Engineering and Specialty Polymers

Engineering and specialty thermoplastics offer outstanding properties in one or more areas when compared with commodity thermoplastics such as polystyrene and polyolefins (see Chapter 9). Advantages may include high thermal stability or excellent chemical resistance, low creep compliance, and high tensile, flexural, and impact strength. Not unexpectedly, these properties come at a premium in price. In many cases, these polymers can be used as replacements for metals, particularly where a high strength-to-weight ratio is an important consideration, such as in automotive and aerospace applications.

The classification between engineering and specialty plastics is somewhat arbitrary. For purposes of discussion, the term *engineering plastics* will refer to those polymers that are used in the manufacture of premium plastic products where high-temperature resistance, high impact strength, chemical resistance, or other special properties are required. The important engineering plastics are normally considered to include aliphatic polyamides (nylon-6 and nylon-6,6), ABS resin, polycarbonate,

poly(phenylene oxide), acetal, polysulfones, poly(phenylene sulfide), engineering polyesters, and fluoroplastics. Properties of some of these engineering thermoplastics are given in Table 10-1. By comparison, *specialty plastics* are significantly more expensive but achieve very high performance in one or more areas. These plastics find limited but critical use in aerospace composites, as membranes for gas and liquid separations (see Section 12.1), as flame-retardant textile fabrics for firefighters and race car drivers, and as material for sutures and surgical implants. The most important class of specialty plastics is the polyimides. Other specialty polymers include polyetherimide, poly(amide-imide), polybismaleimides, polybenzimidazoles, ionic polymers, poly(aryl ether ketones), polyphosphazenes, polyarylates and related aromatic polyesters, ultrahigh-molecular-weight polyethylene and other specialty polyolefins, and dendritic polymers.

Table 10-1   Representative Properties of Some Important Engineering Thermoplastics

Property	PA-6[a]	PA-6,6[a]	ABS[b]	PC	PPO	Acetal	PSF	PPS
Specific gravity (D 792)	1.12– 1.14	1.13– 1.15	1.03– 1.06	1.20	1.06	1.42	1.24	1.34
Tensile strength, MP[c] (D 638)	69	76	41–52	66	66	66–83	70	74
Tensile modulus, GPa[d] (D 638)	0.69	NA	2.1– 2.8	2.4	2.4	3.6	2.6	3.3
Elongation-to-break, % (D 638)	300	300	5–25	110	20– 60	25–75	50– 100	3
Flexural strength, MPa[d] (D 790)	34	42	76–90	93	93	97	106	138
Flexural modulus, GPa[d] (D 790)	9.7	12–28	26–28	23	25– 28	26–30	27	41
Impact strength, notched Izod, m^{-1} [e] (D 265)	160	112	160– 320	854	96– 267	69– 123	160– 320	11
HDT, °C at 455 kPa (66 psi) (D 648)	150– 185	180– 240	102– 107	138	137	124	150– 175	137

[a] Moisture conditioned.
[b] Medium-impact grade.
[c] To convert MPa to psi, multiply by 145.
[d] To convert GPa to psi, multiply by 1.45×10^5.
[e] To convert J m^{-1} to lb$_f$ in.$^{-1}$, divide by 53.38.

10.1 Engineering Plastics

10.1.1 Polyamides

Polyamides can have either all aliphatic- or all aromatic-chain backbones. The aliphatic polyamides, particularly nylon-6 and nylon-6,6, are the most widely used engineering thermoplastics. In addition to their important fiber applications (see Section 8.2.3), aliphatic polyamides may be used as molded parts for automotive and other applications. Commercial nylon resins for molding applications may be modified for improved flame retardancy and impact strength, or reinforced with minerals or glass fibers to increase modulus as well as to lower cost. Fibers made from aromatic polyamides, such as Nomex and Kevlar, provide outstanding high-temperature resistance and high tensile strength for use as fire-retardant fabric and for tire cord. As a class, polyamides exhibit excellent resistance to wear and abrasion, a low coefficient of friction, good resilience, and high impact strength. Properties of nylon-6 and nylon-6,6 are given in Table 10-1. The chemical structures of the repeating units of the most important aliphatic and aromatic polyamides and the monomers from which they are polymerized are given in Table 10-2.

Table 10-2   Chemical Structures of Important Polyamides

Monomer(s)	Polymer	Structure
Caprolactam	Poly(ε-caprolactam) (nylon-6)	$-[NH-\overset{O}{\overset{\|\|}{C}}-(CH_2)_5]-$
Hexamethylene diamine adipic acid	Poly(hexamethylene adipamide) (nylon-6,6)	$-[NH-(CH_2)_6-NH-\overset{O}{\overset{\|\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|\|}{C}}]-$
Hexamethylene diamine sebacic acid	Poly(hexamethylene sebacamide) (nylon-6,10)	$-[NH-(CH_2)_6-NH-\overset{O}{\overset{\|\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|\|}{C}}]-$
Isophthaloyl chloride m-phenylenediamine	Poly(m-phenylene isophthalamide) (Nomex)	$-[HN-\langle\bigcirc\rangle-NH-\overset{O}{\overset{\|\|}{C}}-\langle\bigcirc\rangle-\overset{O}{\overset{\|\|}{C}}]-$
Terephthaloyl chloride p-phenylenediamine	Poly(p-phenylene terephthalamide) (Kevlar)	$-[HN-\langle\bigcirc\rangle-NH-\overset{O}{\overset{\|\|}{C}}-\langle\bigcirc\rangle-\overset{O}{\overset{\|\|}{C}}]-$

All nylons are water sensitive due to the hydrogen-bonding character of the amide groups. For example, nylon-6,6 absorbs about 9% water during equilibrium at ambient temperature and 100% relative humidity. Water absorption decreases

with decreasing amide-group concentration in the polymer backbone as in the case of nylon-11 (1.9% water absorption) obtained by the ring-opening polymerization of 11-aminoundecanoic acid. Water acts as a plasticizer, which reduces tensile strength and modulus (and, therefore, dimensional stability), while increasing elongation-to-break and consequently toughness. Care must be taken to reduce water content of nylon resins to below 0.3% before melt processing to avoid embrittlement due to hydrolytic degradation.

Nylon-6,6 and nylon-6 dominate the non-fiber polyamide market. Nylon-6,6 has higher rigidity, but nylon-6 is more weather and thermally resistant. Due to its good barrier properties, nylon-6 film is used for packaging of some oxygen-sensitive foods. Other aliphatic nylons having more specialized markets include nylon-11, nylon-12, and nylon-4,6. For example, nylon-11 and nylon-12 have been used in the manufacture of fuel lines and compressed-air brake tubing.

Aromatic Polyamides. In the 1960s, aromatic polyamides, often called *aramids*, were developed to improve the heat and flammability resistance of nylons. Poly(*m*-phenylene isophthalamide) (Nomex) is a highly heat-resistant nylon (decomposes at about 370°C) obtained by the solution or interfacial polymerization of a *meta*-substituted aromatic diacid chloride and diamine, as illustrated in Figure 10-1. Nomex may be used as a substitute for asbestos in many applications, such as flame-resistant protective clothing and hot-gas filtration equipment. Nomex in the form of thin pads has been used to isolate the fragile sintered silica-fiber mats of the space shuttle from stress and vibration during flight.
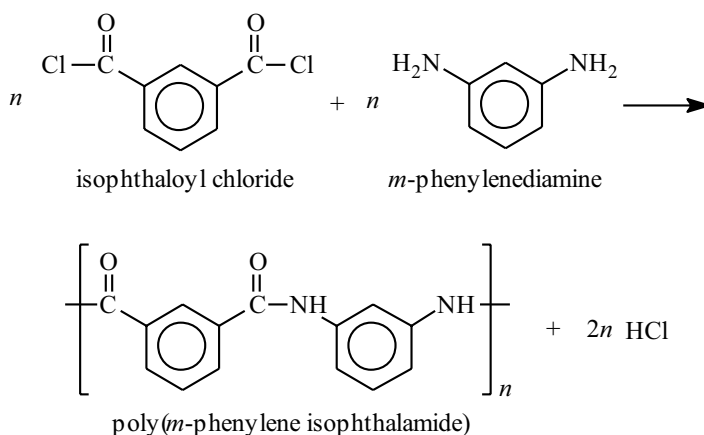

Figure 10-1   Synthesis of an aromatic polyamide, poly(*m*-phenylene isophthalamide) (Nomex).

The corresponding linear aromatic polyamide, poly(p-phenylene terephthalamide) (PPT) (Kevlar) (see Table 10-2), decomposes only above 500°C. Fibers of Kevlar have higher strength and modulus than steel on an equal weight basis. It has been used as a substitute for steel in belted radial tires (i.e., aramid fiber) and in the manufacture of mooring lines, as well as bullet-resistant vests and other protective clothing. Kevlar fiber is also used in the manufacture of fiber-reinforced plastics (see Chapter 7). Fabric made from Kevlar has been used as the skin covering for the first human-powered aircraft, the *Gossamer Albatross*, which was flown across the English Channel.

10.1.2 ABS

Another important thermoplastic with a major market share is ABS, which represents a resin containing acrylonitrile, butadiene, and styrene. ABS is a high-impact, high-HDT grade of polystyrene (see Table 10-1) that, together with the thermoplastic nylons, marks the boundary in price and performance between commodity and engineering thermoplastics. Uses for ABS include automotive applications, consumer products including small and large appliances, and business machines and telecommunications where good impact strength at moderate cost is required.

ABS was first developed in the 1950s by grafting a styrene–acrylonitrile copolymer (SAN) onto semi-crosslinked particles of polybutadiene (PBD). The PBD component of ABS increases impact strength over that of SAN alone. Developments during the 1960s led to a variety of methods to obtain ABS, including bulk, emulsion, and suspension polymerizations, although emulsion processes (free-radical polymerization of styrene and acrylonitrile in the presence of PBD or butadiene copolymers) are still the most widely used. A typical ABS formulation contains <15% butadiene and <20% acrylonitrile. The morphology of an ABS resin, as can be seen by scanning electron microscopy aided by staining the unsaturated sites of the butadiene component, varies with the production process. In general, immiscibility of PBD with SAN results in phase separation whereby PBD is dispersed in the form of small PBD particles contained within a matrix of SAN, as shown in Figure 10-2. Rubber particles produced by bulk or suspension processes are larger (0.5 to 5 μm) than those produced by emulsion methods (0.1 to 1 μm). Graft polymerization of SAN and PBD provides good interfacial adhesion between the dispersed and matrix phases. When ABS is mechanically deformed, the PBD particles act to modify the deformation process by either promoting craze formation (see Figure 10-2) or shear banding (see Section 4.4.1). As a result, the total energy-to-fail (i.e., impact strength) of ABS is increased over that of unmodified PS or SAN.
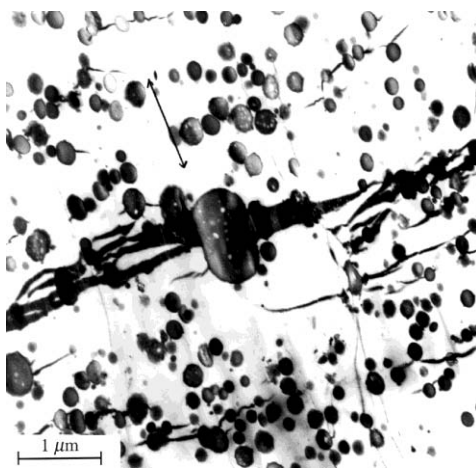
Figure 10-2   Electron micrograph of a section cut parallel to the surface of a deformed sample of ABS. The arrow shows the direction of applied strain. The dispersed phase (dark regions) consists of PBD particles. Crazes appear as dark lines running across the photograph. These craze structures are oriented perpendicular to the strain direction and pass through a number of PBD particles. Reproduced from M. Matsuo, Polymer Engineering & Science, 1969. **9**, p. 206 (1969). © 1969 Society of Plastics Engineering, Inc. Reprinted by permission of John Wiley & Sons, Inc.

