

5

Polyamides and polyimides

5.1 NYLONS

5.1.1 Introduction

The term nylon, originally a trade name, later became the generic name given to linear aliphatic polyamides. Nylons can be obtained from a single monomer such as amino acids or their cyclic lactams by self-polycondensation or by ring opening polymerization, respectively. Other nylons are based on two monomers, namely aliphatic diamines and dicarboxylic acids from which they are prepared by polycondensation. The polymeric chains of nylons contain only methylene and amide groups.

Nylons are designated by a numbering system. In the case of single monomer nylons the digits that follow the nylon name represent the number of carbon atoms between two successive amide groups, such as nylon 6 and nylon 12. For nylons based on diamines and dicarboxylic acids, the numeral is composed successively of the number of carbons in the diamine and diacid molecules, respectively. Thus, nylon 6,12 (or 612) is made of 1,6-hexamethylenediamine and 1,12-dodecanoic acid. Copolyamides are described by the numerals of their components such as nylon 6/6,6.

The USA's production of nylons was estimated at approximately 1.15 million tons in 1993 [1]. Nylons are used as fibers (80–90% of the total volume), as engineering plastics, adhesives and rubbers [2,3].

The most important nylons produced commercially are:

1. nylon 4,6: $-\text{NH}(\text{CH}_2)_4\text{NH}-\text{CO}(\text{CH}_2)_4\text{CO}-\text{}$, poly(tetramethylene adipamide);
2. nylon 6,6: $-\text{NH}(\text{CH}_2)_6\text{NH}-\text{CO}(\text{CH}_2)_4\text{CO}-\text{}$, poly(hexamethylene adipamide);
3. nylon 6,9: $-\text{NH}(\text{CH}_2)_6\text{NH}-\text{CO}(\text{CH}_2)_7\text{CO}-\text{}$, poly(hexamethylene azelamide);

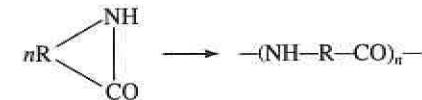
4. nylon 6,10: $-\text{NH}(\text{CH}_2)_6\text{NH}-\text{CO}(\text{CH}_2)_8\text{CO}-\text{}$, poly(hexamethylene sebacamide);
5. nylon 6,12: $-\text{NH}(\text{CH}_2)_6\text{NH}-\text{CO}(\text{CH}_2)_{10}\text{CO}-\text{}$, poly(hexamethylene dodecanedioamide);
6. nylon 6: $-\text{NH}(\text{CH}_2)_5\text{CO}-\text{}$, polycaprolactam;
7. nylon 11: $-\text{NH}(\text{CH}_2)_{10}\text{CO}-\text{}$, poly(11-aminoundecanoic acid);
8. nylon 12: $-\text{NH}(\text{CH}_2)_{11}\text{CO}-\text{}$, poly(12-aminododecanoic acid).

Various copolyamides are also commercially available such as nylon 6,6/6 or 6,6/10.

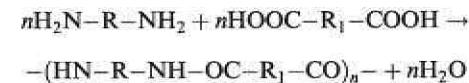
The first synthesis of a polyamide, namely nylon 6,6 is due to Carothers and his coworkers at Du Pont in 1935 as a result of his intensive research work on condensation polymers. The polymer was produced commercially in 1939 and originally used for fibers and later, in 1941, it was used for moldings [4(a)]. Almost at the same time, P. Schlack at I.G. Farbenindustrie in Germany investigated fiber forming polymers not covered by the Du Pont patents and as a result nylon 6 was produced on a commercial scale in 1940 [4(b)]. The production of nylon 11 and 12 was reported in France in 1955 and 1960, respectively [4(c)]. Nylons 7 and 9 were synthesized and investigated as fiber forming materials by Russian chemists [5].

Of the total volume of the above-mentioned polymers, about 80% is represented by only two nylons, 6 and 6,6; these have achieved large scale worldwide production and uses. All other nylons are designed for specific applications and are produced in restricted geographic areas.

Based on raw materials and on polymerization processes, two types of nylons are produced even if their physical properties are very similar. Those based on a unique monomer (polyamides 6–8 above) and designated by a single number are obtained either by the self-condensation of ω -amino acids or by ring opening polymerization of cyclic lactams:



The second type of polyamides (1–5 above) designated by two numbers are synthesized by the polycondensation of aliphatic diamines with aliphatic dicarboxylic acids:



5.1.2 Synthesis of aliphatic polyamides

(a) Nylon 6

Caprolactam is the raw material for nylon 6. It is preferred to ω -amino-caproic acid because it is easier to produce and to purify. Caprolactam may be prepared by various procedures based on the reactions presented in Figure 5.1.

The bulk of manufacture starts from cyclohexane (obtained by the fractionation of petroleum and natural gas) which is air oxidized to cyclohexanone. Cyclohexanone is also produced by the catalytic hydrogenation of phenol. In the next step, cyclohexanone is treated with hydroxylamine sulfate to form cyclohexanone oxime. The oxime is stirred with oleum (sulfur trioxide in sulfuric acid) and undergoes Beckmann rearrangement to yield the caprolactam. In this process, a cumbersome amount of 4–5 tons of ammonium sulfate per ton of caprolactam is obtained as a by-product. To avoid the use of hydroxylamine sulfate, the oxime can be alternatively prepared by catalytic ammoxidation of cyclohexanone with ammonia and hydrogen peroxide [6]. Another method, which avoids such high quantities of ammonium sulfate, involves a photochemical reaction of nitrosyl chloride with cyclohexane and gives cyclohexanone oxime directly [7].

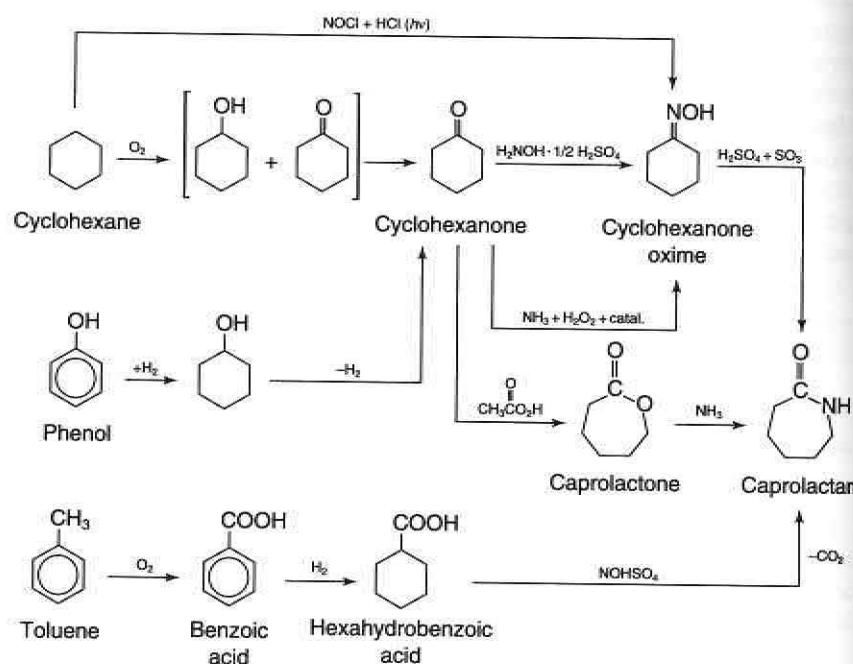
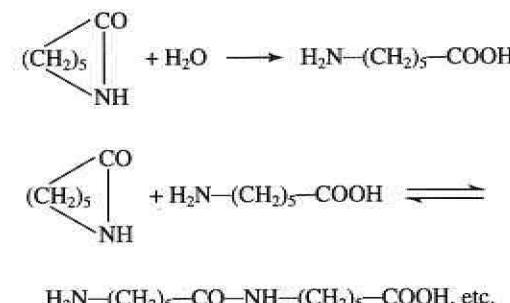


Figure 5.1 Various methods for caprolactam synthesis.

Caprolactam can be prepared from cyclohexanone via caprolactone. Cyclohexanone is oxidized with peracetic acid (made by air oxidation of acetaldehyde) to caprolactone which is then treated with ammonia to form caprolactam [7]. A different process involves oxidizing toluene to benzoic acid in air, followed by reduction to hexahydrobenzoic acid and treatment with nitrosylsulfuric acid to give caprolactam.

Pure caprolactam is a white, hygroscopic, crystalline solid melting at 69.3°C.

Nylon 6 is prepared by hydrolytic or anionic ring opening polymerization of caprolactam [8,9,10]. The water initiated polymerization is believed to begin by the hydrolysis of caprolactam to form the amino acid which subsequently reacts with lactam by ring opening:



Water initiated polymerization can be brought about by both batch and continuous processes. In a typical batch procedure, the molten caprolactam is mixed with 5–10% water by weight, which constitutes the catalyst, and with 0.1% acetic acid as the MW regulator. All the operations are effected under a nitrogen blanket in order to prevent discoloration. The mixture is maintained at 250°C and 1.5 MPa for 12 hours. The resultant polyamide is extruded as ribbon and cut into chips. The product contains up to 10% low MW compounds (unreacted caprolactam, higher lactams and amino acids). A good quality product is obtained by the demonomerization of the raw polymer either by leaching with water at 85°C or by heating at 180°C and 5 kPa.

Similar reaction conditions are used in the continuous polymerization process. The reaction mixture is continuously fed and resides in the reactor for about 18 hours at 250°C.

The flow chart of the hydrolytic polymerization process of caprolactam is presented in Figure 5.2.

Rapid polymerization of caprolactam, achieved by the use of anionic initiators, was developed for the casting polymerization procedure *in situ* and for the reaction injection molding technique (RIM).

Anionic polymerization of caprolactam is carried out under anhydrous conditions using strong bases ($B^- M^+$) such as metal hydrides, metal

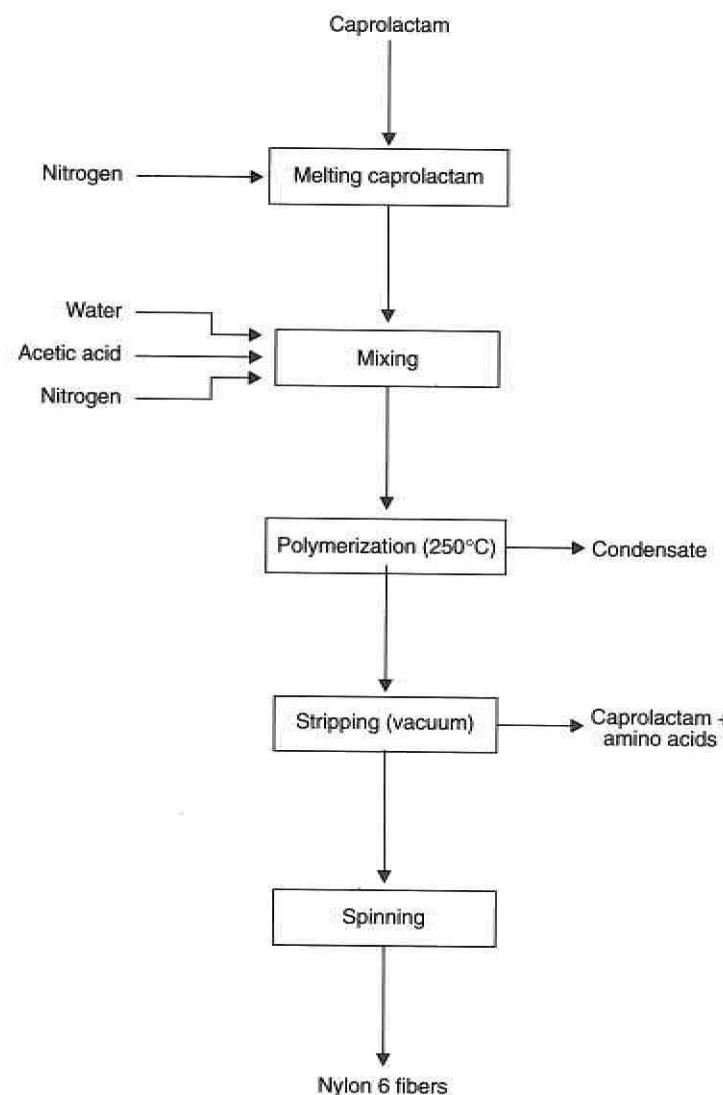


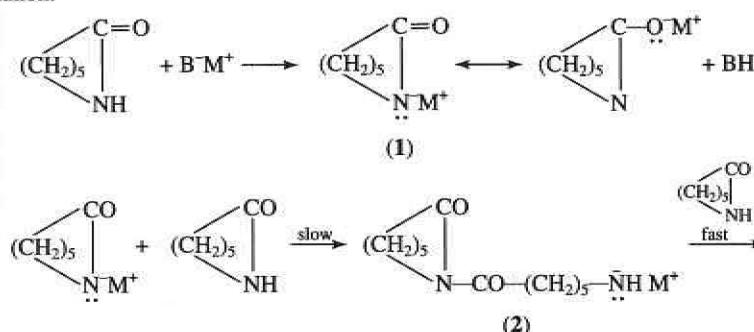
Figure 5.2 Hydrolytical polymerization of caprolactam.

