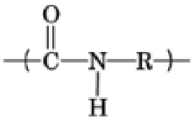
Kirk-Othmer Encyclopedia of Chemical Technology.

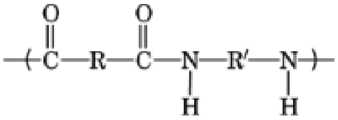
POLYAMIDES, GENERAL

Polyamides, often also referred to as nylons, are high polymers which contain the amide repeat linkage in the polymer backbone. They are generally characterized as tough, translucent, semicrystalline polymers that are moderately low cost and easily manipulated commercially by melt processing. However, significant exceptions to all these attributes occur. The regularity of the amide linkages along the polymer chain defines two classes of polyamides: AB and AABB.



$$-\!\left(\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-R\right)\!-$$

AB



$$-\!\left(\overset{\overset{\displaystyle O}{\|}}{C}-R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-R'-\underset{\underset{\displaystyle H}{|}}{N}\right)\!-$$

AABB

Type AB, which has all the amide linkages with the same orientation along the backbone, can be viewed as being formed in a polycondensation reaction from ω-amino acids to give a polymer with the repeat unit AB. Type AABB, where the amide linkages alternate in orientation along the backbone, can be viewed as being formed from diacids and diamines in a polycondensation reaction to form a polymer with the repeat unit AABB. The R and R′ groups in these structures are hydrocarbon radicals and can be aliphatic, aromatic, or mixed. Because the chemical and physical properties of polyamides differ drastically between those that contain greater than $\sim$15% aliphatic character, ie, nylons, and those that are predominately aromatic, ie, aramids, the aromatic polyamides are treated separately in this article.

1. Nomenclature

The nomenclature (qv) of polyamides is fraught with a variety of systematic, semisystematic, and common naming systems used variously by different sources. In North America the common practice is to call type AB or type AABB polyamides nylon-*x* or nylon-*x,x*, respectively, where *x* refers to the number of carbon atoms between the amide nitrogens. For type AABB polyamides, the number of carbon atoms in the diamine is indicated first, followed by the number of carbon atoms in the diacid. For example, the polyamide formed from 6-aminohexanoic acid [60-32-2] is named nylon-6 [25038-54-4]; that formed from 1,6-hexanediamine [124-09-4] or hexamethylenediamine and dodecanedioic acid [693-23-2] is called nylon-6,12 [24936-74-1]. In Europe, the common practice is to use the designation “polyamide,” often abbreviated PA, instead of “nylon” in the name. Thus, the two examples above become PA-6 and PA-6,12, respectively. PA is the International Union of Pure and Applied Chemistry (IUPAC) accepted abbreviation for polyamides. Occasionally abbreviations such as Ny-6 or Ny-6,12 are seen, but these are to be avoided. More complex organic radicals, eg, branched, alicyclic, or aromatic, that appear between the amide functions are generally designated by special abbreviations; many of the more common ones appear in Table 1. Copolymers are generally designated by writing the symbols for the two polymers separated by a slash, eg, nylon-6,6/6,T, with the component in the higher concentration listed first. This method is readily extended to polymers containing three or more components.

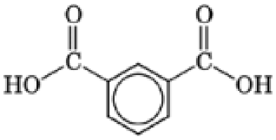
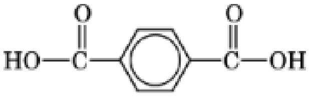
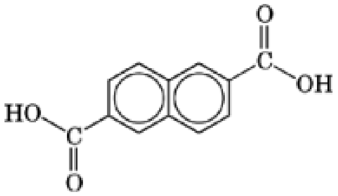
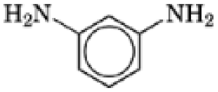
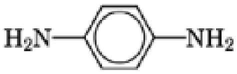
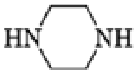
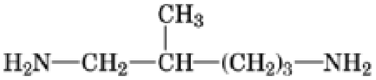
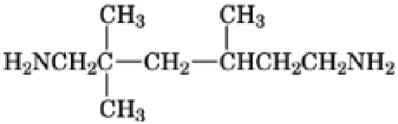
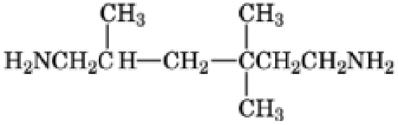
Another common naming scheme, termed source-based (or component monomer) nomenclature, is the practice of naming the polyamide after the monomer from which the polymer is made, eg, poly(caprolactam) for nylon-6. The use of poly(hexamethyleneadipamide [9011-55-6] for nylon-6,6 is a variation of this naming procedure, where the repeat unit is used instead of the specific starting materials. One of the significant disadvantages of source-based nomenclature is that since a given polymer can be prepared from different monomers, it can have several different names; for example, nylon-6 could also be named poly(6-aminohexanoic acid). Trivial as well as systematic names are used to designate various monomers or repeating structural portions of the polymer.

All of these methods of nomenclature are slowly falling out of use, in favor of the systematic nomenclature based on the constitutional repeat unit (CRU), advocated by the IUPAC (1, 2) and used with modification as the structural repeat unit (SRU) in *Chemical Abstracts* to index polymers. In the IUPAC scheme polyamides are named as derivatives of repeating divalent, nitrogen-substituted (designated as imino-) carbon backbones. The carbonyl function is designated as a divalent oxygen (oxo-) substitution on the carbon backbone. Thus nylon-6 becomes poly[imino-(1-oxo-1,6-hexanediyl)] and nylon-6,6 becomes poly[imino(1,6-dioxo-hexanediyl)imino-hexanediyl]. The general template for naming type AB polymers is as follows: nylon-x becomes poly[imimo(1-oxo-R)].

Because the rules for organic nomenclature determine the priority of naming different carbon chains from their relative lengths, the systematic names for type AABB polyamides depend on the relative length of the carbon chains between the amide nitrogens and the two carbonyl functions of the polymer: for aliphatic nylon-x,y, when $x < y$, the IUPAC name is poly[imino-R′ imino(1,y-dioxo-R″)]. When $x \geq y$, then the name is poly[imino(1,y-dioxo-R″)imino-R′]. Table 2 presents the alternative names of the hydrocarbon radicals for the various common polyamides (3). Although the systematic nomenclature appears complicated, and perhaps needlessly so for simple polyamides, it provides several advantages: (*1*) a unique, chemically specific name is assigned to each structure; (*2*) chemical derivatives of the linear polyamides are named in a straightforward and unequivocal manner from their linear analogues; and (*3*) the use of special, nonchemical designations is avoided. The IUPAC systematic nomenclature also provides appropriate methods for designating end groups, copolymers, and nonlinear polymers (1, 4).