10.1.3 Polycarbonates

The polycarbonate obtained from bisphenol-A is the engineering thermoplastic with the second-highest sales volume. Polycarbonate (PC) is an amorphous polymer with attractive engineering properties (see Table 10-1), including high impact strength, low moisture absorption, low combustibility, good dimensional stability, and high light transmittance (up to 88%). The latter property has resulted in the application of PC as an impact-resistant substitute for window glass. Another important application for PC is its use as the material for compact discs. Among the disadvantages of PC are its limited chemical and scratch resistance and a tendency to yellow with long-term ultraviolet exposure. These problems have been addressed by the introduction of silicone-coated and free-radical stabilized polycarbonate resins.

Polycarbonate can be synthesized by the polycondensation of bisphenol-A and phosgene, as shown in Figure 10-3. For each repeating unit that is formed, two molecules of hydrogen chloride are liberated. Alternatively, if the *sodium salt* of bisphenol-A is used in the polymerization, the by-product becomes sodium chloride rather than hydrogen chloride. This is an obvious advantage because the salt will precipitate out of the organic solvent used in the polymerization and, therefore, can

be easily and safely removed. In contrast, the production of strongly acidic hydrogen chloride requires special consideration for disposal and in the selection of construction material used in the polymerization reactor.
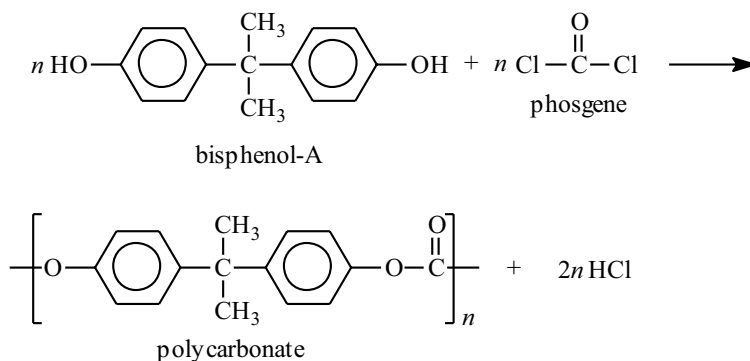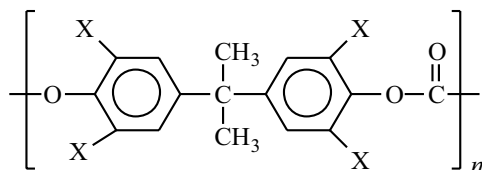

bisphenol-A

polycarbonate

Figure 10-3 Synthesis of bisphenol-A polycarbonate by the polycondensation of bisphenol-A and phosgene.

Other polycarbonates can be polymerized by modified interfacial condensation or by melt transesterification of tetrasubstituted bisphenols. These polycarbonates have the general structure

where X represents a halogen, especially bromine, or a methyl group. One example is tetramethylbisphenol-A polycarbonate (TMPC), $X = CH_3$, which has a higher heat-distortion temperature (HDT) and better hydrolytic stability than PC. The HDT or T_g is a result of the greater rigidity of the TMPC chain due to the steric hindrance of the substituent methyl groups. One disadvantage of TMPC is its low impact resistance; however, this may be improved through blending with impact-resistant resins such as HIPS, ABS, and MBS (see Section 7.2.2). The styrene component of these impact modifiers forms a homogeneous phase with TMPC. Impact-modified grades of TMPC can also be used to increase the HDT of PVC. Tetrabromobisphenol-A polycarbonate (TMBPC), $X = Br$, can be blended with PC to increase HDT. Copolymers of bisphenol-A and tetrabromobisphenol-A or tetrachlorobisphenol-A provide better flame retardancy. The polycarbonate obtained from cyclohexanonebisphenol can be blended with PC to increase the HDT from 160° to 205°C.

10.1.4 Modified Poly(phenylene oxide)

Another large-sales-volume engineering thermoplastic having substantially higher
HDT than PC is poly(2,6-dimethyl-1,4-phenylene oxide) or PPO, which is obtained
from the free-radical, step-growth, oxidative-coupling polymerization of 2,6-
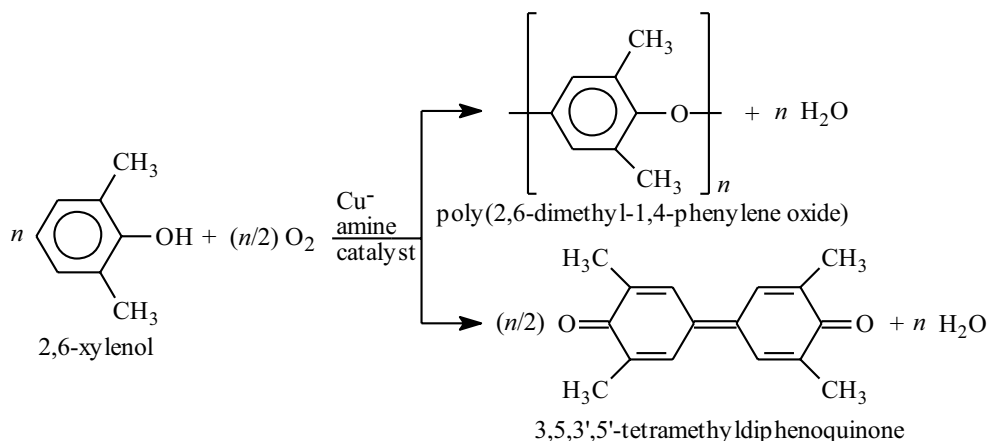xylenol [1], as shown in Figure 10-4.

Figure 10-4   Oxidative-coupling polymerization of 2,6-xylenol. 3,5,3′,5′-tetramethyl-
                     diphenoquinone (DPQ) is a by-product of this polymerization. The con-
                     centration of DPQ impurity depends upon the choice of catalyst and
                     conditions of the polymerization. For example, the yield of DPQ is
                     about 3 wt% using a cupric formate and pyridine catalyst.

A related polymer, poly(2,6-diphenyl-1,4-phenylene oxide), originally consid-
ered for fiber applications, has limited commercial use as a packing for GC col-
umns. A good review of oxidative-coupling polymerization and the com-
mercialization of PPO has been given by Hay [2]. PPO has many attractive proper-
ties (see Table 10-1), including high impact strength, chemical stability to mineral
and organic acids, and low water absorption. A limitation that had restricted its
commercialization is its high glass-transition temperature ($T_g \approx 214°C$) in relation to
the susceptibility of its methyl groups to thermal oxidation, which poses problems
for melt processing. For these reasons, commercial resins (Noryl) are made by
blending PPO with high-impact polystyrene (HIPS), which serves to reduce the
processing temperature, although heat-distortion temperature is reduced as well.
Like impact-modified grades of TMPC, the styrene component of HIPS forms a
homogeneous phase with PPO. Noryl resins are also available in flame-retardant
and filled grades and are used in many electrical and automotive applications.

In addition to PPO/HIPS blends, commercial resins of PPO and polyamides (PA) are available for improved thermal stability required for certain electrical and electronics applications. In this case, a compatibilizer (see Section 7.1.1) such as a PA-grafted styrene–maleic anhydride copolymer serves to improve blend properties. Blends of PPO with polyesters and polyolefins offer better dimensional stability than PPO/PA resins at the expense of lower thermal stability.

10.1.5 Acetal

Polyacetal, sometimes known simply as acetal or as polyformaldehyde and polyoxymethylene (POM), may be the first universal polymer. In 1987, mass spectral data revealed the presence of POM in the gas cloud of Halley's comet. On earth, POM may be obtained by the anionic or cationic polymerization of formaldehyde or by the cationic ring-opening polymerization of trioxane, as shown in Figure 10-5. The highly regular chain structure of polyacetal contributes to its high crystallinity and excellent chemical resistance. Properties of a typical acetal resin are given in Table 10-1.
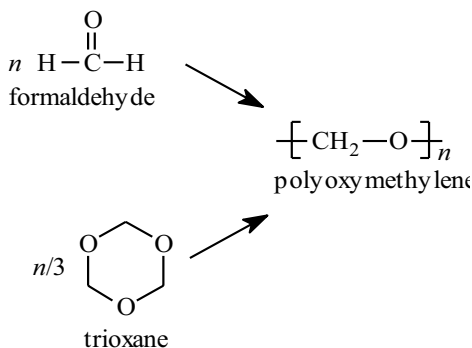

$$n \ \ H-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

formaldehyde

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

polyoxymethylene

$$n/3$$ trioxane

Figure 10-5   Two routes for the synthesis of polyoxymethylene.

Acetal is degraded by UV radiation, leading to color change and loss of toughness and tensile strength; however, acetal can be stabilized against UV degradation by the usual UV absorbers and hindered-amine light stabilizers (HALS). Carbon black and titanium dioxide fillers are also effective for light and UV screening. A particularly attractive property of acetal is its high dimensional stability (creep resistance), which allows acetal to be used as a replacement for metals in gears and machine parts. Rubber-toughened grades of polyacetals are available for applications where higher impact strength, flexural strength, and tensile-fracture resistance are desired. Automotive and electrical/electronic use accounts for approximately two-thirds of worldwide acetal production. Another important consideration for the

continued growth of acetal resins is that acetal can be chemically recycled to monomer.

10.1.6 Polysulfones

Polysulfones comprise a class of engineering thermoplastics with high thermal, oxidative, and hydrolytic stability and good resistance to aqueous mineral acids, alkalis, salt solutions, oils, and greases. Their high biocompatibility and ability to be sterilized by a variety of techniques make them highly suitable for medical applications [3]. Polysulfones also have high permeability and permselectivity which make them attractive as membrane polymers in gas separations (see Section 12.1.2). Chemical structures and representative properties of three aromatic polysulfones are given in Tables 10-3 and 10-4, respectively.