amides and alkali metals as catalysts. The mechanism using base B^- involves initial formation of a resonance stabilized anion (1) which reacts slowly with the monomer and gives the amine anion (2) which is not stabilized by resonance.

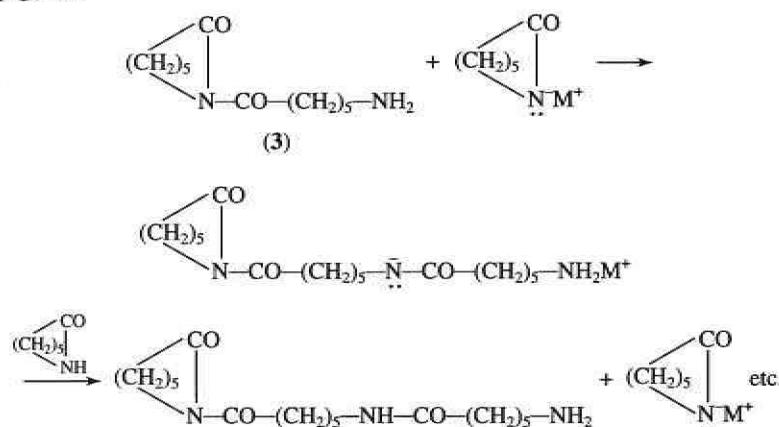
Because the second step is slow, this type of ring opening polymerization by strong bases alone is characterized by an induction period [11]. Once the active amine anion (2) is formed it undergoes rapid proton transfer;

the acyllactam (3) which is formed participates in the propagation.

Initiation:



Propagation:



The induction period may be eliminated by the addition of co-initiators (called activators) such as *N*-acyllactams that ensure rapid polymerization. A typical initiating system consists of a mixture composed of 0.15–0.50 mol% catalyst and 0.1–1 mol% of initiator. Common catalysts are caprolactam magnesium bromide and sodium caprolactam. The initiators used most often are bis-acyllactams and reaction products of diisocyanates or of isocyanate terminated prepolymers with caprolactam [7,12]. The reaction temperature is initially about 150°C but during the polymerization it rises to about 200°C. The liquid mixture is poured into a mold and polymerized *in situ* in four minutes. Very large moldings, up to one ton in weight, have been produced by casting techniques [13]. A recent study on the kinetics of anionic polymerization of caprolactam demonstrated that the polymerization and crystallization time at 150°C is less than 90 s [14].

RIM technique, a variation of the casting polymerization technique initially developed for polyurethanes, has also been adapted for nylon 6

and used for making mechanical parts such as gears, bumper covers and housings for business machines [15]. Nylon RIM (discussed in Section 5.3) are block copolymers of caprolactam and polyols.

(b) Nylon II

The polymer is prepared by the self-condensation of ω -aminoundecanoic acid, $H_2N-(CH_2)_{10}-COOH$, a crystalline solid melting at 189°C. The raw material for the amino acid is castor oil, a vegetable product composed of the triglyceride of ricinoleic acid. By a sequence of reactions ω -amino-undecanoic acid is obtained. This amino acid may also be produced by telomerization reactions [5].

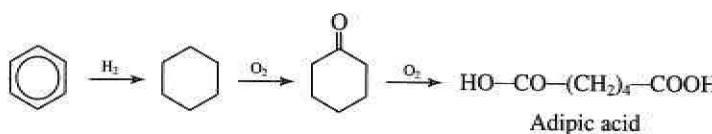
The self-condensation of ω -aminoundecanoic acid is conducted in a continuous process at about 220°C withdrawing water continuously [16]. The latter stages of the process are conducted under reduced pressure. Small quantities of the order of 0.4–0.6% of 12-membered ring lactam are produced by intramolecular condensation but it is not normally removed since its presence has little effect on the properties of the polymer.

(c) Nylon 12

Nylon 12 is obtained by the hydrolytic polymerization of dodecanelactam $\text{HN}-(\text{CH}_2)_{11}-\text{CO}$ prepared from butadiene by a multistaged reaction. The process is conducted at about 300°C in the presence of aqueous phosphoric acid. It is not an equilibrium reaction such as the polymerization of caprolactam and hence the residual monomer concentration is low and the extraction step is eliminated [17].

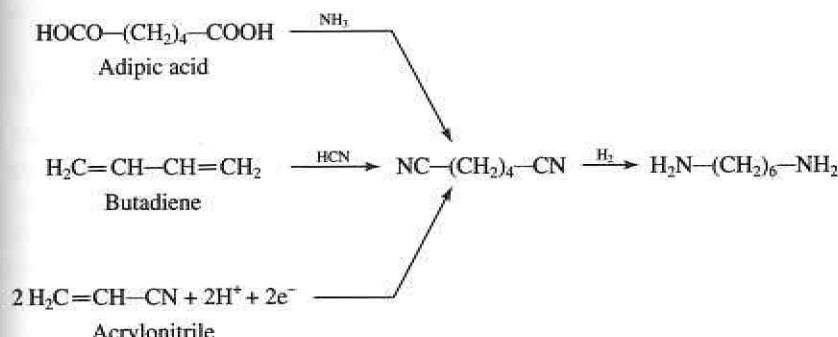
(d) Preparation of nylon 6,6

Nylon 6,6 is prepared by the polycondensation reaction of adipic acid and 1,6-hexamethylenediamine. The raw material for adipic acid is cyclohexane obtained from petroleum or natural gas by fractionation. Another source of cyclohexane is benzene which is hydrogenated using Raney nickel as catalyst. Cyclohexane is oxidized with air using cobalt naphthenate as catalyst. The mixture of cyclohexanol and cyclohexanone obtained in the first step is subsequently oxidized in the second step with 50% nitric acid and an ammonium vanadate–copper catalyst:

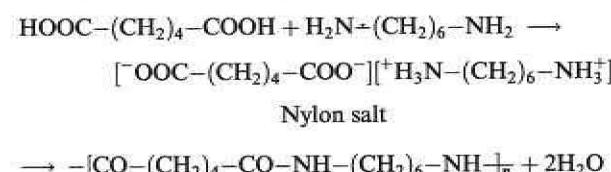


The crystals of adipic acid, HOOC-(CH₂)₄-COOH, are separated from the reaction mass by centrifuging and drying. Their melting point is 152°C.

1,6-Hexamethylenediamine, $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$, is prepared by the hydrogenation of adiponitrile which may be obtained by several commercial procedures. The standard route to adiponitrile is by treatment of adipic acid with ammonia. By other more recent methods, adiponitrile is obtained either by the reaction of butadiene with hydrogen cyanide or by the electrolytic dimerization of acrylonitrile:



In order to obtain high MW nylon 6,6 (10 000–15 000), it is necessary to ensure the equivalence of the number of amino and acid groups. Equivalent amounts of adipic acid and hexamethylene diamine form the hexamethylene-diammonium adipate known as ‘nylon salt’:



The first step, prior to polycondensation, is the preparation of nylon salt. Two commercial procedures are employed. One of them consists of the exact neutralization, determined electrometrically, of an aqueous solution of adipic acid with hexamethylenediamine followed by its concentration to 75-80%. In the other method the salt is prepared by mixing the acid and the amine in boiling methanol from which the insoluble salt precipitates out.

The subsequent polycondensation of nylon salt may be carried out as a discontinuous or continuous process. In the batch process, the 75–80% solution of the salt together with acetic acid used as MW regulator are fed into the reactor and heated to 220°C at an autogeneous pressure of about 2 MPa for 1–2 hours. The temperature is then raised to 270–280°C and steam is bled off to maintain the same pressure. The polycondensation is completed by heating for two more hours while reducing the pressure to atmospheric. The molten polymer is extruded by nitrogen on a water cooled drum to

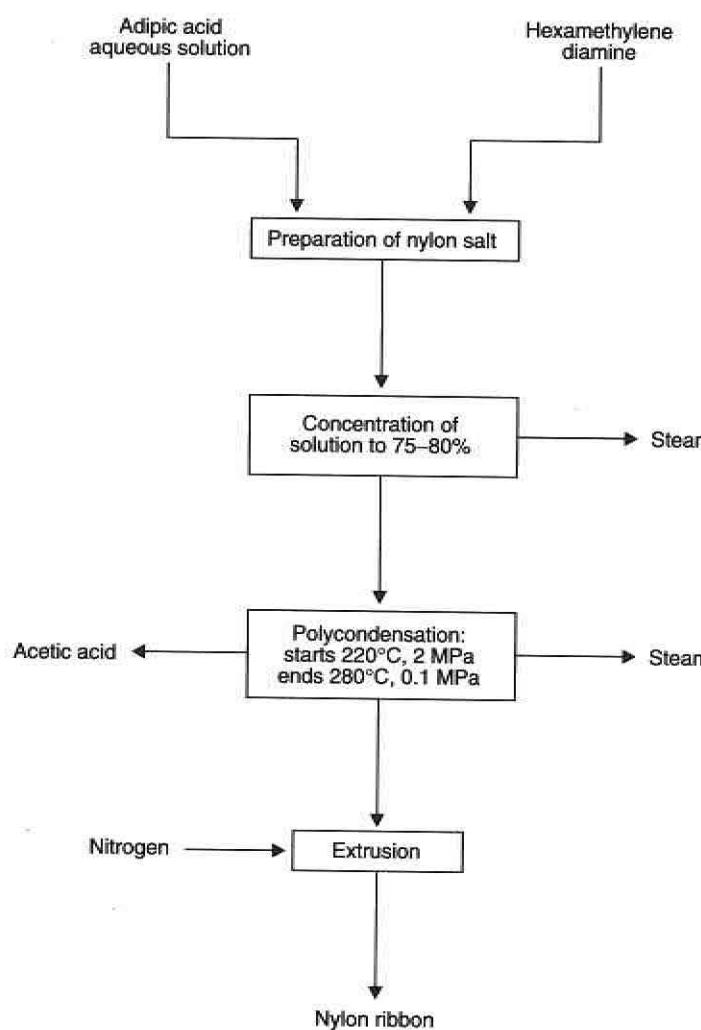


Figure 5.3 Preparation of nylon 6,6.

form a ribbon which is subsequently disintegrated. In the continuous process the reaction mixture traverses slowly different reaction zones in a coiled tube reactor and the polymer is generally directly melt spun into fiber.