Tables 3 and 4 list the CAS Registry Numbers for all the common linear polyamides containing 1–12 carbon atoms in their backbone, except those derived from carbonic acid. Table 3 lists the CAS Registry Numbers for polyamides derived from diacids and diamines (or lactams); additional CAS Registry Numbers may be available for these polymers if they are formed from other monomers such as the reaction of diamines and diacid chlorides (or ω-aminoacids). Table 4 lists the CAS Registry Numbers for the same set of polyamides based on their constitutional repeat unit. To facilitate comparison, the entries are tabulated using their source-based nomenclature even in the case of the constitutional repeat unit (CRU), ie, Table 4. These tables illustrate several important points regarding use of CAS Registry Numbers to identify polymeric materials in general and polyamides in particular. First, there are at least two sets of CAS Registry Numbers for many polymers, especially polyamides; one corresponds to the source-based approach and the other to the CRU approach to the identification of the material. Secondly, depending on the identity of the starting monomer(s), there can be multiple source-based Registry Numbers. Thirdly, in searches of databases (qv) containing Registry Numbers,

Table 1. Codes for Common Polyamide Monomers

Abbreviation or code	Chemical name	CAS Registry Number	Structure
I	isophthalic acid	[121-91-5]	
T	terephthalic acid	[100-21-0]	
N	2,6-naphthalenedicar-boxylic acid	[1141-38-4]	
MPD	*m*-phenylenediamine	[108-45-2]	
PPD	*p*-phenylenediamine	[106-50-3]	
MXD	*m*-xylylenediamine	[1477-55-0]	
Pip	piperazine	[110-85-0]	
MPMD or D	2-methylpentamethyl-enediamine or Dytek A[a]	[15520-10-2]	 $H_2N-CH_2-\overset{CH_3}{C}H-(CH_2)_3-NH_2$
TMD or 6-3	mixture of 2,2,4- and 2,4,4-trimethylhexa-methylenediamine	[3236-53-1] [3236-54-2]	 $H_2NCH_2\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}HCH_2CH_2NH_2$ and  $H_2NCH_2\overset{CH_3}{C}H-CH_2-\underset{CH_3}{\overset{CH_3}{C}}CH_2CH_2NH_2$

[a] Registered trademark of Du Pont Co.

it should not be assumed that the various substance records are cross-referenced. Thus, if a thorough search is desired for a particular polymer, multiple Registry Numbers must generally be used. Finally, the situation can be made even more difficult in searches for information on copolymers since they have additional complexities resulting from the variety of combinations available for several monomers, and they are generally indexed in a source-based format.

Table 2. Systematic Names for Radicals in the SRU Format Appearing in Chemical Abstracts and Other Sources

		Associated systematic name[a]		
x or y[b]	R, R′, or R″[b]	ω-Amino acid replaces 1-oxo-R	Diamine radical replaces R′	Diacid radical replaces 1,y-dioxo-R″
1	1,1-methanediyl	1-oxomethylene	methylene	[c]
2	1,2-ethanediyl	1-oxoethylene	ethylene	oxalyl
3	1,3-propanediyl	1-oxotrimethylene	propylene, trimethylene	malonyl[d]
4	1,4-butanediyl	1-oxotetramethylene	tetramethylene	succinyl
5	1,5-pentanediyl	1-oxopentamethylene	pentamethylene	glutaryl
6	1,6-hexanediyl	1-oxohexamethylene	hexamethylene	adipoyl
7	1,7-heptanediyl	1-oxoheptamethylene	heptamethylene	heptanedioyl, pimeloyl
8	1,8-octanediyl	1-oxooctamethylene	octamethylene	octanedioyl, suberoyl
9	1,9-nonanediyl	1-oxononamethylene	nonamethylene	nonanedioyl, azelaoyl
10	1,10-decanediyl	1-oxodecamethylene	decamethylene	decanedioyl, sebacoyl
11	1,11-undecanediyl	1-oxoundecamethylene	undecamethylene	undecanedioyl
12	1,12-dodecanediyl	1-oxododecamethylene	dodecamethylene	dodecanedioyl
13	1,13-tridecanediyl	1-oxotridecamethylene	tridecamethylene	tridecanedioyl

[a] Not used in *Chemical Abstracts*, but appear in other references, eg, Ref. 3.

[b] In poly[imino(1-oxo-R)], poly[imino-R′ imino(1,*y*-dioxo-R″)], and poly[imino-(1,*y*-dioxo-R″)imino-R′], as explained in text.

[c] Polymers based on carbonic acid and diamines are considered polyureas.

[d] The systematic name of a small radical can replace the trivial name, eg, propanedioyl for malonyl.

2. History

The first patent for the production of synthetic polyamides was issued in 1937 to Wallace H. Carothers, who was working at Du Pont Company (5). His pioneering work in the development of polymeric materials led in a few years to the commercialization of nylon-6,6 as the first synthetic fiber. In 1941 P. Schlack at I. G. Farbenindustrie in Germany was issued a patent for nylon-6 based on the polymerization of caprolactam [105-60-2] (6). Ironically, Carothers' first attempt to synthesize polyamides in 1930 was to make nylon-6 from 6-aminohexanoic acid, but for unexplained reasons he was only able to produce a low molecular weight polymer (7). At this time he and his co-workers also made other polyamides from dibasic acids and aliphatic diamines (8); however, owing to their low solubility and high melting point, this work was also abandoned for the next five years while they worked on other polymers, including neoprene and polyesters. In July 1935, nylon-6,6 was chosen by Du Pont to be the specific polyamide for commercial introduction. This choice was based on its balance of physical properties making it suitable for fiber production and the potential for a low cost source of starting materials from six-member ring carbon compounds derived from coal (qv) (9). In less than one year, Du Pont scientists and engineers built the first commercial plant in Seaford, Delaware, which began production in 1939.

The magnitude of the intellectual achievement of Carothers often overshadows the tremendous effort and success that followed in building the necessary industrial infrastructure and developing the numerous scientific and engineering innovations required to make nylon a successful commercial venture. One of the first of these was the development of a route to produce the starting materials from “coal, air, and water,” and the first intermediates plant was built at Belle, West Virginia (10). Another was the invention of the autoclave polymerization process using balanced salt and acetic acid end termination to control the molecular weight of the final polymer. Because nylon-6,6 was insoluble in all common solvents, a new melt-spinning process was required to form fibers and wind them onto packages. Also, the two-step drawing process was invented to develop the full strength of the fibers. Additional inventions were required for effective downstream processing of this new synthetic fiber in order to dye and form it into finished goods. Finally, strong markets were required