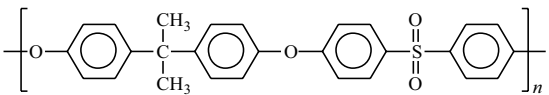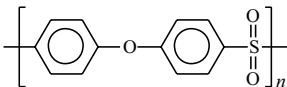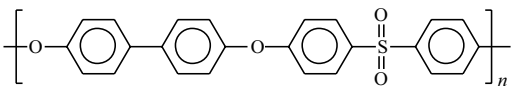**Table 10-3   Chemical Structures of Commercial Polysulfones**

Polysulfone	Structure of Repeating Unit
Polysulfone	
Polyethersulfone	
Polyphenylsulfone	

Table 10-4   Representative Properties of Commercial Polysulfones

Property	PSF	PES	PPS
Specific gravity (D 1505)	1.25	1.37	1.29
Tensile strength at yield, MPa[a] (D 638)	70.3	84.1	71.7
Tensile modulus, GPa[b] (D 638)	2.48	2.70	2.14
Elongation to break, % (D 638)	50–100	40–80	60
Flexural strength, MPa[a] (D 790)	106	129	85.5
Flexural modulus, GPA[b] (D 790)	2.69	2.57	2.30
Impact strength (notched Izod), J m^{-1} D 256)[c]	69	85	641
HDT, °C, at 455 kPa (66 psi) (D 648)	174	203[d]	200–204

[a] To convert MPa to psi, multiply by 145.
[b] To convert GPa to psi, multiply by 1.45×10^5.
[c] To convert J m^{-1} to lb$_f$ in.$^{-1}$, divide by 53.38.
[d] Reported at 1.82 MPa (264 psi).

Polysulfones can be synthesized by condensation polymerizations involving nucleophilic substitution of alkali salts of bisphenates with activated aromatic dihalides. The synthesis of bisphenol-A polysulfone (PSF) is illustrated in Figure 10-6. As shown, the use of the sodium salt of bisphenol-A results in the condensation of NaCl that can precipitate from organic solution rather than corrosive HCl that would result from the polycondensation of the unmodified bisphenol-A monomer. In addition, polysulfones can be synthesized by electrophilic substitution (Friedel–Crafts) of sulfonyl chlorides by use of Lewis acid catalysts, as in the polymerization of polyethersulfone (PES) shown in Figure 10-7. Polysulfones are widely used in the automotive, aerospace, and medical industries for such applications as quartz-iodine headlamp reflectors for cars, sterilizable medical devices, overhead passenger-service modules on aircraft, and specialized battery housing, as shown in Figure 10-8.

Figure 10-6 Polycondensation of bisphenol-A polysulfone.

Figure 10-7 Polycondensation of a polyethersulfone.

Figure 10-8   UDEL polysulfone is used for the transparent containers holding the potassium hydroxide electrolyte of a nickel–cadmium battery for electrical backup in railroad applications. The polysulfone container is unaffected by the alkaline electrolyte and is resistant to shock, vibration, and moisture. Courtesy of Solvay Advanced Polymers, L.L.C.

10.1.7 Poly(*p*-phenylene sulfide)

Poly(*p*-phenylene sulfide) (PPS), or poly(thio-1,4-phenylene), is another important engineering thermoplastic with many attractive properties (Table 10-1), such as outstanding chemical resistance, good electrical properties, excellent flame retardance, low coefficient of friction, and high transparency to microwave radiation. As illustrated in Figure 10-9*,* PPS can be prepared by the polycondensation of *p*-dichlorobenzene and sodium sulfide.

p-dichlorobenzene   sodium sulfide   poly(p-phenylene sulfide)
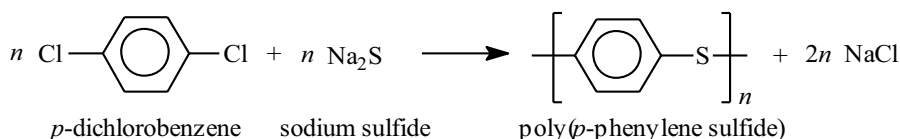
Figure 10-9   Synthesis of poly(*p*-phenylene sulfide).

PPS is highly crystalline with a relatively high melting temperature (285°C) and is insoluble in organic solvents below 200°C. This means that special processing techniques must be used to manufacture products from this engineering resin. For example, PPS coatings are obtained by spraying an aqueous *slurry* of PPS particles and heating the coated object to temperatures above 370°C. PPS can be injection- and compression-molded at high temperatures (300° to 370°C) at which PPS particles soften and undergo an apparent crosslinking reaction to yield a totally

insoluble product. Principal applications of PPS include cookware, bearings, and pump parts for service in various corrosive environments. PPS is frequently produced as reinforced grades (typically filled with glass fiber and mixtures of minerals such as talc and chalk) that have higher strength and HDT.
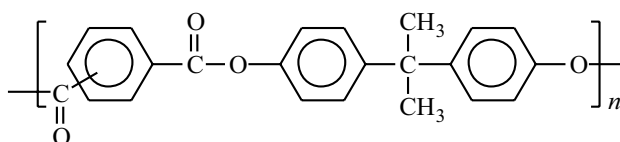
10.1.8 Engineering Polyesters

The slow rate of crystallization of poly(ethylene terephthalate) (PET), which is widely used as a textile fiber (see Section 8.2.3), normally results in poor surface quality and release properties of molded parts. Modified grades of PET have enabled penetration of this polyester into the beverage-bottle market and use in other molding applications (see Section 9.1.3). In the non-bottle market, PET is in competition with a related engineering polyester, poly(butylene terephthalate) (PBT)

$$\left[O-(CH_2)_4-O-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{}{\bigcirc}-\overset{\overset{\displaystyle O}{\|}}{C}\right]_n$$
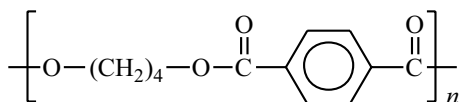
which was introduced by several companies in the early 1970s. Principal applications for PBT include injection-molded parts for electrical and electronic use and for automotive markets. Both polyesters, like polycarbonates, are moisture sensitive (hydrolytic instability) but have high strength, rigidity, and toughness, excellent dimensional stability, low coefficient of friction, abrasion resistance, and good resistance to chemicals and grease.

In the late 1970s, an all-aromatic polyester (polyarylate, PAR) produced by the condensation polymerization of bisphenol-A and mixed phthalic acids

$$\left[\underset{\underset{\displaystyle O}{\overset{\displaystyle \|}{C}}}{\bigcirc}-\overset{\overset{\displaystyle O}{\|}}{C}-O-\bigcirc-\underset{\underset{\displaystyle CH_3}{}}{\overset{\overset{\displaystyle CH_3}{}}{C}}-\bigcirc-O\right]_n$$

was marketed in the United States. Unlike PET and PBT, polyarylate is amorphous and has high clarity, as well as high heat-distortion temperature (T_g in the range of 150° to 200°C), UV stability, inherent flame retardance, and good electrical properties. Typical outdoor applications for polyarylate include solar collectors, safety devices, construction, and transportation. Other uses include the manufacture of plastic parts for electronic and electrical hardware such as lighting fixtures. Unfortunately, a variety of factors, including competition with polysulfone and polycarbonate and poor processability, have virtually eliminated the market for PAR.

Another engineering polyester gaining recent interest is poly(dimethylene cyclohexane terephthalate) (PCT)
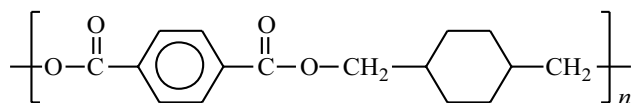
which has high thermal stability and finds applications in some electronic compo-
nents. Like PET, PCT crystallizes slowly and, therefore, nucleating agents and
"hot" oil-cooled molds must be used in order to process PCT in a reasonable time
scale.

Recently, interest has focused on the monomer naphthalene dicarboxylate
(NDC)
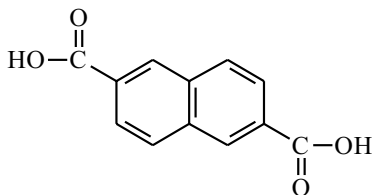
which can be copolymerized with DMT to yield a copolyester with better barrier
and heat resistance for bottle and packaging applications. NDC can also be poly-
merized (with ethylene glycol) to yield poly(ethylene naphthalate) (PEN)
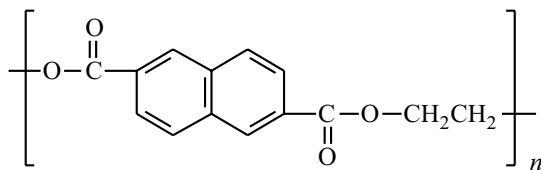
which can be blended with PET to improve properties. PEN can be extruded and
blow-molded and has better mechanical strength, higher heat and chemical resis-
tance, better dimensional, thermal, UV, and hydrolytic stability, and improved bar-
rier properties compared to PET. The higher thermal resistance of PEN (T_g of
120°C compared to approximately 78°C for PET) expands the potential market for
polyester bottles to those such as baby food jars that need to be steam-sterilized.
Current applications for PEN include industrial fiber cord for rubber reinforcement,
blood evacuation tubing, and electronic film, such as long-lasting video-recording
tape. Other potential markets include electrical and electronic parts (e.g., motor in-
sulation, magnetic tapes, and capacitors) and microwaveable packaging for medical
and other applications.

10.1.9 Fluoropolymers

Among the most important fluoropolymers is polytetrafluoroethylene (PTFE or Teflon), obtained by the emulsion free-radical polymerization of tetrafluoroethylene (TFE). Teflon was accidentally discovered by Roy J. Plunket and Jack Rebok who had been working on new refrigerants at DuPont in 1938. On the morning of April 6, Plunket and Rebok noticed that TFE gas stored in a high-pressure vessel in dry ice solidified into a smooth, waxy white powder that seemed impervious to liquids and could not be charred or melted under ordinary conditions. Commercially produced PTFE, introduced in 1950, is highly dense (2.1 to 2.3 g cm^{-3}) with high-temperature stability, low-temperature flexibility, an extremely low coefficient of friction, low dielectric constant and dissipation factor, and chemical inertness. Many of these properties are similar to those of PPS described earlier. Also like PPS, PTFE is extremely difficult to process by conventional techniques. Limited processability is attributed to its extremely high crystallinity and high crystalline-melting temperature (T_m = 327°C), resulting from its highly regular structure and unusually high molecular weight. For coating applications, PTFE is sintered at high temperature and pressure. Recently, researchers at ETH in Zurich have shown that it is possible to melt-process PTFE from medium-viscosity/molar mass micropowders, obtained by γ- or electron-beam irradiation, into a product with good mechanical properties [4].

Improvement in melt processability can also be obtained by incorporating a small concentration of a comonomer such as hexafluoropropylene (Teflon FEP), ethylene (ETFE), or more perfluoroalkoxy (PFA) fluorocarbon resins. In these cases, copolymerization serves to reduce crystallinity. A more recent example of an important TFE copolymer is "amorphous" Teflon (TEFLON-AF)
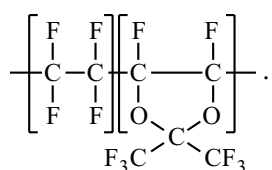
This fluoropolymer can be made by statistical copolymerization of TFE with a fluorinated cyclic ether, perfluoro-(2,2-dimethyl-1,3-dioxole). Incorporation of the cyclic ether prevents crystallization and contributes to better processability, although at a sacrifice in some properties.

In addition to PTFE, several other partially fluorinated polymers listed in Table 10-5 have achieved commercial importance. These include polychlorotrifluoroethylene (CTFE or Kel), which is also available as a copolymer with ethylene or vinylidene fluoride. Applications include electrical insulators, gaskets and seals, and pump parts. Poly(vinylidene fluoride) (PVDF or Kynar), also available as a copolymer with hexafluoroisobutylene (HFIB), is a crystalline polymer (T_m = 170°C) that

finds primary applications in coatings, gasket material, wire and cable insulation, and extruded vinyl siding for houses. Poly(vinyl fluoride) (PVF or Tedlar) is another highly crystalline polymer ($T_m = 197°C$) that can provide tough, flexible films with excellent outdoor weatherability and good abrasion and stain resistance. Applications include protective coatings for materials that are used in the building industry.