The flow chart of the preparation of nylon 6,6 is presented in Figure 5.3.

(e) Nylons 4,6; 6,9; 6,10 and 6,12

Compared to nylon 6 and 6,6, these polymers are prepared in much smaller quantities and are designed for specific applications. They are prepared in an

essentially analogous manner, mostly by discontinuous processes. The nylon salts are synthesized in the first step from hexamethylenediamine and the corresponding dicarboxylic acids [18]:

- azelaic acid, 9 C atoms (obtained from oleic acid) for nylon 6,9;
- sebatic acid, 10 C atoms (obtained from castor oil) for nylon 6,10;
- dodecanoic acid, 12 C atoms (obtained from butadiene) for nylon 6,12.

Nylon 4,6 introduced in the late 1970s is prepared from 1,4-diaminobutane and adipic acid [19].

5.1.3 Properties of nylons

Nylons are linear thermoplastic polymers containing highly polar amide groups $-\text{NH}-\text{CO}-$ separated by flexible aliphatic hydrocarbon chain segments. Amide groups lead to strong intermolecular hydrogen bonding so that polymers are composed of crystalline regions with high cohesive energy density and amorphous zones that impart some flexibility to the polymer.

These structural characteristics determine the general properties of nylons such as:

- sharp melting points, at high temperatures;
- high tensile strength, rigidity, hardness and resistance to creep;
- high heat deflection temperatures;
- high abrasion resistance;
- low thermal coefficient of linear expansion;
- reduced solubility;
- tendency to absorb water from the environment.

The general properties of commercial nylons are presented in Table 5.1.

Nylons with higher concentrations of amide groups have higher T_m , tensile strength and water absorption but lower impact strength. Longer aliphatic segments between amide groups impart more flexibility, higher impact strength and are easier to process because of their lower T_m . The glass transition temperatures of nylons are below room temperature so that materials have a certain flexibility.

The length of aliphatic segments and the even or odd number of methylene groups determine the packing ability of the polymer chains and the frequency of hydrogen bonding, and consequently the percentage of crystallinity and the morphological structure of crystalline regions.

Processing conditions have also a very important influence on the crystallinity of nylons. Slowly cooled and subsequently annealed nylon 6 may reach 50–60% crystallinity compared to only 10% for a rapidly cooled material [13]. Small and uniform spherulites are formed upon slow cooling. Nucleating agents such as fine silica (in amounts of 0.1%) favor the formation of



Table 5.1 General properties of nylons

Property	4,6	6,6	6,9	6,10	6,12	6	11	12	6,6/6,10 (35:65)	6,6/6,10/6 (40:30:30)
Density (g/cm^3)	1.18	1.14	1.09	1.07	1.13	1.04	1.02	1.08	1.09	1.09
Melting temperature ($^\circ\text{C}$)	280	264	205	215	210	185	175	195	195	160
Heat distortion temperature ($^\circ\text{C}$)	—	199	—	160	160–180	150	140	—	—	—
— at 0.5 MPa	—	150–170	100–104	60	66–85	65	54–91	55	50	30
— at 1.8 MPa	100	80	59	59	—	59	76	38	46	52
Tensile strength (MPa)	3	3	—	2.1	—	—	2.8	1.4	1.4	1.4
Tensile modulus (GPa)	30	80–100	—	100–150	150–300	50–100	280–300	200	>200	300
Elongation at break (%)	—	27–53	59	85–107	53–101	53	96	101	107	—
Izod impact strength (J/m)	R123	R118	—	R111	R114	R112	R108	R107	—	R83
Rockwell hardness	14	8.0	—	2.4	3	9.0	2.0	1.8	6.5	10.7
Water absorption at saturation (%)	9.2	10	—	15	9	9.5	15	12	—	—
Coefficient of linear expansion ($10^{-5} \text{ cm}/\text{cm} \cdot {}^\circ\text{C}$)										

such spherulites that give polymers with more uniform structures, enhanced mechanical properties and high abrasion resistance.

The melt viscosity of nylons is rather low due to their high melting temperatures and to relatively low MW.

The solubility of nylons is very reduced because of their crystalline structure. Only those solvents with similar high solubility parameter are capable of interaction with the polymer. These are strong proton donor solvents such as formic and acetic acids, concentrated mineral acids and phenols. Nylons are resistant to aliphatic and aromatic hydrocarbons, lubricants, engine fuels, hydraulic fluids, refrigerants and paint solvents. They are also resistant to aqueous solutions of alkalis and inorganic salts at room temperature.

On exposure to outdoor conditions, particularly in film and filament applications, discoloration and reduction in mechanical properties occur because of relatively poor UV resistance and stabilizers such as carbon black are recommended.

All nylons are hygroscopic to some extent, the higher the content of amide groups, the higher the water absorption. Thus, nylon 4,6 absorbs about 14% of water; it has the highest level of absorption among nylons. The absorbed water acts as plasticizer reducing the tensile strength, tensile modulus, hardness and resistance to creep but increasing the impact strength.

Another effect of water absorption is the dimensional instability: for each 1% of absorbed water there would be a 0.9% increase in volume [18]. In humid conditions of work, nylon 11 and 12 should be chosen as their water absorption is lower. Glass reinforced nylons (30%) retain their dimensions particularly well in a humid environment. At room temperature and under conditions of low humidity, nylons are good electrical insulators at low frequencies.

Polyamides exhibit good oxygen barrier properties but have a high permeability for carbon dioxide [20]. The combination of these two characteristics is put to profit in food packing applications.

Nylons exhibit molding shrinkage specific to crystalline polymers. For nylon 6,6 the molding shrinkage is 0.018 cm/cm [18]. An after-shrinkage effect, especially for nylon 6,6, may occur for periods up to two years due to a very slow relaxation of molding stresses and absorption of water which produces a plasticizing effect. In order to provide more dimensional stability, the after-shrinkage may be accelerated by annealing the parts at temperatures that correspond to maximum crystallization rates.

Various nylon random copolymers based on four, five or more aliphatic and cyclic monomers are developing rapidly, to afford ever-new copolyamide variations. They are prepared commercially either by copolymerizing more than two monomers or by mixing two or more nylons before processing by amide interchange reactions. By copolymerization, products with tailor-made property combinations and improved processability can be

manufactured. As expected, the resulting structures are less regular, which considerably reduces or even cancels the crystallinity. Consequently, nylon copolymers have lower T_m , are easier to process, have lower tensile strength, are more flexible, tougher and more transparent.

Additives significantly change one or more of the properties of nylon resins. They are incorporated into nylons by the manufacturers and only general information is made available. The following additives are used in nylons.

1. Nucleating agents, such as fine silica or phosphorus compounds, are used to control the percentage of crystallinity and the morphological structure of the crystalline regions. They contribute to higher nucleating rates which lead to smaller spherulites. Consequently, polymers have more uniform structures and higher impact strength and abrasion resistance. High melting point polymers such as nylon 6,6 or poly(ethylene terephthalate) may be used as nucleating agents, especially for nylon 6 [13].
2. Heat stabilizers are used in order to obtain good resistance to high temperature aging. They are mercaptobenzimidazole, mercaptobenzothiazole, phenylnaphthylamine, phosphoric acid esters [21] and especially copper salts which are very effective.
3. Light stabilizers such as carbon black improve the performance of nylons in outdoor applications where their resistance to ultraviolet radiation is relatively poor.
4. Impact modifiers are incorporated into impact grade nylons. They are rubber-type materials such as polyurethanes, ethylene-propylene rubbers, ionomers, ABS polymers, acrylates and methacrylates. Rubber droplets are dispersed in the matrix of nylon without any interaction between the two phases.
5. The most common additives for nylon resins are the reinforcing fillers. They may be glass fibers, glass beads, carbon fibers or certain mineral fillers such as talc. They impart a significant increase in stiffness, impact tensile strength, hardness as well as in heat deflection temperature and maximum service temperature. Self-extinguishing properties of glass filled nylons are also improved.

A comparison of the properties for unfilled and filled nylon 6 and nylon 6,6 are presented in Table 5.2.

Glass fillers are added in the amount of 15–50% to the resin. They are treated with silane coupling agents before blending in order to improve the resin–glass bonding.

When glass beads are used as fillers, the composite nylon resin has an increased compressive strength up to eightfold as compared to unfilled material.

Nylon resins may also come with other additives such as plasticizers, lubricants, flame retarders, pigments, fungicides, etc. depending on their specific

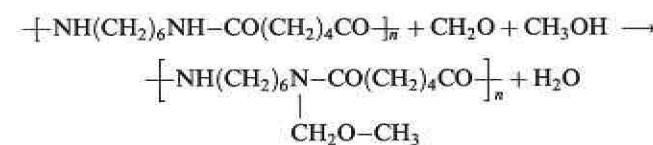
Table 5.2 Effect of glass fiber reinforcement on properties of nylon 6 and 6,6

Property	Nylon 6		Nylon 6,6	
	Unfilled	Filled	Unfilled	Filled
Tensile strength (MPa)	76	115–220	80	160
Elongation (%)	50–100	2–3	80–100	3–5
Flexural modulus (MPa)	2410	5000–11 000	3000	8000
Izod impact strength (J/m)	53	60–190	53	—
Heat deflection temperature under load (°C)				
– 0.5 MPa	160–180	220	200	250
– 1.8 MPa	54–90	190–215	100–104	250
Coefficient of linear expansion (10^{-5} cm/cm · °C)	9.5	—	9.9	2.8
Water absorption at saturation (%)	9	—	8–9	5–6
Maximum service temperature (°C)	180	199	199	241

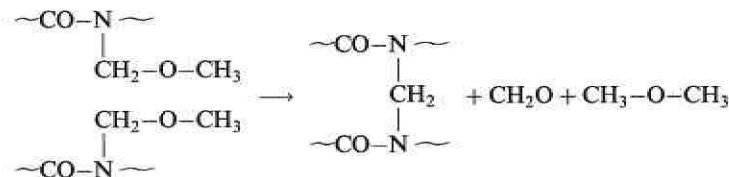
applications. The most frequently used halogen-free flame retarder is based on melamine derivatives [20].

Waste polyamides can be split into their monomers by hydrolysis or recycled and reused, maintaining a good level of properties [20].

Modified nylons with reduced hydrogen bonding, in which about 33% of amide hydrogen atoms have been substituted by methylmethoxy groups, are also available on the market. The methoxymethylation is accomplished by the treatment of the resin dissolved in 90% formic acid with formaldehyde and methanol, in the presence of phosphoric acid as catalyst:



This methylmethoxy nylon is then crosslinked by heating at 120°C with 2% citric acid:



Methylmethoxy nylons have been used as flexible and abrasion resistant coatings.

5.1.4 Applications of nylons

The bulk of about 80% of the total production of nylons goes into fibers where high tensile strength polymers are required [1]. However, due to their outstanding properties, nylons have become indispensable in almost all branches of engineering. Since the price of nylons is almost three times that of general purpose materials (polyethylene and polystyrene), they are used as plastics only in those applications where high mechanical characteristics are required. In 1992, the worldwide market volume of nylons for non-fiber applications reached 1 million metric tons [20].

Several factors such as mechanical properties, dimensional stability and ease of processing have to be considered for the selection of a nylon resin for a specific application. Nylon 6 and 6,6 have the highest tensile strength and are mainly used for fibers. Nylon 6 is the best material for shock-proof parts since it is tough. High mechanical loads are well withstood by nylon 6,6, which has the greatest hardness and stiffness. Nylons 11 and 12 are preferred for cable sheathing, surgical sutures and for precision engineering parts as they are easier to process, have smaller hygroscopicity and are more dimensionally stable.