Table 3. CAS Registry Numbers for Source-Based Monomers

Type AB	C_1	C_2	C_3 [27881-47-6]	C_4 [24968-97-6]	C_5 [25036-00-4]	C_6 [9012-16-2]
Type AABB	Methylene, CH_6N_2	Ethylene, $C_2H_8N_2$	Trimethylene, $C_3H_{10}N_2$	Tetramethylene, $C_4H_{12}N_2$	Pentamethylene, $C_5H_{14}N_2$	Hexamethylene, $C_6H_{16}N_2$
oxalic, $C_2H_2O_4$		[89394-22-9]				[29322-30-3]
malonic, $C_3H_4O_4$	[138251-80-6]			[149508-42-9]	[149508-43-0]	[36863-61-3]
succinic, $C_4H_6O_4$	[138251-81-7]	[65595-82-6]		[26098-28-2]		[34853-53-7]
glutaric, $C_5H_8O_4$	[41510-76-3]		[56467-27-7]		[31781-00-7]	[54215-29-1]
adipic, $C_6H_{10}O_4$	[63289-13-4]	[26936-86-7]	[51025-67-3]	[50327-77-0]	[41510-67-2]	[9011-55-6] [75361-24-9]
pimelic, $C_7H_{12}O_4$					[31781-01-8]	[27136-66-9]
suberic, $C_8H_{14}O_4$		[65595-76-8]		[25916-16-9]		[25776-74-3]
azelaic, $C_9H_{16}O_4$		[28551-99-7]		[27136-64-7]		[27136-65-8]
sebacic, $C_{10}H_{18}O_4$		[30585-15-0]	[138260-67-0]	[25776-75-4]	[111519-63-2]	[9011-52-3]
undecanedoic, $C_{11}H_{20}O_4$						[50733-20-5]
dodecanedoic, $C_{12}H_{22}O_4$	[128743-02-2]	[99207-47-3]		[26834-07-1]		[26098-55-5]
tridecanedoic (brassylic), $C_{13}H_{24}O_4$						[26096-69-0] [69665-23-2]
isophthalic, $C_8H_6O_4$		[30585-16-1]	[130934-29-1]	[35885-42-8]	[130491-44-0]	[25722-07-0]
terephthalic, $C_8H_6O_4$		[29319-66-2]	[103691-99-2]	[73276-93-4]	[32761-06-1]	[24938-03-2]

to support the financial investment necessary for this revolutionary product; fortunately, nylon was extremely well suited to compete in the high value silk markets.

Shortly after the commercial introduction of nylon, World War II began and most of the nylon produced was used for military purposes such as in ropes, parachutes, and tires. After the war, nylon production expanded rapidly, first into the apparel and tire markets, and then into carpets and plastic parts. During the following three decades (1950–1980), numerous technical developments were achieved to provide increased nylon capacity and cost effectiveness. These include the development of intermediates production from petroleum-based feedstocks; the invention of the continuous polymerization (CP) and solid-phase polymerization (SPP) processes; coupled draw-spinning and the invention of interlace to replace twisting of the fiber bundle; and the invention of numerous additives to improve the performance of nylon in special end uses, such as thermal and photostabilizers and rubber tougheners. This development of technology continues where high productivity–low cost, intensely competitive worldwide markets, and environmental friendliness are key factors driving the development of the polymer industry.

Table 4. CAS Registry Numbers for Constitutional Repeat Unit

Type AB	C_1 [28725-43-1]	C_2 [25734-27-4]	C_3 [24937-14-2]	C_4 [24938-56-5]	C_5 [24938-57-6]	C_6 [25038-54-4]
Type AABB	Methylene, CH_6N_2	Ethylene, $C_2H_8N_2$	Trimethylene, $C_3H_{10}N_2$	Tetramethylene, $C_4H_{12}N_2$	Pentamethylene, $C_5H_{14}N_2$	Hexamethylene, $C_6H_{16}N_2$
oxalic, $C_2H_2O_4$	[51735-52-5]	[36812-63-2]	[88007-14-1]	[91277-46-2]		[31694-58-3]
malonic, $C_3H_4O_4$	[108390-54-1]	[113040-39-4]	[41706-21-2]	[113040-38-3]	[113040-25-8]	[32027-68-2]
succinic, $C_4H_6O_4$	[109672-46-0]	[27496-28-2]	[68821-49-8]	[26402-74-4]		[24936-71-8]
glutaric, $C_5H_8O_4$	[41724-64-5]	[68821-50-1]	[56467-06-2]		[32473-29-3]	[33638-80-1]
adipic, $C_6H_{10}O_4$	[138255-69-3]	[26951-61-1]	[51344-88-8]	[50327-22-5]	[41724-56-5]	[32131-17-2]
pimelic, $C_7H_{12}O_4$					[32552-84-4]	[28757-64-4]
suberic, $C_8H_{14}O_4$	[67937-41-1]	[41724-62-3]		[26247-04-1]		[24936-73-0]
azelaic, $C_9H_{16}O_4$	[67937-40-0]	[28775-08-8]		[28757-62-2]		[28757-63-3]
sebacic, $C_{10}H_{18}O_4$	[67937-42-2]	[32126-82-2]	[105063-18-1]	[26247-06-3]	[105063-19-2]	[9008-66-6]
undecanedoic, $C_{11}H_{20}O_4$						[50732-66-6]
dodecanedoic, $C_{12}H_{22}O_4$	[128853-03-2]	[41724-60-1]		[26969-09-5]		[24936-74-1]
tridecanedoic (brassylic), $C_{13}H_{24}O_4$						[26916-49-4]
isophthalic, $C_8H_6O_4$		[32126-83-3]	[119495-33-9]	[28757-32-6]	[119495-34-0]	[25668-34-2]
terephthalic, $C_8H_6O_4$	[67937-43-3]	[25722-35-4]	[35483-54-6]	[35483-53-5]	[32985-25-4]	[24938-70-3]

3. Economic Aspects

Since its introduction in the 1940s as the polymer base for the first synthetic fiber, nylon has been a significant commercial polymeric material. Table 5 shows the relative percentage of the world's consumption for the principal polymers. Nylon represents approximately 4% of the total, 4.5×10^6 metric tons in 1993, of which nylon-6,6 and nylon-6 comprise 85–90%. These two polyamides are produced worldwide in the following approximate percentages: nylon-6, 60%, and nylon-6,6, 40%; their relative proportions vary among the geographic markets globally. In North America, nylon-6,6 dominates; in the Asia/Pacific area, nylon-6 is the predominant polyamide; and in Europe, the market is about equally split. The rate of growth for polyamides in the developed economies of North America and Europe is roughly equal to the overall growth rate of these economies; however, the recent rapid growth in the Asia/Pacific area is expected to continue. South America and Africa represent nascent markets with growth potential in the twenty-first century.

Table 6 shows the principal end uses for polyamides and the approximate relative percent of the total consumption, where the "other" category includes monofilaments and nonwovens. Synthetic fiber, comprising almost 75% of the total, still represents the principal end use for nylon polymer. As shown in Figure **1a**, the

Table 5. Percentage of World Consumption of Polymers by Type in 1990[a]

Type	Percentage
polyethylene	27
poly(vinyl chloride)	18
polypropylene	13
polyester	11
thermosets	10
polystyrene	9
acrylics	4
nylon	4
ABS/SAN	3
other	1

[a] Calculated on a 102×10^6 metric ton basis for total production.