Table 10-5 Chemical Structures of Some Important Fluoropolymers

Fluoropolymer	Repeating Unit
Polytetrafluoroethylene	$-\!\!\left[CF_2-CF_2\right]\!\!-$
Fluorinated ethylene-propylene copolymer (FEP)	$-\!\!\left[CF_2-CF_2\right]_m -\!\!\left[CF_2-\underset{CF_3}{CF}\right]_n$
Polychlorotrifluoroethylene (CTFE)	$-\!\!\left[CF_2-\overset{Cl}{\underset{F}{C}}\right]\!\!-$
Poly(vinylidene fluoride) (PVDF)	$-\!\!\left[CH_2-\overset{F}{\underset{F}{C}}\right]\!\!-$
Poly(vinyl fluoride) (PVF)	$-\!\!\left[CH_2-\overset{F}{CH}\right]\!\!-$

Fluorinated polymers also find significant applications as highly thermally and chemically resistant elastomers, as discussed in Section 9.2.2. These include amorphous copolymers of vinylidene fluoride and hexafluoropropylene, which can be crosslinked in the presence of diamines and basic oxides through dehydrofluorination followed by amine addition. Elastomers can also be made from copolymers of TFE and perfluoroalkyl vinyl ethers, such as perfluoromethyl vinyl ether, and copolymers of vinylidene fluoride and hexafluoroisobutylene. Network formation can be achieved by incorporation of comonomers containing nitrile pendant groups, which when heated can form triazine structures.

10.2 Specialty Polymers

Specialty polymers have small but important commercial markets in the aerospace and electronics industries and as materials for biomedical applications. The most important of these include polyimides, ionomers, polyaryletherketones, polyorganophosphazenes, certain aromatic polyesters and high-performance fibers, polyacetylenes and other electrically conductive polymers, and dendrimers.

10.2.1 Polyimides and Related Specialty Polymers

Polyimides represent an important class of high-temperature, solvent-resistant polymers. Typical uses for polyimides include electronics, sleeve bearings, and valve seatings, and as the matrix component of graphite composites for compressor vanes in jet engines and other aerospace applications. Often, polyimides are formed by a two-stage process. The first step involves the polycondensation of an aromatic dianhydride and aromatic diamine to form an intermediate poly(amic acid). Dehydration of the poly(amic acid) at elevated temperatures yields the polyimide (PI) structure. A representative polymerization of a polyimide is shown in Figure 10-10. Unlike the intermediate poly(amic acid), the cured (i.e., fully imidized) PI is insoluble and infusible and has high temperature and oxidative stability and good electrical-insulation properties and radiation resistance.
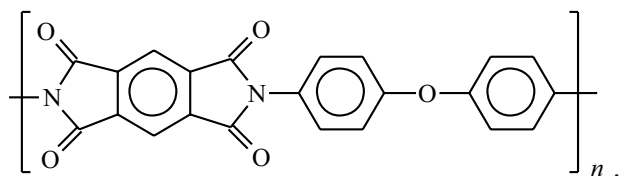
diamine   pyromellitic dianhydride

poly(amic acid)
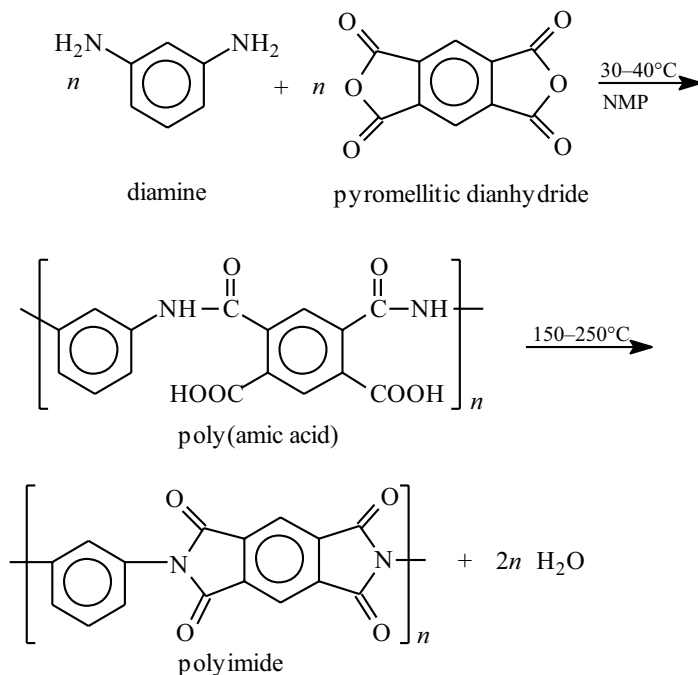
polyimide

**Figure 10-10**   Polymerization of a polyimide.

A large variety of PI structures are possible, limited only by the number of available dianhydrides and diamines. An example of a commercially important PI is a polypyromellitimide available as film called Kapton (DuPont), whose imidized structure is

Kapton is obtained by the condensation polymerization of pyromellitic anhydride
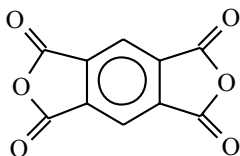
and 4,4-diamino diphenyl ether
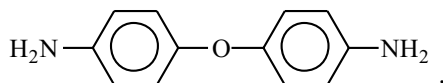
Properties of Kapton are given in Table 10-6.

Table 10-6   Properties of a Polyimide, Polyetherimide, and Poly(amide–imde)

| Property	PI[a]	PEI[b]	PAI[c]
Density (g cm^{-3})	1.42	1.27	1.42
% Elongation at 23°C			15
at yield		7–8	
at break	70	60	
Flexural modulus (GPa), tangent at 23°C		3.31	5.0
Flexural strength (MPa)	—	—	241
HDT, °C at 1.82 MPa (264 psi)	—	200	278
Impact strength, Izod (J m^{-1})			
notched	—	53.4	144
unnotched	—	1335	1068
Tensile modulus (GPa), 1% secant	3.0	3.0	4.8
Tensile strength (MPa) at 23°C, at yield	172	105	192
T_g (°C)	385	217	—
Water absorption, % over 24 h and RT and 40% RH	2.9	0.25	0.33

[a] Kapton H.

[b] Ultem 1000.

[c] Torlon 4203L; contains 3% TiO$_2$ and 0.5% fluorocarbon.

Some disadvantages of these "imidizable" polyimides are the limited shelf life of the precursor poly(amic acids) and possible structural weakness of the fully im-

idized product due to void formation as a result of water release in the curing process. In addition, some thermoplastic polyimides are available. These polyimides are fully imidized but can be melt-processed at high temperatures or can be solution-cast. Solubility in relatively nonpolar liquids is achieved by incorporation of aromatic polyether linkages in the backbone or pendant phenyl and alkyl groups introduced through appropriate selection of the aromatic diamine.

Another approach to PI synthesis, particularly suited for structural composites, is the use of thermoset PIs. A thermoset PI is one prepared by heating a fully imidized PI-prepolymer having a reactive functional group at each end that can react with another prepolymer. An example of a thermoset PI is Thermid resin, which uses acetylene-terminated prepolymers for network formation. The structure of Thermid is given as
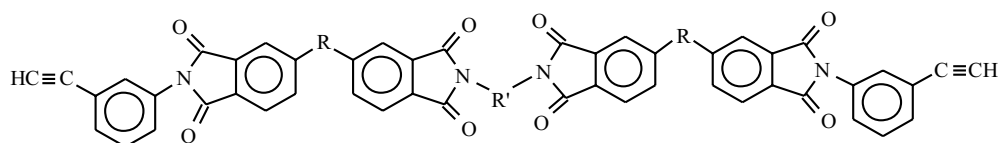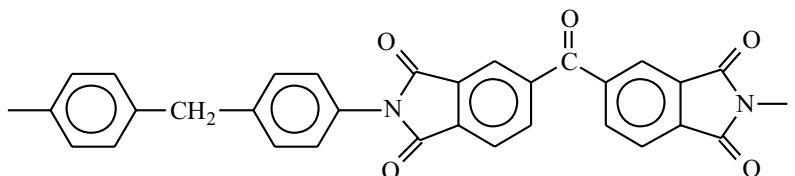

where R is a carbonyl (C=O) or a hexafluoropropane (6F) functionality, $C(CF_3)_2$, and R' is the aromatic group
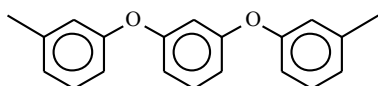

Another important example of a thermoset PI is PMR-15, which has been widely used as the matrix for graphite composites for aerospace applications. PMR-15 uses a norbornene end functionality for network formation
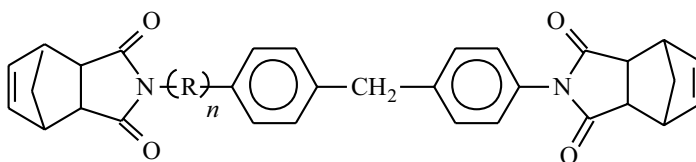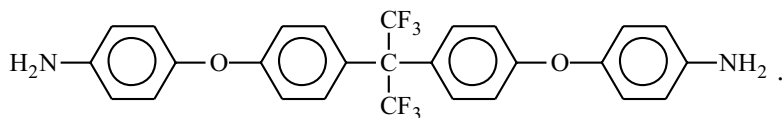

where R ($n \approx 2$) has the aromatic structure

In general, polyimides having excellent thermal and thermooxidative stability (although at much higher cost) can be obtained from fluorinated dianhydrides, especially 6FDA[*]
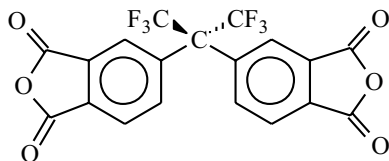
or fluorinated diamines such as 2,2-bis[(4-aminophenoxy)phenyl]hexafluoropropane

Poly(amide-imide) and Polyetherimide. To improve the melt processability of polyimides, the basic imide structure can be combined with more flexible aromatic groups, such as aromatic ethers and amides. For example, poly(amide-imide) (PAI) (e.g., Torlon)
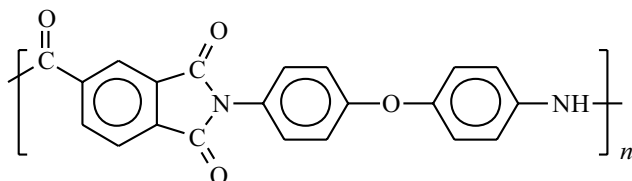
is obtained from the polycondensation of trimellitic anhydride (TMA) and an aromatic diamine (e.g., 4.4'-oxydianiline). Another imide-type engineering thermoplastic is polyetherimide (PEI, Ultem), obtained by a nitro-displacement reaction [5] involving bisphenol-A, 4,4'-methylene-dianiline, and 3-nitrophthalic anhydride.

