermoplastics next to polyamides. Their preparation involves the linking together of aromatic dihydroxy compounds, usually 2,2-bis(4-hydroxyphenyl) propane or bisphenol A, by reacting them with a derivative of carbonic acid such as phosgene (Equation 2.33) or diphenyl carbonate (Equation 2.34).





The melting point of polycarbonates is decreased from 225 ^{o}C to 195 ^{o}C when the methyl pendant groups are replaced by propyl groups. The polycarbonate prepared from bis(4-hydroxyphenyl)ether also has a lower melting point and lower glass transition temperature.

Polycarbonates and polycarbonate-polyester copolymers are used for glazing, sealed beam headlights, door seals, popcorn cookers, solar heat collectors, and appliances. Polycarbonate tends to stress-crack in the presence of gasoline, but a 50–50 blend (Xenoy) is unusually resistant to gasoline.

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.

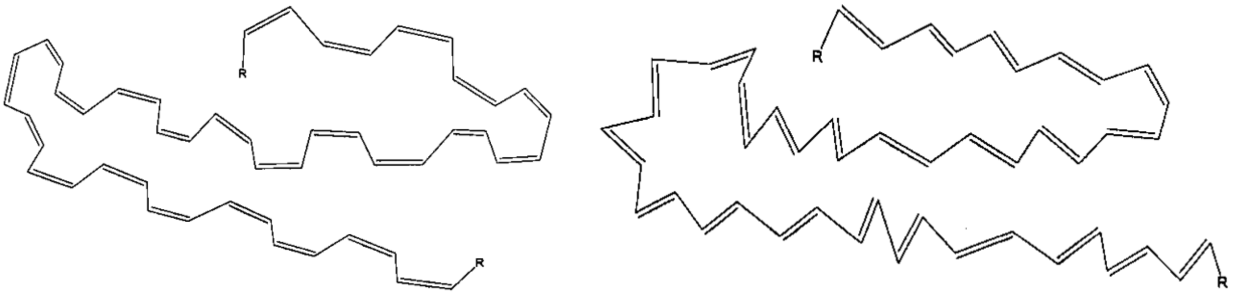
Polycarbonates are processed by all the conventional techniques for processing thermoplastics. The balanced combination of properties permits polycarbonates to be used in a variety of applications. Markets for polycarbonates include automotive, construction, electronics, appliances, and lighting, while 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.

Conducting Polymers

Most polymers are nonconductive and in fact, are employed in the electronics industry as insulators. The Nobel Prize in Chemistry for 2000 was given to Alan MacDiarmid, Alan Heeger, and Hideki Shirakawa for the discovery and development of electrically conductive polymers. A critical structural feature for conductive polymers is the presence of conjugated double bonds. Polyacetylene, poly(phenylene vinylene), polypyrrole, polyaniline, polythiophenes are some example of conducting polymers.

Polyacetylene has been produced by several methods, many utilizing the Zeigler-Natta polymerization systems. Both cis- and trans-isomers exist (Fig. 18.2). The cis-polyacetylene is copper-colored with films having a conductivity of about 10^{-8} S/meter. By comparison, the trans-polyacetylene is silver-colored with films having a much greater conductivity on the order of 10^{-3} S/meter. The cis isomer is changed into the thermodynamically more stable trans isomer by heating. As noted above, conductivity is greatly increased when the trans-polyacetylene is doped (to about 102–104 S/cm). Conductivity is dependent on the micro- or fine structure of the fibrils, doping agent, extent, and technique, and aging of the sample.

Grubbs and others have used the ring-opening metathesis polymerization to produce thick films of polyacetylene and polyacetylene derivatives (Scheme 18.2).



Scheme 18.2. cis- (left) and trans- (right) polyacetylene.

For polyacetylene, every backbone carbon is connected by a stronger localized σ bond. They are also connected by a network of alternating less localized and weaker π bonds. While conjugation is present, it is localized enough to prevent ready delocalization of theπ-bond electrons. The dopants cause the introduction of sites of increased or deficiency of electrons. When there is a deficiency of electrons, or a hole, created, electrons flow to fill this hole with the newly created hole causing other electrons to flow to fill the new hole, etc., allowing a charge to migrate within and between the polyacetylene chains.