Table 6. Percentage of World Consumption of Polyamides by End Use

End use or type	Percentage
fibers	
carpet	34
textile	27
industrial	13
engineering resins	15
aramid	4
films/coatings	4
adhesives	1
other	2

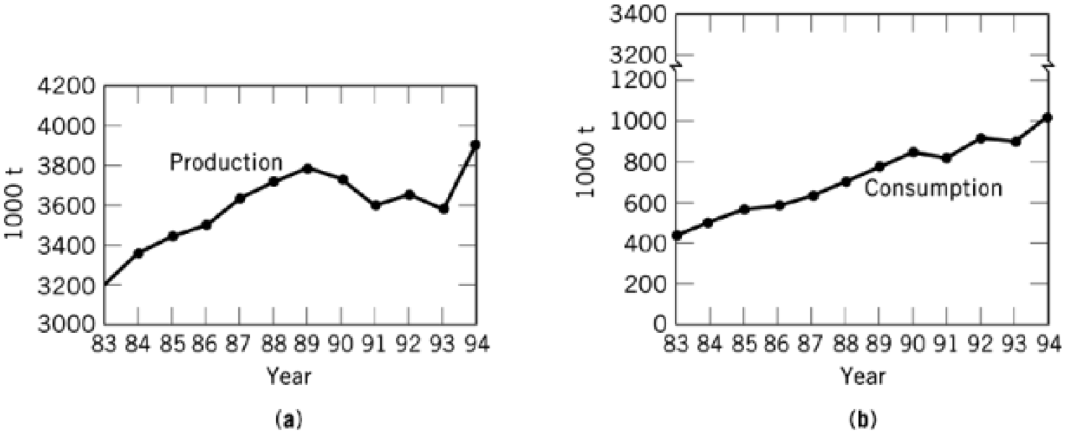


Fig. 1. (**a**) World production of nylon fiber (11); (**b**) world consumption of nylon resins (12).

total of nylon fiber production has declined between 1989 and 1993 (11), primarily as a result of the slowing of the world economy but also as a result of price competition from polyester and polypropylene fibers in many of its less demanding applications. In 1994, production, driven by the rebounding economies worldwide, took a sharp upturn. The long-term outlook for nylon fiber is expected to brighten as a result of the growth of the world economy and the substantial potential of the markets in Asia, especially in India and China (13).

Table 7. Range of Prices for Various Polyamides and Their Primary Product Types

Polymer base and product type	Price/kg
nylon-6,6 and nylon-6	
fiber	\$1.98–\$5.50
resin	\$2.97–\$4.40
other nylons	
resin	\$4.95–\$8.80
meta-aramids	
fiber and paper	\$19.80–\$66.00
para-aramids	
fiber and pulp	\$22.00–\$66.00
other polyamides	
adhesives and coatings	\$0.66–\$3.85

The markets for nylon resins, on the other hand, have shown consistent growth since the mid-1980s (13), with only minor fluctuations owing to the slowing of the world's economies (Fig. **1b**). As a result of the differences in relative growth rates of nylon plastics and fiber, production of the former as a percent of the total production is expected to continue to increase well into the twenty-first century. The position of polyamides as the lowest cost engineering resins or the highest cost (but arguably the highest performing) commodity resin has led to this continuous growth. Although the nylon resin markets, like those for fibers, are dominated by nylon-6,6 and nylon-6, there are many alternative polyamides and copolyamides in this end use. Table 7 gives the price range of many polyamides for various product types. Specialty products and applications can command prices two times higher or greater. In addition to References 11 and 12, price and volume information concerning polyamides can be found in various public sources (14) and private databases that require a client fee for access (15).

4. Physical Properties

4.1. Crystallinity

Linear polyamide homopolymers consist of crystalline and amorphous phases and are termed semicrystalline. Crystallinity enhances yield strength, hardness (qv), abrasion resistance, tensile strength, elastic and shear modulus, and probably resistance to thermooxidation (16), but it decreases moisture absorption and impact strength. Most commercial samples of nylon-6,6 and nylon-6 are 40–50% crystalline by weight, as determined by density measurements. A low degree of crystallinity can be achieved in these polymers by rapidly quenching them below room temperature from the melt, but this state is unstable and the sample quickly crystallizes if it is warmed, subjected to mechanical stress such as drawing, or exposed to moisture or to other plasticizers (qv). A permanent reduction in the degree of crystallinity can be achieved by chemical modification, eg, through the use of unsymmetrical monomers, copolymers, or substitution at the amide nitrogen, but then most of the desirable physical properties are lost. A few properties are improved, however, such as film clarity.

Figure 2 shows the unit cell for nylon-6,6, and Table 8 presents the crystallographic constants for several polyamides. The semicrystalline nature of polyamides and their high melting point are generally attributed to the high degree of hydrogen bonding between adjacent chains in the crystals. The apparent crystal size in polyamides has been determined by wide-angle x-ray scattering (waxs) (20) and small-angle x-ray scattering (saxs) (21). The average size depends on the mechanical and thermal history of the polymer, and in commercial samples it is typically 5–7 nm on each side, but the size distribution is very broad. Chain-folded lamellar, single crystals of polyamides have been formed from dilute solution (22) and from the melt (23). It is generally

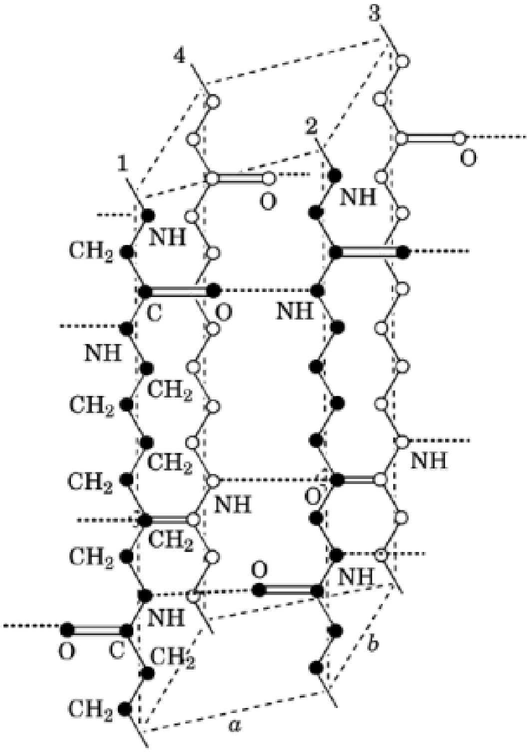


Fig. 2. Unit cell for the α-triclinic form of nylon-6,6 (17).