More than 80% of nylons go into synthetic fiber applications, for clothing, tire cords, ropes and mostly for carpets.

The major engineering field is in the automotive industry as parts for chassis, steering wheels, steering column bearings, bumpers, housings for rear view mirrors, parts for electrical equipment, for transmission systems, for fuel supply system, parts in the engine block and in the lubricating system and many others. For example, fuel tanks are composed of six co-extruded plastic layers, with a central barrier forming polyamide layer.

In mechanical engineering they are used in a large variety of parts such as gears, cams, bearings etc. and particularly where moving nylon parts may often be operated without lubrication and are silent running.

The second largest consumer of polyamides is the electrical industry. In telecommunications nylon resins are used for circuits and relays, for contact makers, for drive units, for cable sheaths, for plug and socket devices, etc. Nylons 11 and 12 are used as coatings for underground cables in hot continents where the resistance to termite attack and formic acid are particularly important.

In building and sanitary industries they are used as water heater tanks, heat exchangers, thermostat casings, fans, chairs and other furniture, sterilizable moldings for medical uses, hair combs, etc.

Nylon films, particularly from nylon 11, are used in packaging pharmaceutical products and foodstuffs especially for those applications that need boil-in-the-bag treatment. Chemical and abrasion resistant coatings are obtained from nylon 11 by fluidized bed dipping and powder spraying techniques.

Nylon 6 is used for the production of large objects such as propellers for marine craft by the polymerization casting of caprolactam, as was already mentioned.

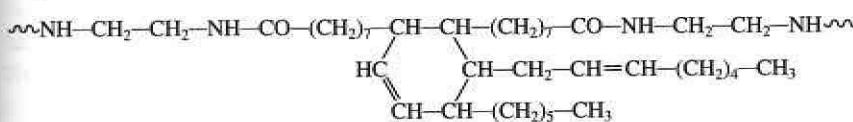
Composite glass reinforced nylon materials have replaced metals in many applications due to their outstanding mechanical properties. Carbon fiber reinforced nylon found use in aerospace and tennis racquet applications [13]. Blends of nylon 6,6 and thermoplastic elastomers such as ethylene-propylene-diene terpolymer and super-tough materials that offer new options for hard-soft composites [20].

Completely novel applications have been opened by blending copolyamides and amylose-containing starch which may be processed into biologically degradable molded articles and films [20].

5.2 ALIPHATIC POLYAMIDES FROM DIMER ACIDS

Drying vegetable oils (tung, soybean and linseed oils) contain a mixture of esters of polyunsaturated acids such as linoleic acid, $C_{18}H_{32}O_2$. The mixture of free acids obtained by the saponification of oils, is subsequently heated in the presence of a catalyst and the unsaturated acids are dimerized, trimerized and polymerized. This complex mixture of inexact structure ranging from dark viscous liquids to brittle resins is known as 'dimer fatty acids' as 60–75% of its content is composed of dimerized acids.

The dimer acid is subsequently used as the acid component for the preparation of polyamides with bulky side groups. Suitable amines are ethylenediamine or diethylenetriamine and the structure of the polyamide may be:



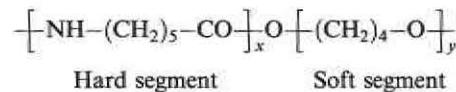
Some of the fatty polyamides are tough and flexible solid resins and find use as hot melt adhesives and as coatings for flexible substrates such as plastic films, paper, etc. Those fatty polyamides prepared with amines that have a functionality of higher than two, are highly branched and liquid. They have free amine groups and are mainly used as curing agents and flexibilizers for epoxy resins intended for adhesives and thixotropic paints.

5.3 POLYAMIDE THERMOPLASTIC ELASTOMERS

Polyamide thermoplastic elastomers are block copolymers that exhibit the characteristics of vulcanized rubber at normal temperatures but behave as

thermoplastics on heating. Similar to other thermoplastic elastomers (polyurethanes and polyesters), the chains of polyamide thermoplastic elastomers are composed of two different alternating blocks, a hard thermoplastic block with a T_g well above room temperature and a soft elastomeric block which has a T_g below room temperature.

The hard segment may be any of the nylon-type polyamides described previously, most frequently polycaprolactam and polylaurinlactam. The soft segments are composed of polyether diols such as poly(oxyethylene) glycol, poly(oxypropylene) glycol or poly(oxytetramethylene) glycol. A typical structure of a polyamide thermoplastic elastomer based on polycaprolactam and poly(oxytetramethylene) glycol is:



The hard segments of different chains are linked to each other by strong hydrogen bondings characteristic to polyamide polymers, and constitute hard thermoplastic semicrystalline domains interspersed in the continuous soft matrix. They act as physical crosslinking points and are responsible for the high tensile strength, abrasion resistance and high service temperature (up to 150°C). The flexibility properties of the material are imparted by the amorphous soft elastomeric matrix. Upon heating, the hard phases melt and the material is fluid and can be easily processed. On cooling, reformation of the physical crosslinks and the separation of phases occur and a rubbery material is obtained.

Polyamide block copolymers may be prepared either by the classical polycondensation process or by the newer reaction injection molding process (RIM) [7,15,22].

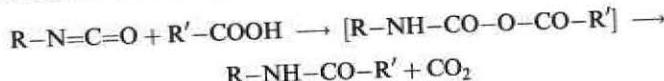
By the first route, a polyamide with MW = 300–15 000 and carboxyl end groups is first prepared, and it is subsequently condensed with the polymeric diol (MW = 100–6000) to give the block copolymer.

In the RIM process for nylons, as in the case of PU, the polymer is formed very rapidly from the reaction components. Two components are used in the nylon RIM process: the first is a solution of the catalyst in caprolactam and the second is the mixture of caprolactam with the initiators. Preferred catalysts are caprolactam magnesium bromide made from caprolactam and alkyl magnesium bromide and sodium caprolactam, made from caprolactam and sodium hydride [7]. The most frequently used initiators are bis-acyl-lactams such as adipyl-bis-caprolactam, the reaction products of diisocyanates with caprolactam or of isocyanate terminated prepolymers with caprolactam [7].

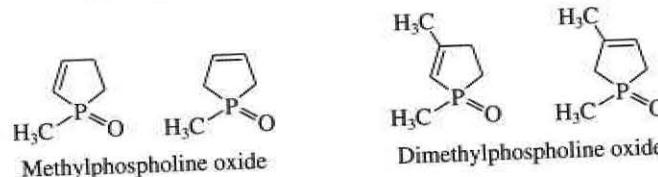
Contrary to PU, nylon–RIM reactions are endothermic and the process is conducted at 130–140°C with cycle times of 2–3 minutes. In the RIM process the injection pressures are low, requiring much lower locking forces of the

mold than in conventional injection molding. This represents an advantage for the processing of large moldings.

One recent development has been the preparation of polyamide elastomers by a new route based on the reaction of dicarboxylic acids with diisocyanates [23–25]. The reaction implies the intermediate formation of unstable carbamic carboxylic anhydride which decomposes to amide with the evolution of carbon dioxide. The reaction is represented schematically below:

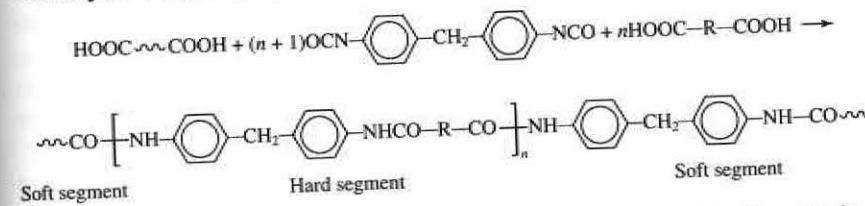


It was shown that the temperature and catalysis affect the distribution of products obtained, as undesirable side reactions can take place [25]. Amide formation is base catalyzed but higher conversions of monomers to amide and consequently higher MW polyamides are obtained using as catalyst a mixture of methylphospholine oxide and dimethylphospholine oxide [26]:



The phospholine oxide catalyst participates in the reaction but is regenerated and recuperated at the end and can be reused. The solvents that gave better results at high polycondensation temperatures were tetramethylene sulfone, diphenyl sulfone and butyrolactone [27].

The polyamide elastomers are based on 4,4'-methylene bis(phenylisocyanate) (MDI), a small molecule dicarboxylic acid and an aliphatic prepolymer of polyester-, polyether- or polycarbonate-type with $M_n = 500–5000$ and carboxylic end groups [23,25]:



The polycondensation can be carried out in two ways. In the solution variant (Figure 5.4), the acid and acid prepolymer are dissolved in the inert solvent and mixed with the catalyst. MDI is then added under stirring to the solution at elevated temperature. Evolved carbon dioxide is vented out. At the end the polyamide is separated from the solvent and catalyst in film evaporators, solid polymer is pelletized and stored while the recovered solvent and catalyst are recycled to the reactor. An alternative and more

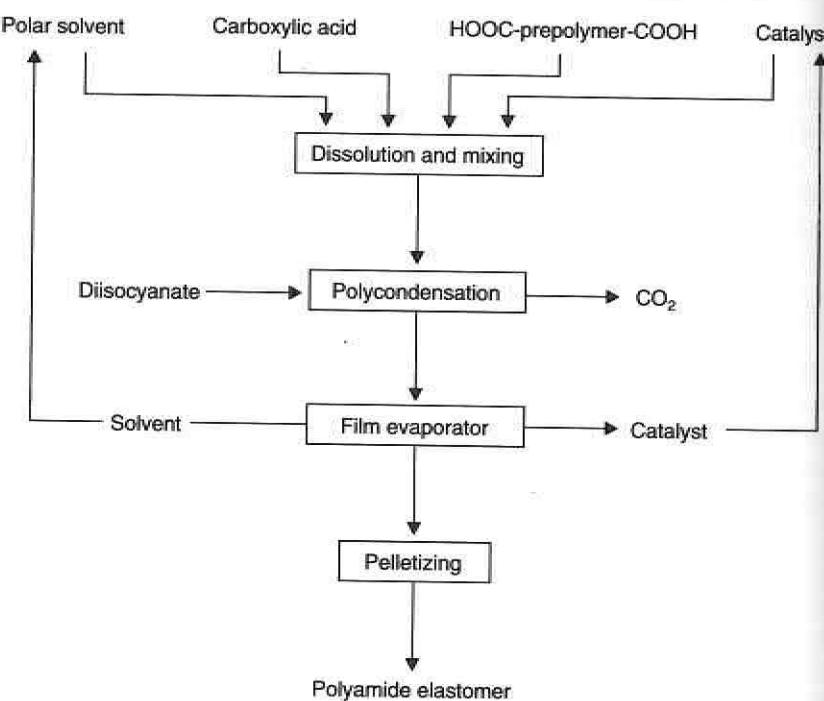


Figure 5.4 Preparation of polyamide thermoplastic elastomers from diisocyanates in an economic way is the melt polycondensation conducted in a properly vented extruder.

The properties of polyamide thermoplastic elastomers are controlled by the appropriate selection of the type, the length and the ratio of the hard and soft blocks. The hardness, the flexibility and the impact strength are maintained over the temperature range -40° to $+80^{\circ}\text{C}$. Polyester based elastomeric polyamides are susceptible to hydrolysis in humid conditions and hydrolytic stabilizers such as polymeric carbodiimides are used. Abrasion resistance is as good as in the case of PU. UV stability is excellent even without stabilizers. The general range of properties of polyamide thermoplastic elastomers are presented in Table 5.3.