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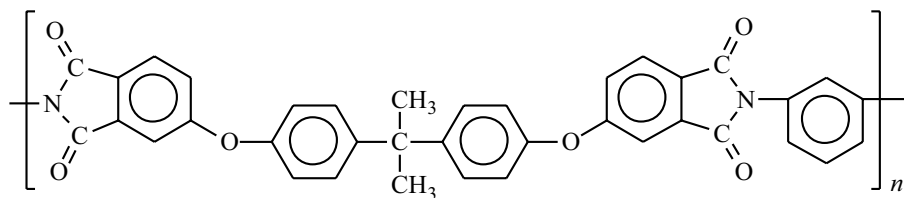
[*] 5,5'-(2,2,2-trifluoro-1-(trifluoromethyl)ethylidene)-bis(1,3-isobenzofuranedione).

Both PAI and PEI have high heat-distortion temperature, tensile strength, and modulus. Properties of a representative polyimide (Kapton H) and two representative grades of PEI and PAI are compared in Table 10-6. Once imidized, Kapton is no longer melt-processable, unlike PAI and PEI, which are compromised by lower softening temperatures (T_g or HDT). Kapton has an HDT of 357°C and a continuous-use temperature of ca. 270°C. One advantage of PAI and PEI over Kapton is their lower water absorption, which is especially important for composite applications. Applications for PAI and PEI include high-performance electrical and electronic parts, microwave appliances, and under-the-hood automotive parts.

Polybismaleimides. A related imide-type polymer is the polybismaleimide (Kerimid, Kinel). A repeating unit can be represented as
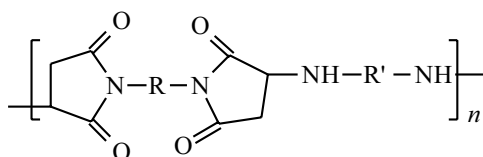
where R and R' represent a variety of aromatic groups. Polybismaleimide is obtained by a (Michael) *addition* of diamine to the unsaturated sites at the ends of a bis-maleimide having a structure similar to
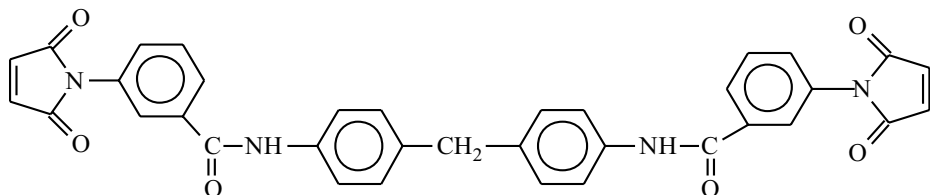
Applications for polybismaleimides include use as composite resin for filament winding and laminates (see Chapter 7), friction pads, gears, and bearings.

Polybenzimidazole. Polybenzimidazole (PBI)[*] is a product of the polycondensation of an aromatic tetramine and an aromatic dicarboxylic acid or derivative [6]. An example of the synthesis of a polybenzimidazole is given in Figure 10-11. As a class, polybenzimidazoles have very high thermal and hydrolytic stability but are often infusible. PBI can be used in fiber form for high-temperature composite and other applications (see Section 10.2.8). It is also being actively considered as a fuel-cell membrane as discussed in Section 12.1.2.

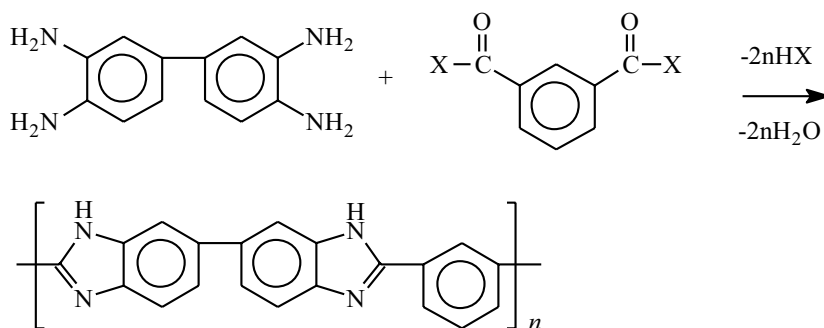[*] Poly[2,2'-(*m*-phenylene)-5,5´-bibenzimidazole].

Figure 10-11   Synthesis of a polybenzimidazole from 3,3'-diaminobenzidine and an aromatic dicarboxylic acid. X represents one of several possible reactive sites including OH, Cl, OCH_3, and OC_6H_5.

Ladder Polymers. At the extreme in high-temperature stability are polymers that incorporate highly fused-ring backbones such as polyimidazopyrrolones. They are obtained by a two-step cure process involving the initial condensation of an aromatic tetracarboxylic acid and aromatic tetramine (Figure 10-12). Such materials, which are sometimes known as *ladder polymers* because their fused-ring structure resembles the rungs of a ladder, are capable of withstanding temperatures in excess of 500°C (see also Section 6.1.1). The first ladder polymers were synthesized in the mid-1960s due to their potential for high thermal stability. More recently, conjugated ladder polymers have been studied for their linear and nonlinear optical properties (see Section 12.4.1) [7].
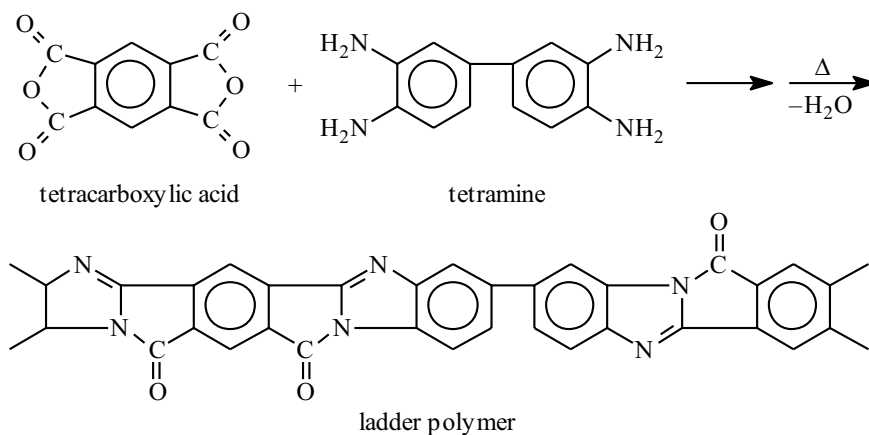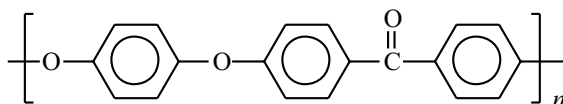

tetracarboxylic acid   tetramine

ladder polymer

Figure 10-12   Polymerization of a ladder polymer, polyimidazopyrrolone.

10.2.2 Polyaryletherketones

A important entry into the engineering thermoplastic market is the poly(aryl ether ketones) (PAEK), of which polyetheretherketone (PEEK, Victrex)

is the most important [8]. As indicated by the data given in Table 10-7, PEEK is semicrystalline but can be melt-processed at elevated temperatures. Attractive properties include good abrasion resistance, low flammability and emission of smoke and toxic gases, low water absorption, and resistance to hydrolysis, wear, radiation, and high-temperature steam. The high solvent resistance, good impact strength, and good thermal stability (maximum continuous working temperature of 260°C) of PEEK make it a good candidate as a thermoplastic matrix for graphite composites (see Section 7.3). Other applications include solvent-resistant tubing for chromatography, wire and cable insulation for hostile environments, and magnet-wire coating.

High-molecular-weight PEEK can be synthesized by the solution polycondensation of alkali bisphenates with activated aromatic dihalides (typically difluoride) at high temperatures, as shown in Figure 10-13. A wide variety of other arylene ether homopolymers and copolymers with T_g values ranging from 114° to 310°C can be prepared by the nucleophilic displacement of aromatic dihalides and potassium bisphenates [9].

Table 10-7   Typical Properties of PEEK

Property	Value
T_g (°C)	143
HDT, °C at 1.82 MPa (264 psi)	148
Crystallinity, %	
Typical	20–35
Maximum	48
Heat of fusion, ΔH_f (J g^{-1})	130–161
Density (g cm^{-3})	
Amorphous	1.263
Crystalline	1.400
Water absorption, % over 24 h and 40% RH	0.15
Solubility parameter (cal/cm^3)$^{1/2}$	9.5
Tensile strength (MPa) at 23°C	91.0
Elongation at 23°C, %	150
Flexural modulus at 23°C, GPa	3.89
Impact strength, Charpy (J m^{-1})	1388

Figure 10-13 Condensation polymerization of polyetheretherketone (PEEK).

10.2.3 Specialty Polyolefins

Polyethylene, having molecular weight in the range of 1 to 5 million (i.e., ultrahigh-molecular-weight PE or UHMWPE), has exceptional impact and tensile strength, tear and puncture resistance, high abrasion resistance, low coefficient of friction, chemical inertness, and good fatigue resistance. Applications for UHMWPE include orthopedic implants, battery separators, grocery sacks, and additives for improving the sliding and wear behavior of other thermoplastics [10]. Melt processability of this high-viscosity polymer can be improved by limiting branching during its polymerization or by incorporating a controlled amount of low-molecular-weight polyethylene, which results in a distinctive bimodal molecular-weight distribution. UHMWPE is processed mainly by compression sintering and ram extrusion into sheet and rod. There has also been interest in the gel spinning of UHMWPE fibers, which combine high tensile strength with low density.

Another member of the specialty polyolefin market is poly(4-methylpentene-1) or PMP, whose structure is

Isotactic PMP, having moderate (40% to 65%) crystallinity, may be polymerized by use of homogeneous Ziegler catalysts like those used in the preparation of i-PP (see Chapter 2). Compared to i-PP, PMP has a higher T_g (18°C compared to -20°C), much higher T_m (300°C compared to 165°C), lower density (0.83 compared to 0.90), and better transparency. The commercial material (TPX) is a copolymer containing a small amount of linear olefins for improved impact resistance and transparency.

10.2.4 Ionic Polymers

Ionic sites may be introduced into polymers through chemical modification or co-polymeriation. Ionic polymers derived from synthetic organic polymers and containing up to 10 to 15 mol % ionic content are called *ionomers*. Those with higher ionic content are called *polyelectrolytes*. Polyelectrolytes are soluble in water but insoluble in common organic solvents. Typical applications for ionomers include ion-exchange resins, membranes for liquid and facilitated gas separations, superacid catalysts, and most importantly as separators in chloralkaline electrolytes.

Ionic sites are typically pendant carboxylic or sulfonic acid groups that are partially or completely neutralized to form the polymeric salt. Counterions may be sodium, zinc, ammonium, or a halide. Typical nonionic polymer backbones include polyethylene, polystyrene, and copolymers of fluorocarbons such as TFE. Due to the general incompatibility of ionic and nonionic segments, micro-phase separation of the ionic groups is typical of ionic polymers. Small aggregates consisting of only ionic material are termed *multiplets*, while larger aggregates that also include nonionic material are called *clusters*. Multiplets, consisting of only a few ions or ion pairs, act as moderately strong, temporary, ionic crosslinks. The larger clusters also act as mechanical reinforcement.