Table 8. Lattice Constants for Some Polyamides[a]

		Lengths, nm			Angles, °			
Polyamide	Crystal system	a	b	c	α	β	γ	Z^b
nylon-6,6	α-triclinic	0.49	0.54	1.72	48.5	77	63.5	1
nylon-6	α-monoclinic	0.956	0.801	1.724	90	90	67.5	8
	γ-monoclinic	0.914	0.484	1.668	90	90	121	4
nylon-6,10	α-triclinic	0.495	0.54	2.24	49	76.5	63.5	1
nylon-12	α-monoclinic	0.479	3.19	0.958	90	120	90	4

[a] Refs. (17–19).
[b] Z = number of chemical repeat units per unit cell.

accepted that such lamellar structures are present as crystallites in isotropic samples (24), though extended chain crystals may be formed in highly oriented systems such as fibers. The crystallites can form ordered three-dimensional superstructures called spherulites which are detectable by optical microscopy using polarized light. In drawn fibers and films the crystallites as well as the polymer chains in the amorphous regions are preferentially oriented in the direction of the applied strain. The large-scale structure in bulk polyamides is usually unoriented and spherulitic, though some orientation can occur at the surface and elsewhere in the polymer where stresses were induced by flow during melt processing such as injection molding. A comprehensive review of crystallinity and structure in polyamides has been published (25), and extensive crystallographic data are also available (26).

4.2. Solubility

In general, the homopolymer aliphatic polyamides are insoluble in common organic solvents at room temperature. However, they are soluble in formic acid [64-18-6], phenols, chloral hydrate, minerals acids, and fluorinated alcohols such as 1,1,1,3,3,3-hexafluoroisopropyl alcohol [920-66-1] (HFIP) and 2,2,2-trifluoroethanol [75-89-8] (TFE) (27). Mixtures of TFE and methylene chloride in a 3:1 ratio are recommended as effective nmr solvents (28). Formic acid in 90% concentration, 96% sulfuric acid [7664-93-9], *m*-cresol [108-39-4], and HFIP are commonly used as solvents for relative viscosity measurements, and HFIP has been recommended as the preferred solvent for size exclusion chromatography (29). Also, HFIP is an excellent solvent for uv-visible spectroscopy, because it has virtually no absorption in the wavelength range 200–900 nm. At higher temperatures, lithium or calcium chloride–methanol mixtures are effective solvents, as are benzyl alcohol [100-51-6], unsaturated alcohols, alcohol–halogenated hydrocarbons, and nitro alcohols (30). Copolymers of aliphatic polyamides and polyamides with substitution on the amide nitrogen, both of which significantly reduce the degree of crystallinity, are more soluble, and methanol–chloroform mixtures can often be used. Predominately or wholly aromatic polyamides require powerful solvents, such as trifluoroacetic acid [76-05-1] (TFA) or concentrated sulfuric acid. Lower molecular weight aromatic polyamides are often soluble in basic solvents such as *N*,*N*-dimethylacetamide [127-19-5] and *N*-methyl-2-pyrrolidinone [872-50-4], usually with the addition of lithium chloride [7447-41-8] or calcium chloride [10043-52-4]. When polyamides are used in solution to characterize the bulk polymer, such as relative viscosity or spectroscopy, care must be taken to ensure that the very high molecular weight portion of the linear distribution or branched polymers are not left behind as small amounts of insoluble material.

4.3. Piezoelectric Effect

The electrical properties of piezoelectricity, ie, the ability to generate an electrical signal in response to a mechanical stress; pyroelectricity, ie, the ability to generate an electrical signal in response to a temperature change; and ferroelectricity, ie, the ability to respond repeatedly to reversing external electric fields, have been recognized in polymers for many years (31). Materials with these properties find application in microphones, tone generators, hydrophones, ir detectors, electromechanical transducers, and in numerous other devices. The odd-numbered nylons possess a strong piezoelectric effect, with their piezoelectric strain and stress coefficients, d_{31} and e_{31}, being second in magnitude for polymeric materials only to those of poly(vinylidene fluoride) [24937-79-9] and its copolymers (32). The phenomenon has been observed in nylon-11 [25035-04-5], nylon-9 [25035-03-4], nylon-7 [25035-01-2], and nylon-5 [24138-57-6] (33), and is believed to result in part from the alignment of the high dipole moment of the amide group in the periodic array of the crystalline regions of the polymer during the process called poling; the ordered array is stabilized by hydrogen bonding between adjacent amide groups. During poling, a sample of the polymer, positioned between the plates of a capacitor, is subjected to a high electric field of up to 900 kV/cm. Heating the polymer above the glass-transition point, T_g, and allowing it to cool while the electric field is maintained increase the effectiveness of the poling process. Figure 3**a** shows how the amide groups in a crystal of nylon-7 are aligned in an all-trans conformation to reinforce their dipole moments perpendicular to the chain axis; this arrangement produces a microscopic polarization within the crystal. These microscopic crystalline domains must then be aligned and maintained in a mutual orientation, on average, within the polymer sample during poling in order for the macroscopic polarization to be achieved. The dipole moments are also reinforced in odd–odd nylons, as shown in Figure 3**b**. The α-crystalline form has been associated with the development of piezoelectric properties in nylon-7 by means of ^{13}C and ^{15}N solid-state nmr (34). However, waxs studies associate the piezoelectric effects with crystal orientation (35). In nylons containing even-numbered segments, the amide groups alternate direction periodically within the crystal; thus this arrangement mutually cancels the effect of their dipole moments at the microscopic level, as shown in Figure 3**c**.

The odd-numbered nylons exhibit an additional useful property in that their piezoelectric constants increase with increasing temperature almost to the melting point of the polymer. This increase is attributed to the persistence of the hydrogen bonding in polyamides up to the melting point. This property of odd-numbered nylons is in contrast to that of poly(vinylidene fluoride), whose piezoelectric constants remain approximately unchanged with increasing temperature (36) (Fig. 4). Thus nylon could find useful application as a high temperature polymer piezoelectric material. Bilaminate films of nylon-11 and poly(vinylidene fluoride) have been prepared and appear to show enhancements of properties above those exhibited when either polymer is used individually (37).

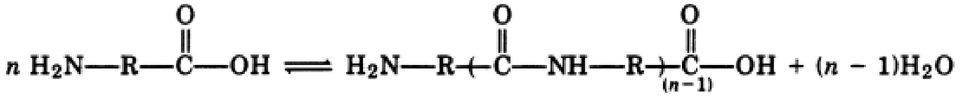
Organic plasticizers (38) and water (39), also a plasticizer for nylons, affect the development of piezoelectric properties in nylon-11 and nylon-7. If these are applied after the samples are poled, the piezoelectric coefficients show an increase with increased plasticization. This effect is interpreted as showing that the alignment of dipoles in the amorphous region also plays a significant role in the bulk polarization. Because both the melting point and weight percent of moisture regain increase as the number of amide bonds increases, nylon-3 [25513-34-2] would be expected to demonstrate superior piezoelectric performance. To support this, the remanent polarization, ie, the polarization that remains after the sample has been poled and the applied field removed, was determined for several nylons and appears to increase linearly as the number of carbon atoms decreases from 55 mC/m^2 for nylon-11 to 135 mC/m^2 for nylon-5. This effect has been extrapolated to approximately 180 mC/m^2 for nylon-3 (40) (Fig. 5). Similarly, ferroelectric behavior has been observed for partially fluorinated odd–odd nylons, eg, nylon-3,5, nylon-5,5, nylon-7,5, and nylon-9,5, based on perfluoroglutaric acid (32, 41). In addition, remanent polarizations have been measured for a series of polyamides containing *m*-xylylenediamine (42) and for those containing 1,3-bis(aminomethyl)cyclohexane (43). Pyroelectricity has been observed in nylon-11 (44) and nylon-5,7 (45).