The properties of thermoplastic polyamide elastomers place them on top of all other thermoplastic and thermoset elastomers but they are also the most expensive [28]. They share 2.5% of the market of all thermoplastic elastomers. Thermoplastic elastomers have the major environmental advantage over thermoset rubbers that they are completely recyclable at the end of their service life.

Polyamide elastomers can be favorably blended with nylons, PET and PBT. They accelerate the crystallization rates of PET and PBT [25]. Usual fillers are glass fibers and minerals.

Table 5.3 Some properties of polyamide thermoplastic elastomers

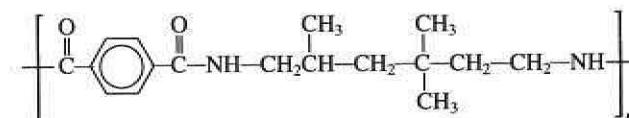
<i>Property</i>	<i>Value</i>
Density (g/cm ³)	1.01–1.15
Melting temperatures (°C)	120–270
Maximum service temperature (°C)	150
Tensile strength (MPa)	18–42
Tensile modulus at 300% (MPa)	18–33
Elongation (%)	270–500
Hardness (Shore)	60A–63D
Flexural modulus (MPa)	20–410
Water absorption (% vol.)	1.2–120

Applications include automobile bumpers and fascia, housings for business machines, gaskets and seals, watch straps, high performance athletic goods, military shoes, etc. The worldwide consumption of polyamide thermoplastic elastomers in 1992 was estimated at 7000 tons [20].

5.4 PARTIALLY AROMATIC POLYAMIDES

Partially aromatic polyamides include those polyamides in which at least one of the components is aromatic. This group of polyamides constitutes high performance engineering thermoplastics with excellent temperature stability. They comprise a large variety of materials from completely amorphous and transparent to partially crystalline [13,20,24]. Aliphatic and cycloaliphatic amines are preferred to aromatic amines which have poor reactivities and high melt viscosities. The acids generally used are terephthalic and isophthalic acids. Polyamides based on aromatic amines have also been prepared, but by using an alternative route based on commercially available aromatic diisocyanates and various dicarboxylic acids [25].

1. Poly(trimethylhexamethylene terephthalamide) is an amorphous copolyamide prepared by the polycondensation of terephthalic acid with a 1/1 mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diamine:



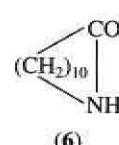
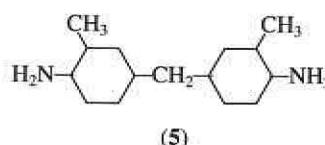
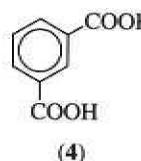
The presence of substituent methyl groups on both amine molecules as well as the irregular structure of the copolymer prevent the crystallization of the amorphous material, which is consequently highly transparent and more soluble than nylons. The aromatic structures in the polymer chain account

Table 5.4 Some properties of poly(trimethyl hexamethylene) terephthalamide

Property	Value
Density (g/cm ³)	1.12
Tensile strength (MPa)	68
Tensile modulus (MPa)	3000
Elongation (%)	70
T _g (°C)	150
Deflection temperature at 1.8 MPa (°C)	130
Molding shrinkage (cm/cm)	0.007
Refractive index	1.566

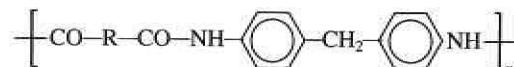
for a T_g as high as 150°C, good heat deformation resistance, rigidity and hardness. Compared to nylon, the material has lower water absorption and better electrical insulation properties and very low molding shrinkage. Some properties are given in Table 5.4.

2. Another amorphous and transparent copolyamide with similar properties is prepared from isophthalic acid (4), bis-(4-amino-3-methylcyclohexyl) methane (5) and laurinlactam (6):



This copolyamide has a very low water absorption and the lowest density (1.06 g/cm³) among polyamides.

3. Various transparent copolyamides have been prepared by the condensation of 4,4'-diphenylmethane diisocyanate with (a) a 30/70 mixture of adipic (C6) and azelaic (C9) acids and (b) a 50/50 mixture of isophthalic and azelaic acids and 2,4-toluylene diisocyanate. The general structure of type (a) polyamide is given below:



where R = (CH₂)₄/(CH₂)₇ = 30/70.

High MW polyamides are obtained when the condensation is conducted by adding MDI to a solution that contains the mixture of carboxylic acid and phospholine oxide catalysts at temperatures above 150°C [26]. The best solvents are tetramethylene sulfone, diphenyl sulfone or butyrolactone [27]. At the end of the polycondensation, the solution is fed into evaporators where the solvent and the catalyst are stripped and the polymer

Table 5.5 Some properties of MDI based polyamides

Property	Value	
	Polyamide 70/30	Polyamide 50/50
Density (g/cm ³)	1.17	1.16
T _g (°C)	140	180
Heat deflection temperature at 1.8 MPa (°C)	127	160
Tensile strength (MPa)	83	82
Tensile modulus (MPa)	1869	2289
Elongation at break (%)	80	30
Mold shrinkage (cm/cm)	0.005	0.0035

is pelletized and stored. The solvent and the catalyst are recycled and reused.

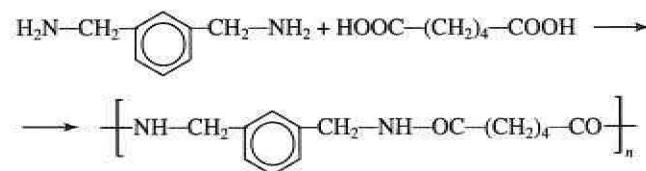
An alternative polycondensation process may be run in the melt by reactive extrusion with adequate venting of carbon dioxide by-product [26].

Mechanical properties compare favorably with those of polycarbonate and polysulfone plastics. Electrical properties are much less influenced by moisture because of the high aromatic content and their relatively high T_g. Some properties of MDI based polyamides are given in Table 5.5.

All these amorphous and transparent polyamides compete with poly(methyl methacrylate) for their transparency but they are as tough as polycarbonate and polysulfone. Their aging and chemical resistance are also good.

Partially aromatic polyamides are used for transparent flow meter parts, sight glasses and spectacle frames, counters and containers for solvents, transparent housings for different equipment, X-ray apparatus windows and sanitary fittings.

4. Partially crystalline polyamides are produced by the polycondensation of adipic acid with *m*-xylylene diamine:



These polyamides have T_m values in the range 235–240°C, T_g = 100°C and low heat deflection temperatures of about 96°C. Therefore these polyamides are not suited for high temperature applications and they are used only in composite materials which have improved heat deflection temperature and mechanical characteristics. Glass fibers (30–50%), carbon fibers

Table 5.6 Some properties of glass filled composites

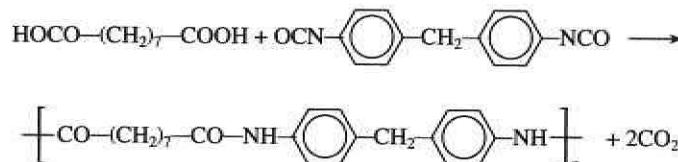
Property	Value
Tensile strength (MPa)	185
Flexural modulus (GPa)	10
Heat deflection temperature at 1.8 MPa (°C)	220–230
Molding shrinkage (cm/cm)	0.003–0.006

and particulates can be chosen as reinforcing fillers. Other additives such as impact modifiers and fire retardants are used specifically.

Some characteristics of glass filled composites are presented in Table 5.6.

Composite polyamides may replace metals in some applications. They are used as shafts and gears, electrical plugs and sockets, machine components and other mechanical parts.

5. Another semicrystalline polyamide is prepared by the condensation of MDI and azelaic acid in a similar way to that described in 3 above:



This polyamide has a relatively high T_m at 290°C and T_g at 135°C. Combined with suitable reinforcing and nucleating agents, the polyamide is a valuable engineering thermoplastic with high modulus and tensile strength, high heat resistance, dimensional stability, good electrical properties and excellent chemical resistance. It is used in automotive under-the-hood and other harsh industrial applications. Blends with 15–30% bottle grade PET or PBT are engineering resins with good properties and lower cost.

Table 5.7 Some properties of unfilled and glass reinforced semicrystalline polyamides

Property	Glass reinforced		
	Unfilled	30% glass	40% glass
Density (g/cm ³)	1.17	1.40	1.49
Tensile strength (MPa)	71	148	195
Tensile modulus (MPa)	1681	5757	7193
Elongation (%)	5.0	4.0	4.1
Flexural modulus (MPa)	2459	7648	10 018
Heat deflection temperature at 1.8 MPa (°C)	130	247	247

Some properties of unfilled and reinforced polyamides of this group are presented in Table 5.7.

5.5 AROMATIC POLYAMIDES

Aromatic polyamides or aramid fibers, according to the definition of the US Federal Trade Commission, are 'manufactured fibers in which the fiber-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings'.

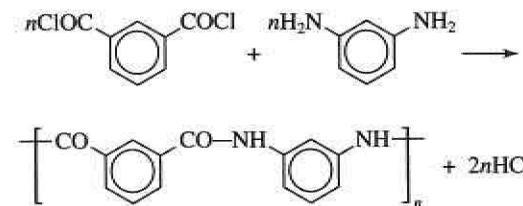
The synthesis of aromatic polyamides is not possible by the direct condensation of acids and amines as aromatic amines are less reactive than aliphatic and would not lead to macromolecular products. On the other hand, the very high melting temperatures and the discoloration and decomposition in the molten state make the bulk polycondensation technique impracticable. For these reasons, aromatic polyamides are obtained by the more costly solution and interfacial polycondensation methods of diacid chlorides and diamines [30–35].

Few details are made available on the synthesis of aramid fibers. A flow chart of the general method of interfacial polycondensation applied to aramid fibers is presented in Figure 5.5.

The acid chloride is dissolved in an organic solvent immiscible with water such as methylene chloride, carbon tetrachloride or cyclohexanone. The diamine is brought into an aqueous solution containing sodium carbonate as acid acceptor. As the monomers are very reactive to each other, the polycondensation is effected by vigorous mixing of the two immiscible solutions. The reaction takes place at the liquid interface or just inside the solvent boundary. The material is supplied by the manufacturers as fibers, obtained by spinning into hot air the solution of polymer in dimethylformamide containing lithium chloride.

Several aramid fibers are available on the market.