The introduction of ionic groups can have significant effects on the properties of polymers. For example, ionic sites can increase T_g, modulus, and melt viscosity. The extent of property modification depends upon the dielectric constant of the backbone, the position and type of ionic group, the type of counterion, ionic concentration, and the degree of neutralization. The concentration of ionic groups and the strength of interaction between the anion and cation determine the increase in T_g with a relationship given as

$$T_g = \frac{cq}{a} \tag{10.1}$$

where c is the concentration of ionic repeat units in the backbone, q is the charge of the counterion, and a is the distance of closest approach between the centers of charge of anion and cation. Generally, T_g is observed to increase 2° to 10°C per mol % of ionic repeat units.

Ionomers. A common commercial ionomer is Surlyn, a copolymer of ethylene and about 15% methacrylic acid. About 33% of the methacrylic acid comonomers are neutralized with sodium hydroxide to produce the sodium salt, as illustrated in Figure 10-14. Ionic bonding provides a tough material, often used for covering golf balls as a replacement for gutta percha, in packaging applications such as a coating for safety bottles to store hazardous chemicals, and in the manufacture of automotive bumper strips and guards.
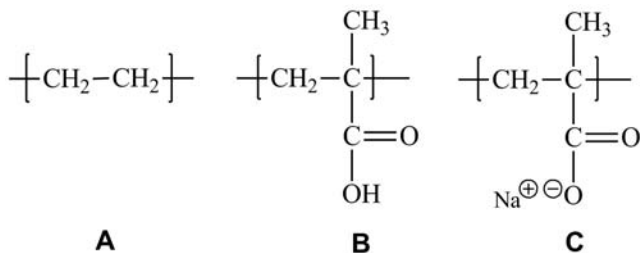
$$+CH_2-CH_2+ \quad +CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{\underset{C=O}{|}}}+ \quad +CH_2-\underset{\underset{Na^{\oplus}\ominus O}{|}}{\overset{\overset{CH_3}{|}}{\underset{C=O}{|}}}+$$

A   B   C

Figure 10-14   Comonomer units in Surlyn A. **A**. Ethylene. **B**. Methacrylic acid. **C**. Sodium salt of methacrylic acid.

Another important class of ionomers is the *perfluorosulfonate ionomers* (PFSI). These are copolymers of TFE and a perfluorinated vinyl ether containing a terminal sulfonyl fluoride (SO_2F) group, as shown in Figure 10-15. The most important commercial PFSI product is Nafion ($y = 1$ in Figure 10-15) manufactured by DuPont, while a related PFSI ($y = 0$) has been developed by Dow Chemical Company. Commercial PFSI films are extruded but can also be solution-cast under special conditions. After film formation, the sulfonyl fluoride groups are converted to sulfonate groups by reaction with sodium or potassium hydroxide, with further conversion to the commercial sulfonic acid (SO_3H) form (Nafion-H). Other ionic forms (e.g., Na^+, Li^+, K^+, Ag^+, Ca^{2+}, and Al^{3+} salts) can be obtained by ion exchange with the appropriate salts. Nafion has selective permeability to ions and can, therefore, be used in the production of chlorine and caustic by electrolysis of salt solutions; it has also been evaluated for use in many other applications, such as a membrane for gas separations, organic electrosynthesis, fuel cells, electrodes, separation of amino acids, controlled drug release, and biosensors (see Section 12.1.2).
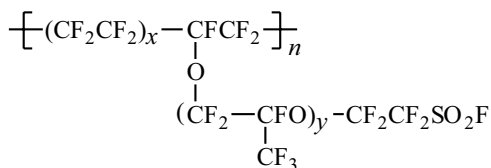
$$+(CF_2CF_2)_x-\underset{\underset{(CF_2-\underset{\underset{CF_3}{|}}{CFO})_y-CF_2CF_2SO_2F}{|}}{\overset{}{\underset{O}{|}}}CFCF_2+_n$$

Figure 10-15   Structure of Nafion perfluorinated ionomer.

10.2.5 Inorganic Polymers

In addition to the polysiloxanes (Section 9.2.2), there are several other polymers having an all-inorganic backbone that have commercial potential for some specialized applications. These include poly(organophosphazenes) and polysilastyrene.
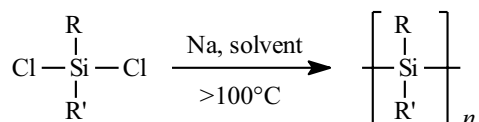
Poly(organophosphazenes). The structure of a poly(organophosphazene) repeat unit, having substituent groups R' and R", is

$$\left[\begin{array}{c} R' \\ | \\ -N=P- \\ | \\ R'' \end{array} \right]_{n.}$$
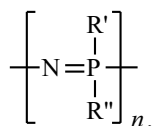
Symmetric substitution (i.e., R' = R") yields crystalline polymers while asymmetric substitution (R' ≠ R") yields noncrystalline rubbery materials suitable for elastomer application. Properties range from highly solvent-resistant, low-temperature flexible elastomers to glassy materials that can be fabricated in film and fiber form. Potential applications of poly(organophosphazenes) include elastomers, coatings, and biomedical encapsulation [11, 12].

Poly(organophosphazenes) may be prepared by substitution of poly(dichlorophosphazene), which is obtained from the radiation or plasma polymerization of hexachlorocyclotriphosphazene. The intermediate polymer, poly(dichlorophosphazene), is unstable due to its high susceptibility to hydrolysis. In the presence of even atmospheric moisture, poly(dichlorophosphazene) decomposes to ammonium phosphates and phosphoric acids. Fortunately, the active chlorine sites can be readily substituted by nucleophiles such as alkoxides, aryloxides, and amines to yield a wide variety of high-molecular-weight polymers that are chemically and thermally stable. Various synthesis routes to prepare poly(organophosphazenes) were discussed in Section 2.4.1.

Polysilanes. Polysilanes, or polysilylenes, are inorganic polymers with an all-silicon backbone. They can be polymerized by a Wurtz-type reaction of a dichlorosilane [13, 14]

$$\text{Cl} - \overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle R'}{|}}{\text{Si}}} - \text{Cl} \xrightarrow[>100°C]{\text{Na, solvent}} \left[\begin{array}{c} R \\ | \\ \text{Si} \\ | \\ R' \end{array} \right]_n$$

where R and R′ are organic substituents. Depending upon the type of side group, polysilanes can be amorphous or highly crystalline. Glass-transition temperatures can range from -50° to 120°C. Polysilanes have good high-temperature thermal stability (up to 250°C or more), are inert to oxygen, and are resistant to hydrolysis. Applications include use as UV photoresists, polymeric photoinitiators, nonlinear optical material, and ceramic precursors. A silane copolymer, polysilastyrene, can be prepared from the solution copolycondensation of dimethyldichlorosilane and phenylmethyldichlorosilane. It is highly soluble and can be spun into fibers, which when heated in an inert atmosphere at very high temperature are converted to a variety of gaseous by-products and β-silicon carbide filaments, as shown in Figure 10-16. Silicon-carbide fibers have extreme strength, as well as exceptional chemical and heat resistance, which makes them suitable for many aerospace applications.
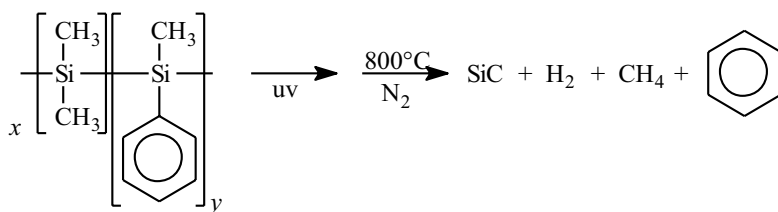
Figure 10-16   Pyrolysis of polysilastyrene to give silicon carbide.

10.2.6 Liquid-Crystalline Polymers

Low-molecular-weight liquid crystals have been known since 1888 when it was shown that heating could cause certain cholesteryl esters to change their optical state from colored and opaque to clear. Flory suggested in 1956 that polymers containing long, rigid units could form anisotropic ordered solutions above some minimum concentration depending upon temperature and the axial (length/diameter) ratio, x, of the polymer chain [15]. According to Flory's lattice theory, the threshold volume fraction, ϕ, is given as

$$\phi = \frac{8}{x}\left[1 - \frac{2}{x}\right] \approx \frac{8}{x} \tag{10.2}$$

for high values of x. Above the critical threshold volume fraction, a stable anisotropic phase is formed from solutions and melts of rod-like polymers. In 1974, liquid-crystal behavior for a polymeric system was first observed in a concentrated solution of poly(benzyl L-glutamate)
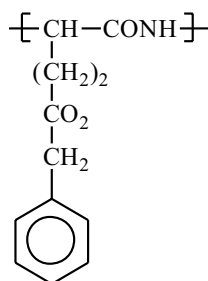
which forms a rod-like α-helical conformation in a variety of organic solvents.

The rigid units or *mesogens* of a liquid-crystalline polymer (LCP) can lie along the polymer backbone or be attached to the backbone as a substituent group (i.e., side-chain LCP) [16]. Polymers that form liquid-crystalline organization in solution are termed *lyotropic*, while those that form from the melt are called *thermotropic*. There are three recognized categories of liquid-crystalline structures. As

illustrated in Figure 10-17, the most ordered structure, the *smectic state*, is observed when all the mesogens are arranged in a parallel and lateral order. The smectic state is rare and has been observed only for thermotropic polymers. More common for polymers is the *nematic* state, in which there is parallel but not lateral order. Aromatic polyamides (aramid) form a nematic liquid-crystalline state in concentrated solution. If mesogens are oriented parallel to one another but the directions vary from one layer to another, the liquid-crystal structure is termed *cholesteric*.

smectic   nematic   cholesteric
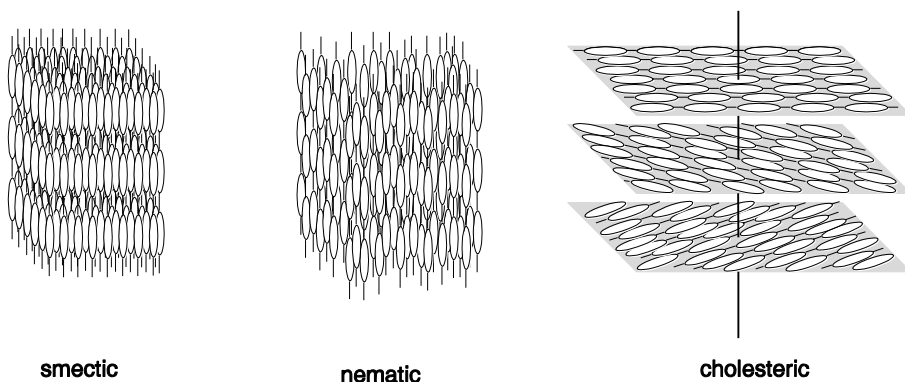
Figure 10-17   Liquid-crystal structures: smectic, nematic, and cholesteric. From R. W. Lenz and J.-I. Jin, *Liquid Crystal Polymers: A New State of Matter*. Polymer News, 1986. **11**: p. 201 Copyright 1986. Reproduced by permission of Taylor & Francis, Inc. http:www.routledgeny.com.