5. Chemical Properties

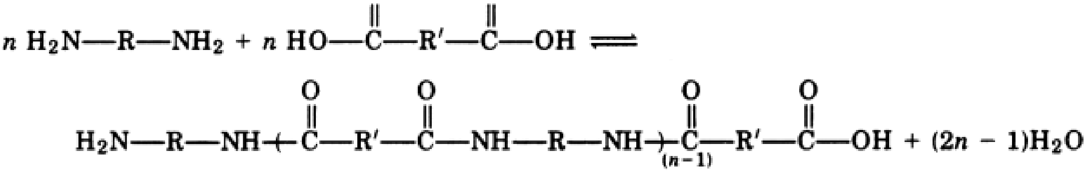
5.1. Preparation

5.1.1. Direct Amidation

The direct reaction of amino acids to form Type AB polyamides (eq. **1**) and diacids and diamines to form type AABB polyamides (eq. **2**) are two of the most commonly used methods to produce polyamides. The

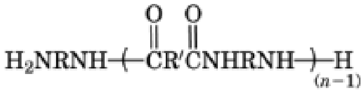


$$n\,H_2N{-}R{-}\overset{\overset{O}{\|}}{C}{-}OH \rightleftharpoons H_2N{-}R\left(\overset{\overset{O}{\|}}{C}{-}NH{-}R\right)_{(n-1)}\overset{\overset{O}{\|}}{C}{-}OH + (n-1)H_2O \tag{1}$$

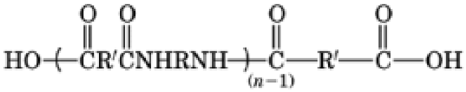


$$\begin{aligned} &n\,H_2N{-}R{-}NH_2 + n\,HO{-}\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}OH \rightleftharpoons \\ &H_2N{-}R{-}NH\left(\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R{-}NH\right)_{(n-1)}\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}OH + (2n-1)H_2O \end{aligned} \tag{2}$$

integer n is called the degree of polymerization (DP). The average DP is approximately 200 for a typical nylon-6, or about 100 for nylon-6,6; thus the numberaverage molecular weight is approximately equal for both, since the monomer, hexamethyleneadipamide, for nylon-6,6 has twice the unit weight as the monomer, ϵ-aminocaproamide, has in nylon-6. Water is released as a by-product of the reaction and depending on the conditions of the reaction can be in equilibrium with the reactants. Ideally for the amino acids, only one homologous series of linear polymers is formed, each member of which possesses one amino and one carboxyl end group, as shown in equation **2**. However, for the type AABB polymers, two additional homologous series of linear polymers are possibly one with two amino end groups and one with two carboxyl end groups:

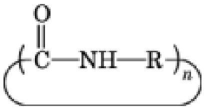


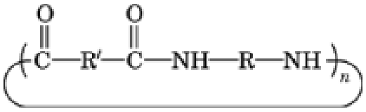
$$H_2NRNH{-}\left(\overset{\overset{O}{\|}}{C}R'\overset{\overset{O}{\|}}{C}NHRNH\right)_{(n-1)}H$$



$$HO{-}\left(\overset{\overset{O}{\|}}{C}R'\overset{\overset{O}{\|}}{C}NHRNH\right)_{(n-1)}\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}OH$$

Polymers from either of these homologous series can be made to predominate by using a small excess of the diamine or diacid, respectively. In addition to these linear polymers, cyclic oligomers are also formed, though in this case *n*



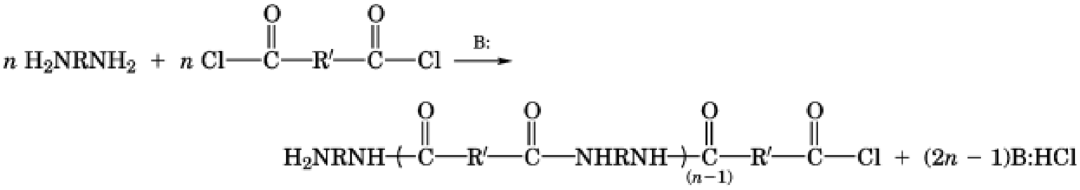


is generally <10 for type AABB and <20 for type AB polymers. Thus, for the Type AB polyamides, direct polyamidation leads ideally to a mixture of two homologous series of polymers, one linear and one cyclic, and for the Type AABB a mixture of four is formed, three linear and one cyclic. Additional complications can arise as a result of side reactions and degradation, which can lead to different end groups, defects along the chain, or branching.

Direct amidation is generally carried out in the melt, although it can be done in an inert solvent starting from the dry salt (46). Because most aliphatic polyamides melt in the range of 200–300°C and aromatic-containing polyamides at even higher temperatures, the reactants and products must be thermally stable to be polymerized via this method.

5.1.2. Acid Chloride Reaction

In situations where the reactants are sensitive to high temperature or the polymer degrades before the melt point is reached, the acid chloride route is often used to produce the polyamide (47). The basic reaction in the presence of a base, **B**:, is as follows:

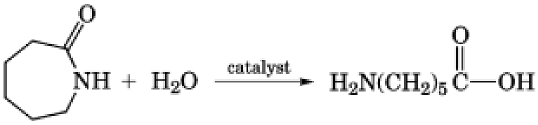


$$n\,H_2NRNH_2 + n\,Cl{-}\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}Cl \xrightarrow{B:} H_2NRNH{-}\left(\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}NHRNH\right)_{(n-1)}\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}Cl + (2n-1)B{:}HCl$$

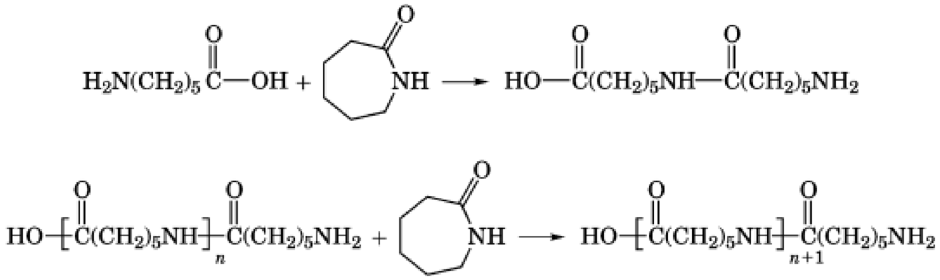
Because almost any diacid can be readily converted to the acid chloride, this reaction is quite versatile and several variations have been developed. In the interfacial polymerization method the reaction occurs at the boundary of two phases: one contains a solution of the acid chloride in a water-immiscible solvent and the other is a solution of the diamine in water with an inorganic base and a surfactant (48). In the solution method, only one phase is present, which contains a solution of the diamine and diacid chloride. An organic base is added as an acceptor for the hydrogen chloride produced in the reaction (49). Following any of these methods of preparation, the polymer is exposed to water and the acid chloride end is converted to a carboxylic acid end. However, it is very difficult to remove all traces of chloride from the polymer, even with repeated washings with a strong base.