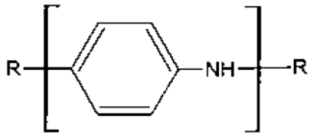
In general, the Huckel theory predicts that π electrons can be delocalized over an entire chain containing adjacient π bonds with the activation energy for delocalization decreasing as the chain length increases. Doping provides a ready mechanism for delocalization to occur.

Polyacetylene has good inert atmospheric thermal stability but oxidizes easily in the presence of air. The doped samples are even more susceptible to air. Polyacetylene films have a lustrous, silvery appearance and some flexibility. Other polymers have been found to be conductive. These include poly(p-phenylene) prepared by the Freidel-Crafts polymerization of benzene, polythiophene and derivatives, poly(phenylene vinylene), polypyrrole, and polyaniline. The first polymers commercialized as conductive polymers were polypyrrole and polythiophene because of their greater stability to air and the ability to directly produce these polymers in a doped form. While their conductivities (often on the order of 104 S/meter) are lower than that of polyacetylene, this is sufficient for many applications.

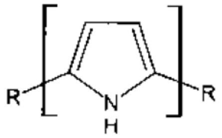
Doped polyaniline is employed as a conductor and as an electromagnetic shielding for electronic circuits. Poly(ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonic acid is used as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions and is also used as a hole injecting electrode material in polymer light-emitting devices. Organic soluble substituted polythiophenes with good conductivities have been prepared. Poly(3-hexylthiophene) has a room temperature conductivity of about 100 S/cm; poly(3-metnylthiophene) has a conductivity of 500 S/cm; and a poly(3- alkylether)thiphene) with a conductivity of about 1000 S/cm has been reported. The unsubstituted polythiophene has a conductivity in the range of 50 to 100 S/cm. The fact that all of these substituted polythiophenes have similar conductivities indicates that there is little twisting of the backbone conjugation as alkyl substituents are added.

Polythiophene derivatives are being used in field-effect transistors. Polypyrrole is being used as microwave-absorbing "stealth" screen coatings and in sensing devices. Poly(phenylene vinylidene) derivatives are being used in the production of electroluminescent displays.

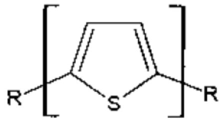
Following are the structures of some of the more common conjugated polymers, along with poly(acetylene), that can be made conductive through doping. As noted before, doping causes and electrical imbalance that allows electrons to flow when an electrical potential is applied. The band gap is the energy needed to promote an election from the valence band to the empty energy or conductive band. Metals have zero band gaps while insulators such as polyethylene have large band gaps, meaning that a lot of energy is needed to promote an electron to an empty band. Semiconductors have small band gaps where valence electrons can be moved into the conductance band through application of relatively small potential energies.



Polyalanine



Polypyrrole



Polythiophene

While the amount of electricity that can be conducted by polymer films and "wires" is limited, on a weight basis the conductivity is comparable to that of copper. These polymeric conductors are lighter, some more flexible, and they can be laid down in wires that approach one atom thickness. They are being used as cathodes and solid electrolytes in batteries, and potential uses include in fuel cells, smart windows, nonlinear optical materials, light-emitting diodes, conductive coatings, sensors, electronic displays, and electromagnetic shielding.

There is a large potential for conducting polymers as corrosion inhibiting coatings. For instance, the corrosion protection ability of polyaniline is pH dependent. At lower pH's, polyaniline-coated steel corrodes about 100 times more slowly than noncoated steel. By comparison, at a pH of about 7 the corrosion protection time is only twice for polyaniline-coated steel. Another area of application involves creation of solid-state rechargeable batteries and electrochromic cells. Polyheterocycles have been cycled thousands of times with retention of over 50% of the electrochromic activity for some materials after 10,000 cycles. Infrared polarizers based on polyaniline have been shown to be as good as metal wire polarizers.

Polyheterocyclic conducting polymers have shown a wide variation in color as they are electronically converted between oxidized and reduced forms. The instability of some of the polymers is being used to monitor moisture, radiation, mechanical, and chemical destruction.