Liquid-crystalline polyesters and copolyesters may have been recognized as early as 1965. Liquid-crystal polyesters have highly aromatic structures such as Vectra (Hoechst Celanese)
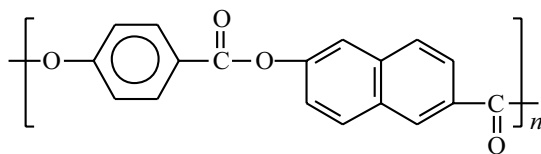
and the thermotropic polyester Xydar (Amoco)
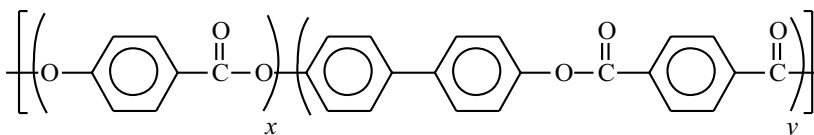
that is made from the polycondensation of *p*-hydroxybenzoic acid (HBA), *p,p*'-biphenol, and terephthalic acid. Such stiff-chain structures lead to ordering of the chains of LCPs in a manner similar to low-molecular-weight liquid crystals.

In general, LCPs are manufactured in a stepwise polycondensation by either a batch or continuous process. The LCP is then mixed with various additives and extruded. A majority of the LCPs sold are reinforced with 30% to 40% glass filler having polymeric sizing to provide a strong interface between the fiber and matrix. Unreinforced grades are injection-molded for specialty applications.

Properties of a part molded from an LCP are highly dependent upon the morphology of the part, which is determined by the conditions of processing. Injection-molded parts exhibit highly oriented skins, with rigid chains oriented in the direction of flow. The core zone beneath this skin is less ordered. This morphology results in very good properties (particularly in the direction of flow) and very high dimensional stability. Other attractive properties of LCPs include exceptional oxygen and barrier properties (100 times that of PETP), very high thermal stability, high modulus and strength, good dimensional stability, and high chemical and solvent resistance. Properties of Xydar are compared to those of a molding-grade PET in Table 10-8.

Table 10-8   Comparison of Properties of PET with Liquid-Crystalline Polyester

| Property	PET[a]	LC Polyester[b]
Tensile strength, MPa	81	126
Tensile modulus, GPa	2.8	8.3
Elongation, %	4–70	5
Flexural strength, MPa	3.0	131
Flexural modulus, MPa		13.1
Izod impact strength, J m^{-1}		
notched		208
unnotched		454
Density, g cm^{-3}		1.35
T_m, °C (or Vicat softening point)	235	358
HDT at 1.8 MPa, °C	80	337

[a] Arnite.
[b] Xydar.

At the moment, the high cost of liquid-crystalline polyesters has limited these resins to specialty applications such as electronic components (e.g., computer memory modules), housings for light-wave conductors, a variety of aerospace applications, and filaments to compete with aramid fibers. This situation could change as monomer costs are reduced through increasing production and supply.

10.2.7 Conductive Polymers

As will be discussed in Section 12.3.1, a number of polymers are electrically conductive or can be made to be conductive by doping with an electron donor or acceptor. Applications include polymeric electrodes for lightweight batteries, variable-transmission windows, electrochromic displays, sensors, and nonlinear optical (NLO) materials. The first of these electrically conductive polymers was polyacetylene. Other specialty polymers in this class that have been extensively studied include polyaniline, polythiophene, poly(p-phenylene), and polypyrrole.

Polyacetylene with molecular weight up to 1 million can be prepared through a complicated process involving a metathesis polymerization (Durham process), as illustrated in Figure 10-18. The *cis* isomer of polyacetylene can be transformed to the more stable *trans* isomer by heating, as follows:

cis-polyacetylene   *trans*-polyacetylene
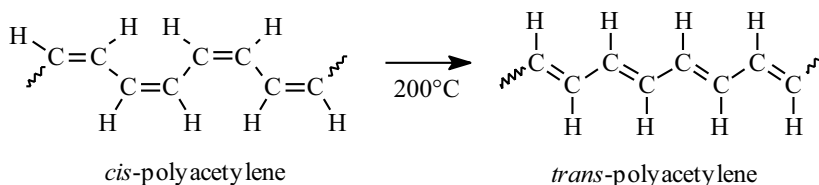
The *trans* isomer has higher conductivity (4.4×10^{-5} S cm^{-1}) than the *cis* isomer (1.7×10^{-9} S cm^{-1}). Conductivity is greatly increased by doping. For example, addition of AsF$_5$ increases conductivity to 400 S cm^{-1}. Polyacetylene has a T_g in the range from -40° to 0°C and good thermal stability (decomposition temperature above 420°C); however, polyacetylene is easily oxidized. Applications include solar cells and batteries.
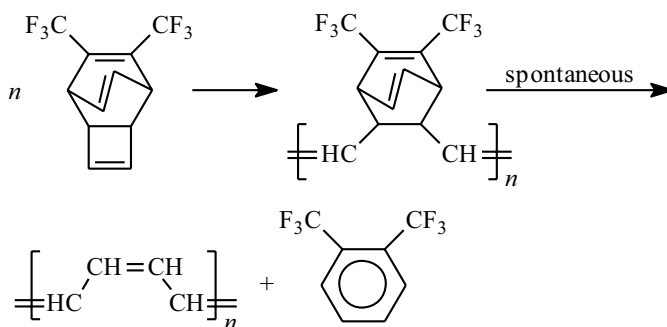

Figure 10-18   Synthesis of *cis*-polyacetylene by metathesis polymerization.

Polyaniline (PANI) can be obtained by the electrochemical or chemical oxidation of aniline in aqueous acidic media using common oxidants such as ammonium

peroxydisulfate. Polyaniline can exist in several oxidation states with vastly differ-ent conductivities (ranging from 10^{-11} to 10^{2} S cm^{-1}). Only the emeraldine salt of polyaniline
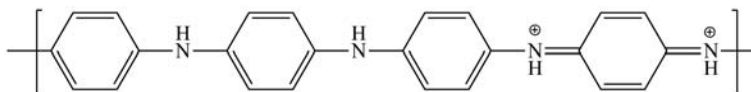

is electrically conductive.

Poly(*p*-phenylene) (PPP) can be prepared by the Freidel–Crafts polymeriza-tion of benzene
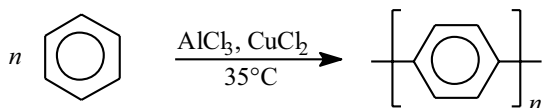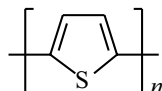

and by other synthesis routes to yield a structurally regular polymer with high strength, solvent resistance, and excellent thermal and thermal oxidative stability [17]. PPP can be converted from an electrical insulator to a highly conductive charge-transfer complex by doping with strong electron donors or acceptors.

Polypyrrole (PPy)
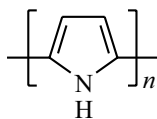

and polythiophene (PT)

are related in structure and properties. Polypyrrole is obtained by the electropoly-merization of pyrrole as a highly colored, dense conducting film while polythio-phene can be polymerized by the anodic oxidation of thiophene. Unlike polyacety-lene, polypyrrole and polythiophene can be synthesized in the doped form and are very stable in air. Unfortunately, their conductivities are lower than that of polya-cetylene (see Section 12.3.1).

Photoconductive Polymers. Some polymers become conductive when illu-minated. The ability to become photoconductive has great importance for the xero-graphic-copier, laser-printer, and duplicator industries. The most important example of a photoconductive polymer is poly(*N*-vinylcarbazole) (PVK)

$$\left[CH_2 - CH \right]_n$$
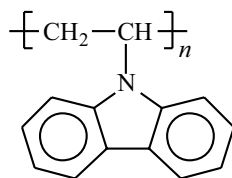
which can be polymerized by free-radical and cationic mechanisms. Both amorphous (free-radical) and tactic PVK can be prepared. Amorphous PVK has a T_g of 227°C and a density of 1.184 g cm^{-3}. In the dark, PVK is an insulator; however, it becomes conductive when exposed to UV radiation. Incorporation of sensitizing dyes or electron acceptors extends the photoconductive response to the visible and near-IR region. In general, photoconductivity can be attributed to the ability to generate free-charge carriers (electron hole) by the absorption of radiation and the subsequent transport of these carriers to the electrodes.

Polyfluorenes. Polyfluorenes are a class of conjugated polymers with both photoactive and electroactive properties with important applications in light-emitting diodes, field-effect transistors, and polymer solar cells [18]. A typical structure of polyfluorene is shown below.
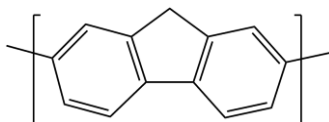
Fluorene can be polymerized by either oxidative coupling or electropolymerization.

10.2.8 High-Performance Fibers

In addition to the aramids, Kevlar and Nomex (see Section 10.1.1), there are several other rigid-rod polymers that can be spun into fibers for high-temperature composite and related applications. These include polybenzimidazole (PBI), polybenzobisoxazole (PBO), and polybenzobisthiazole (PBT).

As discussed in Section 10.2.1, polybenzimidazole is obtained from the polycondensation of an aromatic tetramine and an aromatic dicarboxylic acid or derivative. The most important of the polybenzimidazoles is poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole], shown in Figure 10-11. This polymer is obtained from the polycondensation of tetraaminobiphenyl and diphenyl isophthalate in poly(phosphoric acid) (PPA) in a two-stage process at high temperature [19]. Fiber may be dry-spun from solution in dimethylacetamide and drawn under high temperature to obtain a very high-tensile-strength fiber. PBI has high-temperature stability (in excess of 400°C) and excellent chemical resistance. It will burn only in a high-oxygen-content atmosphere (>48% oxygen). Applications include many of those for which
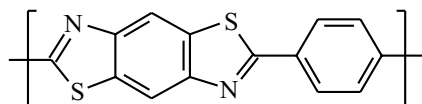
Kevlar may be used, including flue-gas filtration, and generally as a substitute for asbestos.

A related polymer is polybenzobisoxazole (PBO)[*]
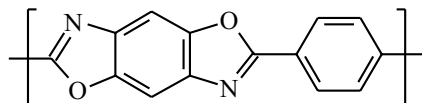
which can be prepared by the polycondensation of 4,6-diamino-1,3-benzenediol dihydrochloride and terephthalic acid in PPA.

Polybenzobisthiazole (PBT)[†]

is obtained from the polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride in PPA.

10.2.9 Dendritic Polymers

Dendritic macromolecules may be classified into dendrons, dendrimers, and hyperbranched polymers. Dendrons and dendrimers are typically prepared by multistep reactions while hyperbranched polymers are synthesized by a one-step self-polymerization of AB_x-type multi-functional monomers where A and B are mutually reactive functional groups [20]. Hyperbranched polymers have a fractal pattern of chemical bonds but branches do not emanate from a central core and may be comb-shaped as an example [21, 22]. The word *dendrimer* comes from the Greek *dendron* meaning "tree" and *meros* meaning "part." Dendrimers have a spherical or globular form similar to that of an ice crystal with many individual branches radiating from the center. A representative dendrimer is shown in Figure 10-19. Some dendrimers can have diameters of more than 10 nm and molecular weights exceeding 1 million. Dendrimers can provide some interesting opportunities. For example, dendrimers can penetrate biological membranes and carry a variety of chemicals or drugs in their low-density interiors. They can be used to remove pollutants from water, serve as nanoscale catalysts and reaction vesicles, control drug release, and moderate chemical reactions. Applications for hyperbranched polymers include coatings, pigment dispersants, and adhesives.