5.1.3. Ring-Opening Polymerization

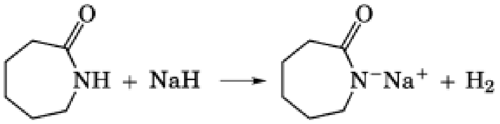
Ring-opening polymerization is the method used to convert lactams to polyamides. There are several variations of the method, but the most commonly practiced method in industry is hydrolytic polymerization, in which lactams containing six or more carbons in the ring are heated in the presence of water above the melting point of the polyamide. The reaction begins with the hydrolytic ring opening of the lactam, which can be catalyzed by an acid or base, an amino acid, or an amine carboxylate, eg, nylon-6,6 salt.



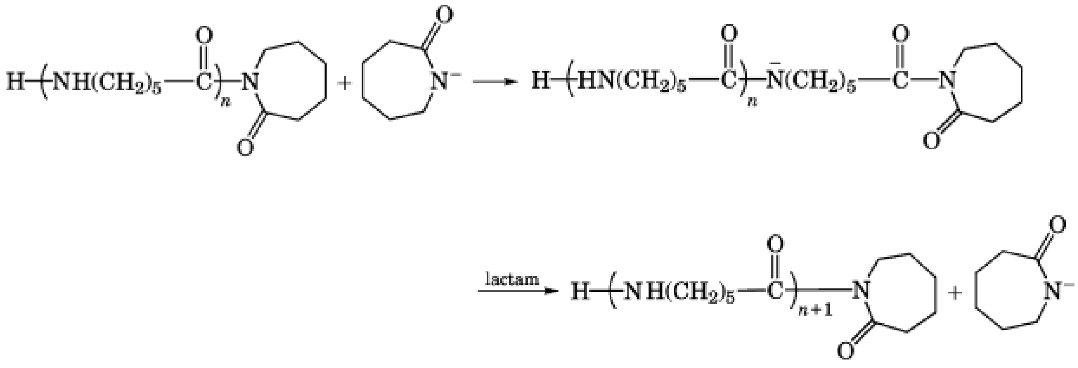
The resulting amino acid then condenses in a stepwise manner to form the growing polymer chain. As in direct polymerization, cyclic oligomers are also formed; hence, caprolactam (qv) can be formed in the reverse of the reaction just shown above.



In anionic polymerization the reaction is initiated by a strong base, eg, a metal hydride, alkali metal alkoxide, organometallic compounds, or hydroxides, to form a lactamate:



The lactamate then initiates a two-step reaction which adds a molecule of the lactam to the polymer chain (50–52):



Lactams can also be polymerized under anhydrous conditions by a cationic mechanism initiated by strong protic acids, their salts, and Lewis acids, as well as amines and ammonia (51–53). The complete reaction mechanism is complex and this approach has not as yet been used successfully in a commercial process.

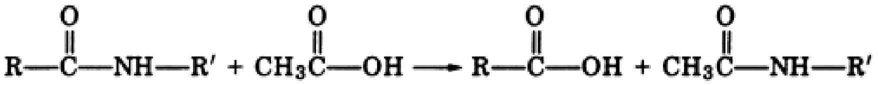
5.1.4. Other Preparative Reactions

Polyamidation has been an active area of research for many years, and numerous methods have been developed for polyamide formation. The synthesis of polyamides has been extensively reviewed (54). In addition, many of the methods used to prepare simple amides are applicable to polyamides (55, 56). Polyamides of aromatic diamines and aliphatic diacids can also be made by the reaction of the corresponding aromatic diisocyanate and diacids (57).

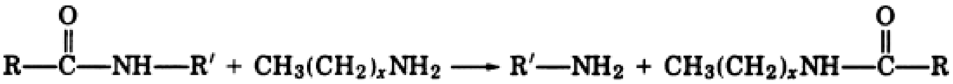
5.2. Reactions of Polyamides

5.2.1. Acidolysis, Aminolysis, and Alcoholysis

When heated, polyamides react with monofunctional acids, amines, or alcohols, especially above the melt temperature, to undergo rapid loss of molecular weight (58, 59), eg, as in acidolysis (eq. **3**) with acetic acid [64-19-7] or aminolysis (eq. **4**) with an aliphatic amine:

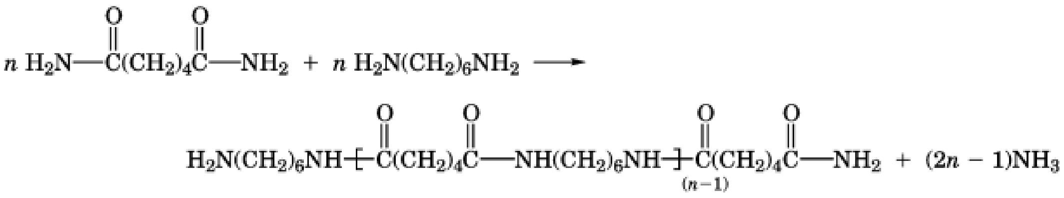


$$R-\overset{\overset{O}{\|}}{C}-NH-R' + CH_3\overset{\overset{O}{\|}}{C}-OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH + CH_3\overset{\overset{O}{\|}}{C}-NH-R' \qquad (3)$$



$$R-\overset{\overset{O}{\|}}{C}-NH-R' + CH_3(CH_2)_xNH_2 \longrightarrow R'-NH_2 + CH_3(CH_2)_xNH-\overset{\overset{O}{\|}}{C}-R \qquad (4)$$

If adipamide reacts with hexamethylenediamine, then nylon-6,6 can be prepared by aminolysis of the adipamide; this could also be viewed as reverse ammonolysis.