1. The first fiber, poly(*m*-phenylene isophthalamide) was produced at the end of 1960 by the polycondensation of isophthaloyl chloride with *m*-phenylenediamine:



The poly(*m*-phenylene isophthalamide) fibers are characterized by their good mechanical properties at elevated temperatures. Even at ambient temperature, their mechanical, chemical and electrical insulation properties

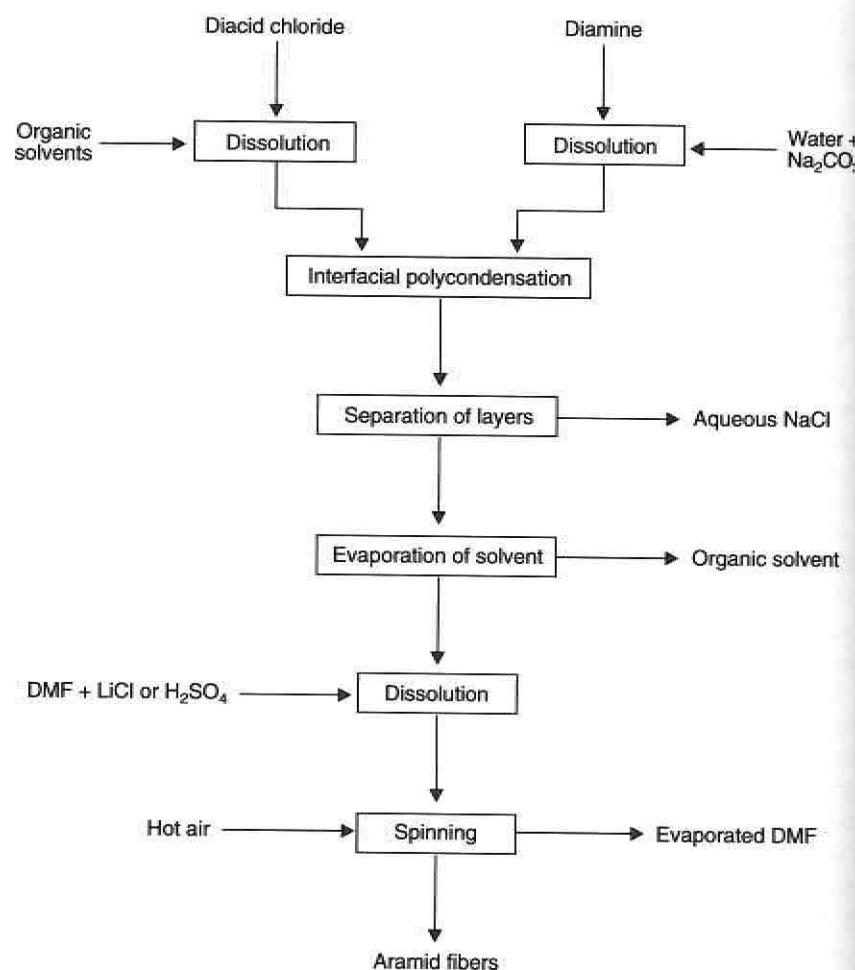
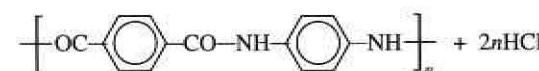
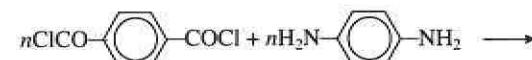


Figure 5.5 Preparation of aramid fibers by interfacial polycondensation.

are similar to those of nylons 6 and 6,6; at 260°C they still retain half of these properties. The crystalline melting point is 368–390°C; the material resists ignition but shrinks considerably.

The fibers are used for heat protective clothing and for electrical insulation at high temperatures.

2. Poly(*p*-phenylene terephthalamide) has the highest strength/density properties among commercially available fibers. It is another aramid fiber and was commercialized in 1972. The polymer is prepared by low temperature solution polycondensation of terephthaloyl chloride with *p*-phenylenediamine in a solvent composed of a 2:1 mixture of hexamethylphosphoramide and *N*-methylpyrrolidone at –10°C:



The polymer is dissolved in sulfuric acid and spun into fibers. In sulfuric acid solution the polymer is lyotropic as it exhibits a liquid crystal phase formed under the influence of the solvent. Extrusion of this solution into fibers and removal of the sulfuric acid results in further alignment of the molecules, with the result that they are even more uniform than could be obtained by drawing. As a general rule, *p*-linked benzene rings give rise to molecules that are rigid along their main axis and are typical for liquid crystal structures [36–41].

Poly(*p*-phenylene terephthalamide) fibers are competitive with glass, carbon and steel fibers. They are advantageously used as fillers in composite materials as they have lighter weight, greater stiffness and higher tensile strength than composites based on glass fiber reinforcement [42]. The heat resistance of the polymer is high as it retains about half of the tensile strength after 100 hours at 250°C. Some comparative properties of poly(*p*-phenylene terephthalamide) and glass fibers are presented in Table 5.8.

The polymer does not melt but begins to carbonize at 425°C. Thermal and electrical insulating properties of aramid based composite materials are better than those of glass fiber counterparts.

The volume of poly(*p*-phenylene terephthalamide) used in 1987 was about 10 tons and continues to grow as new applications are found. It is used as fiber and fabric reinforcement for composite materials, particularly with epoxy resins, in many applications. These advanced composites have replaced conventional aluminum for floors, ceilings, bulkheads, side walls and other parts in the aircraft and aerospace industry, reducing weight, manufacturing costs and maintenance demands [42].

Other uses for poly(*p*-phenylene terephthalamide) reinforced composites are for boat hulls, military protection helmets and filament-wound rocket

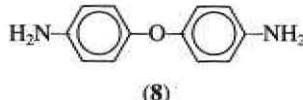
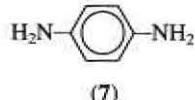
Table 5.8 Comparative tensile properties of aramid fibers and glass fibers

Property	Aramid fiber*	Glass fiber
Density (g/cm ³)	1.44–1.47	2.49–2.55
Tensile strength (GPa)	3.45–3.62	3.10–4.14
Tensile modulus (GPa)	124–186	72–85
Elongation at break (%)	2.0–2.5	4.3–4.8

* Aramid = poly(*p*-phenylene terephthalamide)

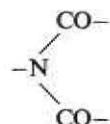
motors. The fibers are also used as reinforcement in radial tires and mechanical rubber goods and for specialty clothing. Modern lightweight bullet-proof vests contain up to 18 layers of woven aramid cloth.

3. Aromatic polyether-amide copolymer fibers that may compete with poly(*p*-phenylene terephthalamide) fibers are prepared by the polycondensation of terephthaloyl chloride with a mixture of *p*-phenylenediamine (7) and 4,4'-diaminodiphenylether (8). The polymer melts at 515°C.



5.6 POLYIMIDES

Polyimides are high temperature engineering materials characterized by the presence in the polymer chains of cyclic structures that contain the imide group:

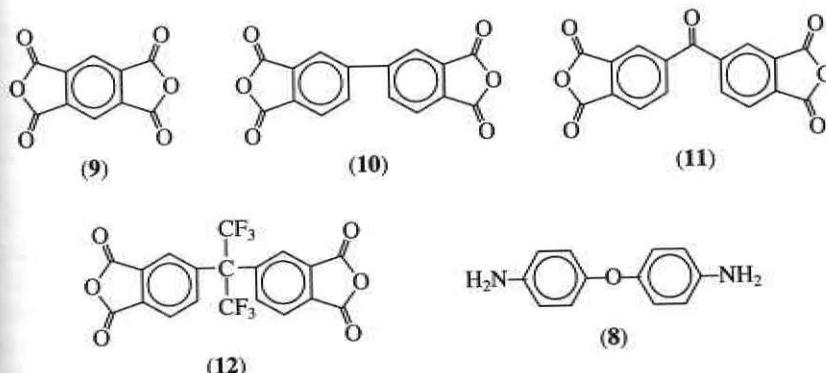


The first polyimide was produced in the early 1960s but only in recent years has there been a rapid development for high strength composites, thermally stable films, molding compounds and adhesives [43–46].

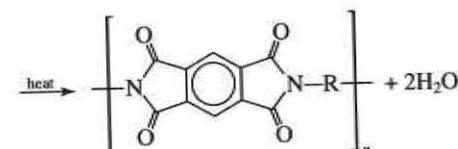
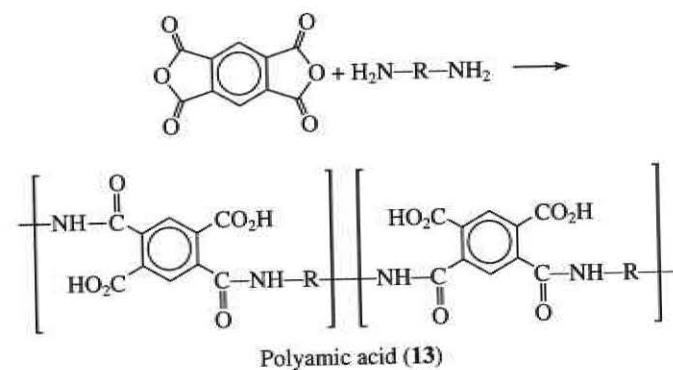
Different types of polyimide polymers are marketed. Some of them contain the imide group as the main functional group and are known as unmodified polyimides. Modified polyimides that include polyamide-imides, polyesterimides, polyetherimides and polybismaleimides were produced in order to provide materials with the same superior physico-mechanical characteristics as unmodified polyimides but which were easier to process.

5.6.1 Unmodified polyimides

Unmodified polyimides are prepared by the polycondensation of aromatic dianhydrides with aromatic diamines. Examples of dianhydrides are pyromellitic dianhydride (9), 3,3',4,4'-biphenyltetracarboxylic dianhydride (10), benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride (11) and the fluorinated dianhydride (12) which has found occasional use in moisture resistant polyimides. The most used aromatic diamine is 4,4'-diaminodiphenyl ether (8). Both dianhydride and diamine are required in high purity.



The synthesis of polyimides is carried out in two stages. The first step is effected by dissolving the diamine in polar solvents such as dimethylformamide, dimethylacetamide or dimethyl sulfoxide and by adding the dianhydride to the solution which is maintained at mild temperatures (under 50°C) in order to avoid cyclization (imidization). The reaction of the diamine with the dianhydride is fast and exothermic and it results in the formation of a viscous solution of polyamic acid prepolymer (13). The second step is the cyclization of the polyamic acid to the polyimide by intramolecular condensation.

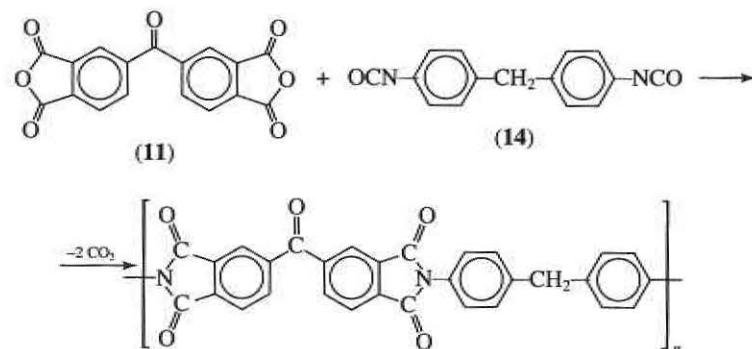


As the resultant cyclic polyimide is infusible and insoluble, the imidization step must be carried out in the solid state, i.e. in the physical form of the final product. The solution of polyamic acid obtained in the first step is cast to film or used for the impregnation of glass or carbon fibers for composite

materials. After the evaporation of the solvent by heating for 1–2 hours at 150–200°C, the imidization is completed by an additional heating at 300°C. Careful processing is necessary as water formed as a by-product during the cyclization as well as residual solvent may cause voids that structurally weaken the finished product. Addition of acetic anhydride and pyridine to the polyamic acid solution contribute to easier removal of water.

The formation of five-membered imide rings by intramolecular polycondensation is the favored path of reaction. Nevertheless, some intermolecular condensation may also occur resulting in crosslinking and premature gelation which will bring difficulties in processing by conventional thermoplastic methods.

A simpler one-step process is based on the utilization of diisocyanates instead of diamines, which react with dianhydrides yielding the polyimide directly, with simultaneous evolution of carbon dioxide [47–49]. The polyimide prepared from benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride (11) and a 20/80 mixture of 4,4'-diphenylmethane diisocyanate (14) and 2,4-toluene diisocyanate is available commercially and may be processed either from dimethylformamide or from *N*-methyl pyrrolidone as fibers and films or as compression moldings [25]. The evolution of carbon dioxide from the condensation was turned to profit in the manufacture of polyimide foams used for acoustic insulation of jet engines.



Polyimide polymers, especially in film form, have outstanding heat resistance with heat deflection temperatures as high as 357°C. After 1000 hours of exposure to air at 300°C the polymer retains 90% of its tensile and dielectric strength.