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[*] Poly(*p*-phenylene-2,6-benzoxazole-diyl).

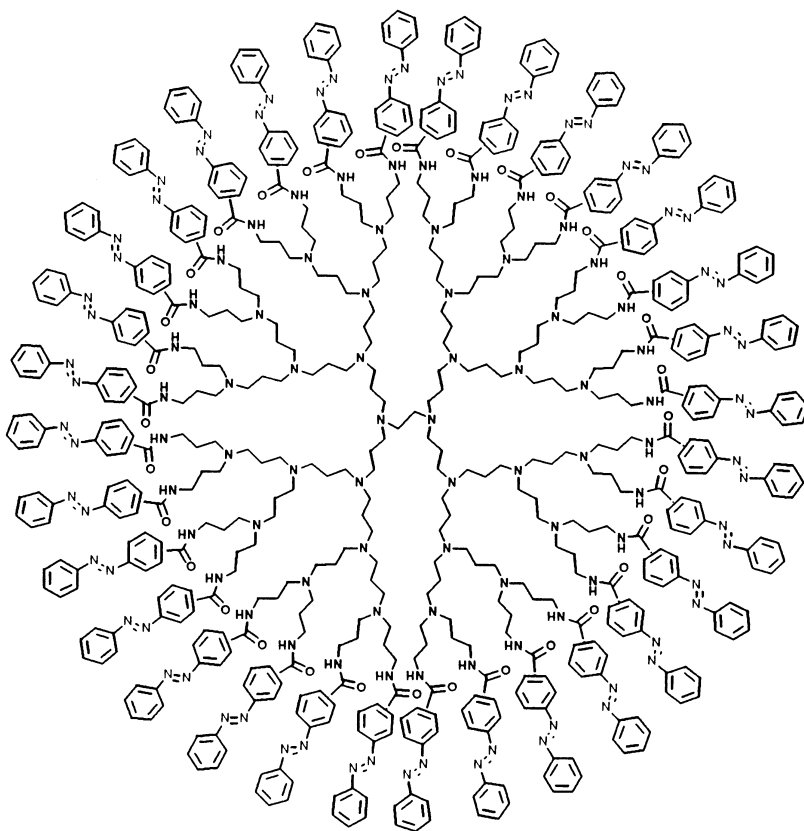[†] Poly(*p*-phenylene-2,6-benzobisthiazolediyl).

Figure 10-19 Azobenzene dendrimer. Reprinted from F. Vögtle, S. Gestermann, R. Hesse, H. Schwierz, and B. Windisch, *Functional Dendrimers*. Progress in Polymer Science, 2000. **25**: p 987–1041. Copyright 2000, with permission from Elsevier Science.

SUGGESTED READING

ENGINEERING PLASTICS

Cebe, P., *Review of Recent Developments in Poly(phenylene sulphide)*. Polymers and Polymer Composites, 1995. **3**: p. 239.

Clarson, S. J., and J. A. Semlyen, *Siloxane Polymers*. 1993, Englewood Cliffs: Prentice Hall.

Feiring, A. F., J. F. Imbalzano, and D. L. Kerbow, *Developments in Commercial Fluoroplastics*. Trends in Polymer Science, 1994. **2**: p. 26.

LeGrand, D. G., and J. T. Bendler, eds., *Handbook of Polycarbonate Science and Technology*. 2000, New York: Marcel Dekker, Inc.

Lopez, L. C., and G. L. Wilkes, *Poly(p-phenylene sulfide)—An Overview of an Important Engineering Thermoplastic*. Journal of Macromolecular Chemistry—Reviews in Macromolecular Chemistry and Physics, 1989. **C29**: p. 83.

Masamoto, J., *Modern Polyacetals*. Progress in Polymer Science, 1993. **18**: p. 1.

Rao, V. L., *Polyether Sulfones*. Journal of Macromolecular Science, Chemistry and Physics, 1999. **C39**: p. 655.

Rigby, R. B., *Polyetheretherketone PEEK*, Polymer News, 1984. **9**: p. 325.

SPECIALTY PLASTICS

Baziun, C. G., and A. Eisenberg, *Ion-Containing Polymers: Ionomers*. Journal of Chemical Education, 1981. **58**: p. 938.

Brostow, W., *Properties of Polymer Liquid Crystals: Choosing Molecular Structures and Blending*. Polymer. 1990. **31**: p. 979.

Dyson, R. W., ed., *Specialty Polymers*. 1987, New York: Chapman and Hall.

Genies, E. M., A. Boyle, M. Lapkowski, and C. Tsintavis, *Polyaniline: A Historical Survey*, Synthetic Metals, 1990. **36**: p. 139.

Gleria, M., and R. De Jaeger, *Aspects of Phosphazene Research*. Journal of Inorganic Organometallic Polymers, 2001. **11**: p. 1.

Hodd, K., *Trends in High Performance Polymers. Part I—Linear High Performance Polymers*. Trends in Polymer Scence, 1993. **1**(5): 129.

Lopyrev, V. A., G. F. Myachina, O. I. Shevaleyevskii, and M. L. Khidekel, *Polyacetylene Review*. Polymer Science USSR, 1988. **30**(10): p. 2151.

Mittal, K. L., ed., *Polyimides: Synthesis, Characterization, and Applications*, vols. 1–2. 1984, New York: Plenum Press.

Negi, Y. S., and P. V. Adhyapak, *Developments in Polyaniline Conducting Polymers*. Journal of Macromolecular Science—Polymer Reviews, 2002. **C42**: p. 35.

Preston, J., *High-Strength/High-Modulus Fibers from Aromatic Polymers*. Journal of Chemical Education, 1981. **58**: p. 935.

Samuel, J., T. Xavier, and T. Kurian, *Ionomers*, Progress in Rubber and Plastics Technology, 2000. **16**: p. 1.

Scherf, U., and D, Neher, eds., *Polyfluorenes*. Advances in Polymer Science, vol. 212. 2008, Heidelberg: Springer Verlag.

Sroog, C. E., *Polyimides*. Progress in Polymer Science, 1991. **16**: p. 561.

Takekoshi, T., *Polyimides*. Advances in Polymer Science, 1990. **94**: p. 1.

Tomalia, D. A., and J. M. J. Fréchet, *Discovery of Dendrimers and Dendritic Polymers: A Brief Historical Perspective*. Journal of Polymer Science, Polymer Chemistry Education, 2002. **40**: p. 2719.

Vögtle, F., S. Gestermann, R. Hesse, H. Schwierz, and B. Windisch, *Functional Dendrimers*. Progress in Polymer Science, 2000. **25**: p. 987.

PROBLEMS

10.1   How is Kevlar synthesized? What is the reason why Nomex was developed before Kevlar?

10.2   Using the material developed in this chapter, suggest the best polymer candidate for each of the following applications and explain your selection:

(**a**) Bullet-proof armor

(**b**) Precision plastic gear

(**c**) Microwave tray

(**d**) Carbonated beverage container

(**e**) Solvent-resistant O-ring

(**f**) Observation window for a deep-dive submarine

(**g**) Golf ball cover

(**h**) Polymeric anode

10.3   Why is PBI an attractive candidate for fuel-cell membranes while the related polymers PBO and PBT are not?

REFERENCES

1.   Hay, A. S., *Polymerization by Oxidative Coupling. II. Oxidation of 2,6-Disubstituted Phenols.* Journal of Polymer Science, 1962. **58**: p. 581–591.
2.   Hay, A. S., *The SPE International Award Address—1975 Polymerization by Oxidative Coupling—an Historical Review.* Polymer Engineering and Science, 1976. **16**(1): p. 1–10.
3.   Dickinson, B. L., *UDEL Polysulfone for Medical Applications.* Journal of Biomaterials Applications, 1988. **3**(4): p. 605–634.
4.   Tervoort, T., et al., *Melt-Processible Poly(tetrafluoroethylene).* Macromolecules, 2000. **33**(17): p. 6460–6465.
5.   Takekoshi, T., *Synthesis of High Performance Aromatic Polymers via Nucleophilic Nitor Displacement Reaction.* Polymer Journal, 1987. **19**(1): p. 1912–02.
6.   Vogel, H., and C. S. Marvel, *Polybenzimidazoles, New Thermally Stable Polymers.* Journal of Polymer Science, 1961. **50**: p. 511–539.
7.   Wang, C.-S., *Properties of Conjugated Ladder Polymers.* Trends in Polymer Science, 1993. **1**(7): p. 199–205.
8.   Nguyen, H. X., and H. Ishida, *Poly(aryl-ether-ketone) and Its Advanced Composites: A Review.* Polymer Composites, 1987. **8**(2): p. 57–73.
9.   Hergenrother, P. M., B. J. Jensen, and S. J. Havens, *Poly(arylene ethers).* Polymer, 1988. **29**(2): p. 358–369.

10. Kelley, J. M., *Ultra-High Molecular Weight Polyethylene.* Journal of Macromolecular Science, 2002. **C42**(3): p. 355–371.

11. Singler, R. E., N. S. Schneider, and G. Hagnauer, *Polyphosphazenes:Synthesis Properties—Applications.* Polymer Engineering and Science, 1975. **15**(5): p. 321–338.

12. Allcock, H. R., *Polyphosphazenes.* Journal of Inorganic and Organometallic Polymers, 1992. **2**(2): p. 197–211.

13. West, R., *The Polysilane High Polymers.* Journal of Inorganic and Organometallic Polymers, 1986. **300**: p. 327–346.

14. Miller, R. D., and J. Michl, *Polysilane High Polymers.* Chemical Reviews, 1989. **89**(6): p. 1359–1410.

15. Flory, P. J., *Statistical Thermodynamics of Semi-Flexible Chain Molecules.* Proceedings of the Royal Society of London, Series A, Mathematical and Physical Science, 1956. **234**(1196): p. 73–83.

16. Lenz, R. W., and J.-I. Jin, *Liquid Crystal Polymers: A New State of Matter.* Polymer News, 1986. **11**: p. 200–204.

17. Gin, D. L., and V. P. Conticello, *Poly(p-phenylene): New Directions in Synthesis and Application.* Trends in Polymer Science, 1996. **4**(7): p. 2172–22.

18. Leclerc, M., *Polyfluorenes: Twenty Years of Progress.* Journal of Polymer Science: Part A: Polymer Chemistry, 2001. **39**: p. 2867–2873.

19. Moelter, G. M., R. F. Tetreault, and M.J. Hefferon, *Polybenzimidazole Fiber.* Polymer News, 1983. **9**: p. 134–138.

20. Dvornic, P. R., and D. A. Tomalia, *Starbust Dendrimers: A Conceptual Approach to Nanoscopic Chemistry and Architecture.* Macromolecular Symposium, 1994. **88**(1): p. 123–148.

21. Jikei, J., and M.-A. Kakimoto, *Hyperbranched Polymers: A Promising New Class of Materials.* Progress in Polymer Science, 2001. **26**: p. 1233–1285.

22. Kim, Y. H., and O. Webster, *Hyperbranched Polymers.* Journal of Macromolecular Science—Polymer Reviews, 2002. **C42**(1): p. 55–89.