Polyimide film has excellent abrasion resistance, flame, solvent and oxidative degradation resistance as well as high energy radiation resistance. Chemical resistance of polyimides is very good, apart from with aqueous acids and alkalis which degrade the polymer.

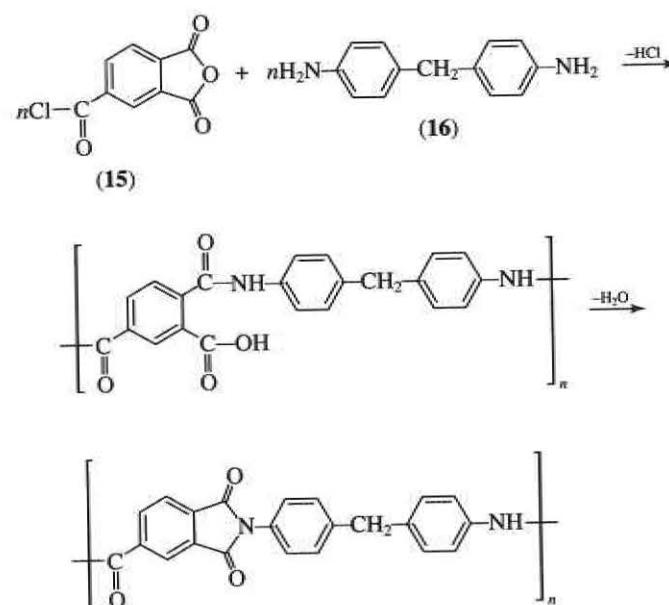
Polyimides have found use as insulating enamels and varnishes for electric motors and cables and for coating glass cloth. Polyimides can be compounded with graphite, molybdenum disulfide, PTFE and metal powders

such as aluminum for use as a wear surface in the manufacture of gaskets and piston rings for jet engines, and in soldering and welding equipment. Compounded with abrasives, polyimide composites are used in grinding wheels [25].

5.7 MODIFIED POLYIMIDES

5.7.1 Poly(amide-imides) (PAIs)

PAIs are produced by the condensation of high purity raw materials, namely the acid chloride of trimellitic anhydride (15) with 4,4'-diaminodiphenylmethane (16) in a solution of *N*-methylpyrrolidone. Hydrochloric acid and water evolve from the condensation.



The polycondensation is stopped before the imidization is completed and the resin is still soluble and fusible. The polymer is marketed in pellet form. It is applied either by solution techniques or by compression and injection molding. Molding temperatures are very high, in the range 330–350°C and so is the viscosity of the melt requiring heavy duty, high temperature processing equipment. Molded or extruded parts are then postcured in high temperature staged ovens. Long postcuring cycles (up to weeks) depend on the part thickness since the reaction by-product (water) must diffuse through the part. Postcuring is thought to increase chain length, to fully imidize the chain and possibly to cause a small amount of crosslinking; this all contributes to high quality products [50].

Table 5.9 Some properties of poly(amide-imides)

Property	At ambient temp.	at 260°C
Density (g/cm ³)	1.14	-
Glass transition temperature, T_g (°C)	275	-
Heat deflection temperature at 1.82 MPa (°C)	270	-
Continuous use temperature (°C)	200	-
Tensile strength (MPa)	185	50
Flexural modulus (GPa)	4.55	3.00
Elongation (%)	12	22

High MW PAIs have been prepared starting from diisocyanates, particularly MDI (**14**), trimellitic anhydride (**17**) or an 80/20 mixture of trimellitic anhydride/isophthalic acid [25]. PAI ignition resistant foams can be prepared based on diisocyanates and the evolution of carbon dioxide from their reaction with dianhydrides [51].

PAI block copolymers have been prepared which are soluble in polar aprotic solvents, have reduced viscosities and T_g at 290°C [52]. A polyamide with amine end groups is prepared in the first step and is subsequently reacted in solution with a mixture of amine and dianhydride; a block PAI is formed by the condensation of the polyamide with the polyamic acid formed *in situ*, followed by cyclization in solution.

Requirements of high purity raw materials, demanding processing conditions and long curing cycles, are the reasons that make PAI products very expensive. As a result, only those applications that require their specific combination of characteristics use PAI materials. The commercial production of PAI was about 250 tons at the end of 1980s [50].

PAIs are hard, tough and creep resistant polymers with exceptionally high temperature stability [53,54]. Some properties of PAIs are given in Table 5.9. Creep modulus under 70 MPa load and 150°C is 1700 MPa in 100 hours. PAIs are resistant to aromatic and halogenated hydrocarbons, to other organic solvents and diluted acids but are attacked by alkalis. They have an excellent resistance to radiation.

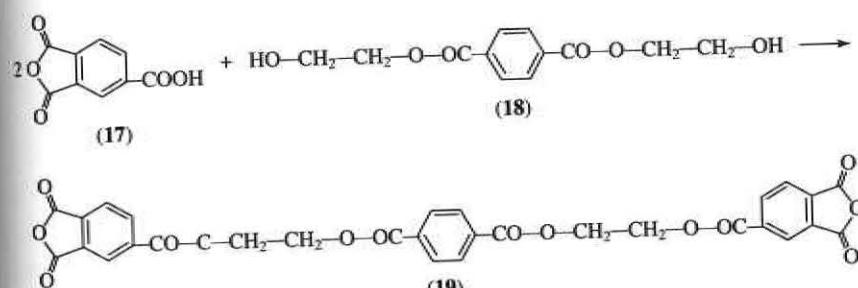
PAIs are used as thermoplastic matrix in high performance composites. Up to 30% of graphite fibers give composites which have a very low coefficient of friction. Glass fibers (30–40%) and PTFE are also used as reinforcing materials.

PAIs are extensively used in the aerospace and automotive industries. They have lower weight and higher strength per unit weight than many high performance metal alloys.

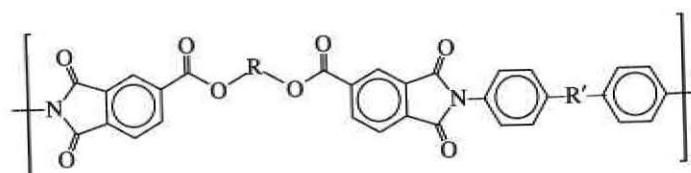
5.7.2 Polyesteramides

Polyesteramides are another type of modified polyimides which contain ester and imide groups in the chain. They are synthesized in three steps. In the first

step, trimellitic anhydride (**17**) is reacted with bis(2-hydroxyethyl) terephthalate (**18**) to give an intermediate product with ester groups in the chain and capped with anhydride groups (**19**):



In the second step, this intermediate anhydride is treated with 4,4'-diaminodiphenyl methane (**16**) or other diamine and the resulting polyamic acid is then imidized in the third step in the same way that was described earlier for polyimides. Their general formula is:

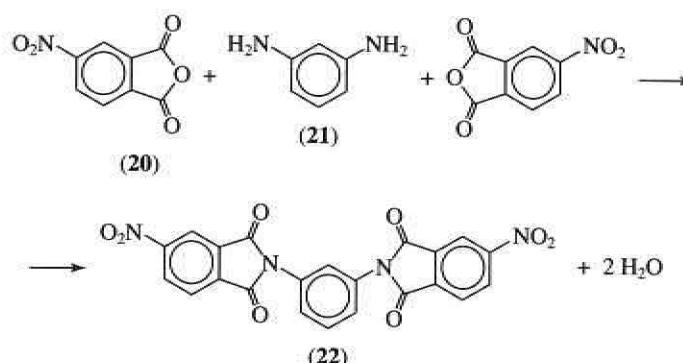


Polyesteramides are used for heat resistant wire enamels.

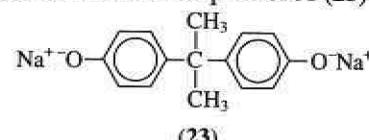
5.7.3 Polyetherimides (PEIs)

PEIs are high temperature high performance engineering thermoplastics materials of the polyimide family and constitute the last entry on the market in 1982. The presence of imide and aromatic units provides materials with the excellent properties characteristic to imide polymers, while the ether groups impart improved processability and melt flow. The synthesis of PEI involves three stages [55–57].

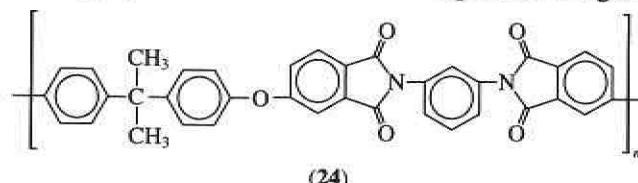
- Firstly, a diamine is end capped with two molecules of nitrophthalic anhydride (**20**) leading to a low MW bisimide intermediate (**22**) with preformed imide groups. *m*-Phenylenediamine (**21**) is preferred commercially but other diamines may be used in order to obtain polyetherimides with different structures and properties.



2. Preparation of the sodium salt of bis-phenol A (23):



3. The polycondensation of bis-phenol A dianion with the bisimide intermediate in aprotic dipolar solvents and mild conditions leads to the formation of polyetherimide chains containing ether linkages (24).



PEIs are amorphous and transparent materials. They have outstanding tensile properties even without reinforcement, an excellent balance of electrical properties and an outstanding thermal stability, retaining their strength at elevated temperatures. Table 5.10 illustrates some properties of PEIs.

PEIs are resistant to hydrocarbons, fully halogenated solvents and mineral acids and have an excellent hydrolytic stability. They are attacked by alkalis and dissolved by partially halogenated solvents. Even without the addition of stabilizers, PEIs are resistant to UV and ionizing radiations.

High flame resistance accompanied by very low smoke generation make PEIs superior to many engineering materials and are in agreement with stricter regulations on the flammability of plastics [13].

PEI resins are processed by injection molding, blow molding and by extrusion. Reinforcing materials such as carbon fiber or glass fiber (up to 40%) are used resulting in a substantial increase in tensile properties due to the excellent adhesion of PEI to the glass fiber [55].

PEIs have found various applications as car under-the-hood components and other mechanical parts, three-dimensional printed circuit boards,

Table 5.10 Some characteristics of polyetherimide resins

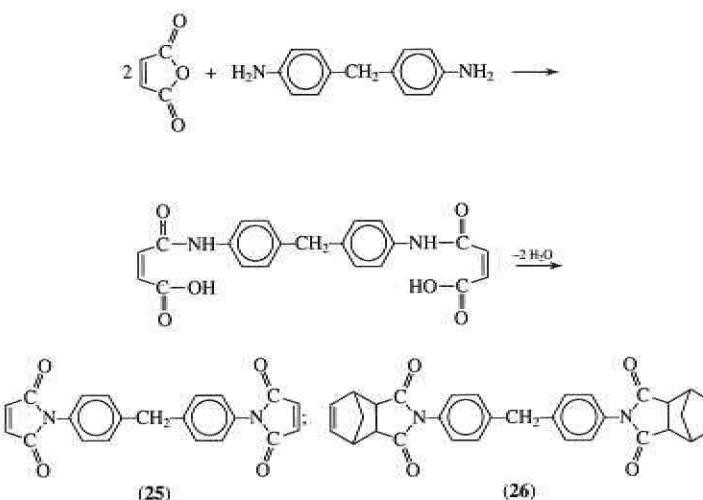
Property	Value
Density (g/cm ³)	1.27
Glass transition temperature, T _g (°C)	217
Heat deflection temperature at 1.84 MPa (°C)	200
Continuous use temperature (°C)	170
Tensile strength (MPa)	105
Tensile modulus (MPa)	3000
Elongation at break (%)	60
Flexural modulus (MPa)	3309
Molding shrinkage (cm/cm)	0.005–0.007

microwave equipment and different components for the aerospace industry [58]. PEI fibers and fabrics have been used for protective clothing for fire fighters and race drivers, for aircraft upholstery and carpets [55]. Film applications include insulating tapes, flexible circuitry and wire insulation.

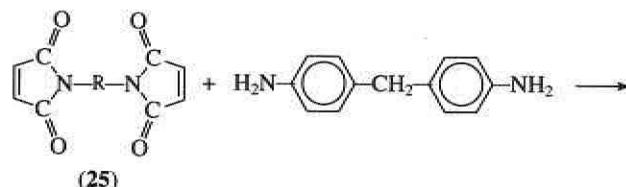
5.7.4 Polybismaleimides

A different route to modified polyimide polymers is used in the preparation of polybismaleimides. They are synthesized from monomers or low MW oligomers which contain preformed imide groups in the chain and double bonds at the end of the chains; they are transformed to final crosslinked polymers by rearrangement reactions and by addition polymerization [59–61]. This avoids the production of volatile by-products during the final stage.

Commercial polymers are based either on maleic anhydride or on nadic anhydride, which are reacted with a diamine to form bismaleimides (25) and bisnadicimides (26), respectively:



These bisimides can be polymerized by thermal free radical polymerization through the end double bonds, but the resultant homopolymers have a high degree of crosslinking and are too brittle. Commercial products are based on chain extended bisimides which lead to reduced crosslink density and brittleness of the finished product. The extension of the chain can be done by the addition of a variety of bifunctional compounds such as diamines, disulfides and aldoximes. Most commonly used is 4,4'-diaminodiphenyl methane:



The reaction is effected by heating the mixture of bismaleimide with a molar deficiency of diamine at temperatures of 200–260°C. Two different reactions take place simultaneously without the formation of any volatile product: (a) the addition of the amino groups to maleic double bonds which extends the chains to form structure (27) which has maleic end groups and (b) thermal free radical polymerization of the remaining maleic end groups to crosslinked structures. Both these reactions take place during the molding process.

Unfilled and filled grades are commercially available. Unfilled polybis-maleimides are applied for compression molded printed circuit boards. Fillers such as glass fibers, carbon fibers, asbestos, graphite and PTFE are used in composite materials which have found use in weapon and aerospace industries.

REFERENCES

1. Reisch, M.S. (1994) *Chem. Eng. News*, 7 November, 10.
2. Moncrieff, R.M. (1975) *Man-Made Fibers*, Butterworths, London, Chapters 19–22.
3. Kohan, M.I. (ed.) (1973) *Nylon Plastics*, Wiley-Interscience, New York.
4. Seymour, R.B. and Kirshenbaum, G.S. (eds) (1986) *History of High Performance Polymers*, Elsevier, New York: (a) p. 19; (b) p. 39; (c) p. 55.

5. Fredlina, L.K. and Karapetian, S.A. (1961) *Telomerization and New Synthetic Materials*, Pergamon, Oxford.
6. Roffia, P. et al. (1987) European Patent 208,311, Montedipe.
7. H. Ulrich (1992) in *Reaction Polymers* (eds W.F. Gum, W. Riese and H. Ulrich), Hanser Publishers, Munich, p. 217.
8. Reimschuessel, H.K. (1977) *J. Polym. Sci. Macromol. Rev.*, **12**, 65.
9. Millich, F. and Seshadri, K.V. (1972) in *Cyclic Monomers* (ed. K.C. Frisch), Wiley-Interscience, New York, Chapter 3.
10. Reimschuessel, H.K. (1969) in *Ring-Opening Polymerization* (eds K.C. Frisch and S.L. Reegen), Marcel Dekker, New York, Chapter 7.
11. Stevens, M.P. (1990) *Polymer Chemistry*, 2nd edn, Oxford University Press, New York.
12. Dai, S.A. et al. (1985) US Patent 4,550,157 to Upjohn; (1986) US Patent 4,604,450 to Upjohn.
13. Brysdon, J.A. (1995) *Plastic Materials*, 6th edn, Butterworths, London.
14. Iobst, S.A. (1985) *Polym. Eng. Sci.*, **25**, 425.
15. Sweeney, F.M. (1990) in *Handbook of Plastic Materials and Technology* (ed. I.I. Rubin), Wiley-Interscience, New York, p. 1273.
16. Jacobs, D.B. and Zimmerman, J. (1977) in *Polymerization Processes* (ed. C.E. Schildknecht), Wiley-Interscience, New York, p. 424.
17. Griehl, W. and Ruestem, D. (1970) *Ind. Eng. Chem.*, **62**(3), 16.
18. Damm, P.O. and Matthies, P. (1990) in *Handbook of Plastic Materials and Technology* (ed. I.I. Rubin), Wiley-Interscience, New York, p. 161.
19. Roerdink, E. and Warnier, J.M.M. (1985) *Polymer*, **26**, 1582.
20. Maskus, P. and Capaul, M. (1993) *Kunststoffe*, **10**, 20.
21. Ellis, T.S. (1988) *J. Appl. Polym. Sci.*, **36**, 451.
22. Mumcu, S., Burzin, K., Feldmann, R. and Feinauer, R. (1978) *Angew. Makromol. Chem.*, **74**, 49.
23. Chen, A.T., Farrissey, W.J. and Nelb, R.G. (1978) US Patent 4,129,715 to Upjohn.
24. Nelb, R.G., Onder, K. and Chen, A.T. (1987) *Thermoplastic Elastomers*, Hanser Publishers, Munich, p. 197.
25. Onder, K. (1992) in *Reaction Polymers* (eds. W.F. Gum, W. Riese and H. Ulrich), Hanser Publishers, Munich, p. 405.
26. Onder, K. (1979) US Patent 4,156,065 to Upjohn.
27. Onder, K., Andrews, P.S., Farrissey Jr, W.J. and Tilley, J.N. (1980) *Polymer Preprints*, **21**(2), 130.
28. Rader, C.P. (1993) *Kunststoffe*, **10**, 36.
29. Nelb, G.R., Onder, K., Raush, K.W. and Vanderlip, J.A. (1987) US Patent 4,672,094 to The Dow Chemical Co.
30. Morgan, P.W. (1965) *Condensation Polymers by Interfacial and Solution Methods*, Wiley-Interscience, New York, Chapter 5.
31. Nikonov, V.Z. and Savinov, V.M. (1977) in *Interfacial Synthesis* (eds F Millich and C.E. Carraher), Vol. 2, Marcel Dekker, New York, Chapter 15.
32. Korshak, V.V. (1972) *Heat-Resistant Polymers*, Halsted Press, New York.
33. Critchley, J.P., Knight, G.J. and Wright, W.W. (1983) *Heat-Resistant Polymers*, Plenum Press, New York.
34. Lenk, R.S. (1978) *Macromol. Revs.*, **13**, 355.

35. Jaffe, M. and Jones, R.S. (1985) in *High Technology Fibers*, Part A (eds M. Lewin and J. Preston), Marcel Dekker, New York, Chapter 9.
36. Gordon, M. (ed.) (1984) *Adv. Polym. Sci.*, **59**, 60–61, Springer-Verlag, New York.
37. Blumstein, A. (ed.) (1978) *Liquid Crystalline Order in Polymers*, Academic Press, New York.
38. Ciferri, A., Krigbaum, W.R. and Meyer, R.B. (eds) (1982) *Polymer Liquid Crystals*, Academic Press, New York.
39. Varshney, S.K. (1986) *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C26**, 551.
40. Lenz, R.W. (1985) *Polym. J.*, **17**, 105.
41. Finkelmann, H. (1987) *Angew. Chem. Int. Ed. (English)*, **26**, 816.
42. Langston, P. and Zahr, G.E. (1990) in *Handbook of Plastic Materials and Technology* (ed. I.I. Rubin), Wiley-Interscience, New York, p. 931.
43. Mittal, K.L. (ed.) (1984) *Polyimides*, Vols 1 and 2, Plenum Press, New York.
44. Beesonov, M.I., Koton, M.M., Kudryavtsev, V.V. and Laius, L.A. (1987) *Polyimides – Thermally Stable Polymers*, Plenum Press, New York.
45. Ranney, M.W. (1971) *Polyimides Manufacture*, Noyes Data Corp., Park Ridge, New Jersey.
46. Cassidy, P.E. (1980) *Thermally Stable Polymers*, Marcel Dekker, New York, Chapter 5.
47. Carleton, P.S., Farissey Jr, W.J. and Rose, J.S. (1972) *J. Appl. Polym. Sci.*, **16**, 2983.
48. Ghatge, N.D. and Mulik, U.P. (1980) *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1905.
49. Alvino, W.M. and Edelman, L.E. (1975) *J. Appl. Polym. Sci.*, **19**, 2961.
50. Throne, J.L. (1990) in *Handbook of Plastic Materials and Technology* (ed. I.I. Rubin), Wiley-Interscience, New York, 225.
51. Nelb, R.G. and Saunders, K.G. (1988) US Patent 4,738,990 to Dow Chemical Co.
52. Phaendner, R. (1992) Ger. Offen. DE 4,332,248 to Ciba-Geigy A.-G.; *CA* (1994), **121**(10), 231660.
53. Billerbeck, C.J. and Henke, S.J. (1985) in *Engineering Thermoplastics: Properties and Applications* (ed. J.M. Margolis), Marcel Dekker, New York, p. 373.
54. Cekis, G.V. (1987) in *Modern Plastic Encyclopedia*, Vol. 63, 10A, McGraw-Hill, New York, p. 37.
55. Serfaty, I.W. (1990) in *Handbook of Plastic Materials and Technology* (ed. I.I. Rubin), Wiley-Interscience, New York, p. 263.
56. Johnson, R.O. and Burlhis, H.S. (1983) *J. Polym. Sci., Polym. Symp.*, **70**, 129.
57. White, D.M. (1981) *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1635.
58. Bailly, C., Sederel, W. and Stahl, P.O. (1993) *Kunststoffe*, **10**, 48.
59. Stenzenberger, H.D., Herzog, H., Romer, W. et al. (1983) *Br. Polym. J.*, **15**, 2.
60. Trivedi, B.C. and Culbertson, B.M. (1982) *Maleic Anhydride*, Plenum Press, New York.
61. Varma, I.K. and Sharma, S. (1984) *Eur. Polym. J.*, **20**, 1101.

Silicone polymers

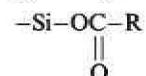
6

6.1 INTRODUCTION

Like carbon, silicon has the possibility of forming covalent compounds. The siloxane bond $-\text{Si}=\text{O}-\text{Si}$ is more stable than the $\text{Si}-\text{Si}$ one. It is the basic bond in the silicone polymers, and the same linkage is present in glass and quartz. Silicon multiple bonds polymers are uncommon; as a result, silicone polymers are obtained only by polycondensation. The combination of inorganic polymer networks with organic groups leads to inorganic–organic polymers. A convenient method for the introduction of organic radicals into a mineral backbone is the use of organo substituted silicoesters in a polycondensation process [1]. In the 1980s, the USA's silicone polymers annual consumption exceeded 60 000 tons. Since 1990 worldwide production of silicones has risen by 8–10% annually on average. In 1991/1992 the world market for silicones, including chip material, was roughly worth 4.5 billion US \$ [2].

Depending on the substituents at the oxygen atom position of the $\text{Si}=\text{O}$ bond, various type of compounds have to be distinguished [3].

- Silanols and their condensation products, the siloxanes: $\text{Si}-\text{OH}$ and $\text{Si}=\text{O}-\text{Si}$
- Organyloxsilanes: $-\text{Si}-\text{OR}$, R = alkyl, aryl
- Acyloxy silanes (also named silyl esters)



- Silylenol ethers



- Cyclic Si–O compounds (e.g. siloxa-heterocycles)