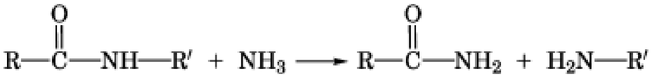
$$n\ H_2N-\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}-NH_2 + n\ H_2N(CH_2)_6NH_2 \longrightarrow$$

$$H_2N(CH_2)_6NH\left[\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}-NH(CH_2)_6NH\right]_{(n-1)}\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}-NH_2 + (2n-1)NH_3$$

Phosphoric acid [7664-38-2] and its derivatives are effective catalysts for this reaction (60). Reverse alcoholysis and acidolysis can, in principle, also be used to produce polyamides, and the conversion of esters to polyamides through their reaction within diamines, reverse alcoholysis, has been demonstrated (61). In the case of reverse acidolysis, the acid by-product is usually less volatile than the diamine starting material. Thus, this route to the formation of polyamide is not likely to yield a high molecular weight polymer.

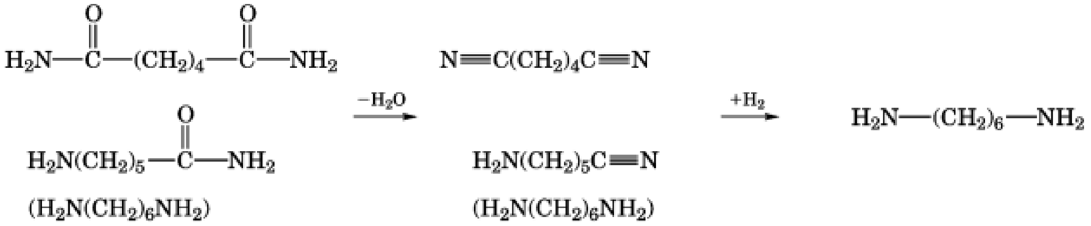
5.2.2. Ammonolysis

In a reaction closely related to aminolysis, ammonia [7664-41-7] reacts with polyamides, usually under pressure and at elevated temperatures (62).



$$R-\overset{O}{\overset{\|}{C}}-NH-R' + NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + H_2N-R'$$

Lewis acids, such as the halide salts of the alkaline-earth metals, Cu(I), Cu(II), zinc, Fe(III), aluminum, etc, are effective catalysts for this reaction (63). The ammonolysis of polyamides obtained from post-consumer waste has been used to cleave the polymer chain as the first step in a recycle process in which mixtures of nylon-6,6 and nylon-6 can be reconverted to diamine (64). The advantage of this approach lies in the fact that both the adipamide [628-94-4] and 6-aminohexanoamide can be converted to hexamethylenediamine via their respective nitriles in a conventional two-step process in the presence of the diamine formed in the original ammonolysis reaction, thus avoiding a difficult and costly separation process. In addition, the mixture of nylon-6,6 and nylon-6 appears to react faster than does either polyamide alone.



$$\begin{array}{ccccc} H_2N-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH_2 & & N{\equiv}C(CH_2)_4C{\equiv}N & & \\ & \xrightarrow{-H_2O} & & \xrightarrow{+H_2} & H_2N-(CH_2)_6-NH_2 \\ H_2N(CH_2)_5-\overset{O}{\overset{\|}{C}}-NH_2 & & H_2N(CH_2)_5C{\equiv}N & & \\ (H_2N(CH_2)_6NH_2) & & (H_2N(CH_2)_6NH_2) & & \end{array}$$

The resulting hexamethylenediamine can then be reused to produce new nylon-6,6. Impurities or contaminants from monomers of other types of polyamides can be readily removed by distillation from either the nitriles or diamine.

5.2.3. Transamidation and Transesteramidation

Transamidation is the mutual exchange of chain fragments in a polyamide, shown as follows where R, R″: and R′, R″: represent polymer chain fragments of any length.

$$R-\overset{O}{\overset{\|}{C}}-NH-R' + R''-\overset{O}{\overset{\|}{C}}-NH-R''' \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH-R''' + R''-\overset{O}{\overset{\|}{C}}-NH-R'$$

It is generally accepted that transamidation is not a concerted reaction, but occurs through the attack of a free end on the amide group via aminolysis (eg, eq. **4**) or acidolysis (eg, eq. **3**) (65). Besides those ends always present, new ends are formed by degradation processes, especially hydrolysis (eq. **5**), through which the amide groups are in dynamic equilibrium with the acid and amine ends.

$$R-\overset{\overset{O}{\|}}{C}-NH-R' + H_2O \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-OH + H_2N-R' \qquad (5)$$

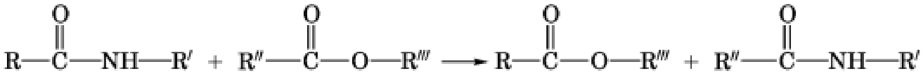
The acid and amine products of equations **3**, **4**, and **5** condense to form new amide end groups (eq. **6**).

$$R-\overset{\overset{O}{\|}}{C}-OH + H_2N-R''' \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-NH-R''' + H_2O \qquad (6)$$

The step in which the free acid and amine ends recombine (eq. **6**) is only accomplished statistically, since it is unlikely that any two particular ends formed in the acidolysis or aminolysis steps would find each other in the melt. Transamidation is catalyzed by both acidic and basic ends, but in general acids appear to be much more effective than bases (59, 65).

Transamidation is an important process in the melt phase for polyamides because it is usually the process by which an equilibrium molecular weight distribution is reestablished and, in the case of the melt blending of two or more polyamides to form a copolymer, it is the process by which randomization of the individual monomers along the chain is effected. In the solid phase, chain mobility is restricted and equilibrium in either case often is not achieved. In the case of blending two homopolymers in the melt, eg, nylon-6,6 and nylon-6, randomization begins by forming copolymers with large blocks of nonrandomized polymer. Then, as the reaction proceeds, the size of the blocks decreases as a result of the interchange of segments between adjacent polymer chains via transamidation, until the monomeric units are distributed randomly along the polymer chain. Industrial practice indicates that the effects of incomplete randomization are usually indistinguishable from full randomization after about 15 min in the melt. However, laboratory studies have shown that complete randomization takes several hours (66). Equilibration of molecular weight distribution also appears to occur relatively quickly, presumably because it requires only a statistical distribution of chain lengths rather than complete randomization of monomeric units. This tendency of polyamides to randomize in the melt makes it virtually impossible to produce block copolymers via such a process.

Transesteramidation is a process similar to transamidation, except that a polyamide is mixed with a polyester rather than another polyamide (67). This is often a convenient route to produce polyesteramides.



$$R-\overset{\overset{O}{\|}}{C}-NH-R' + R''-\overset{\overset{O}{\|}}{C}-O-R''' \longrightarrow R-\overset{\overset{O}{\|}}{C}-O-R''' + R''-\overset{\overset{O}{\|}}{C}-NH-R'$$

Here, R and R' represent polyamide chain fragments, and R'': and R''': represent polyester chain fragments of any length. Polyesters are generally more easily hydrolyzed than polyamides and thus are quite sensitive to the presence of water in the polyamide. During transesteramidation care must be taken not to significantly hydrolyze the polyester before it reacts. The rate constants for randomization of copolyamides by transamidation are an order of magnitude slower than that for copolyesters by transesterification (68).

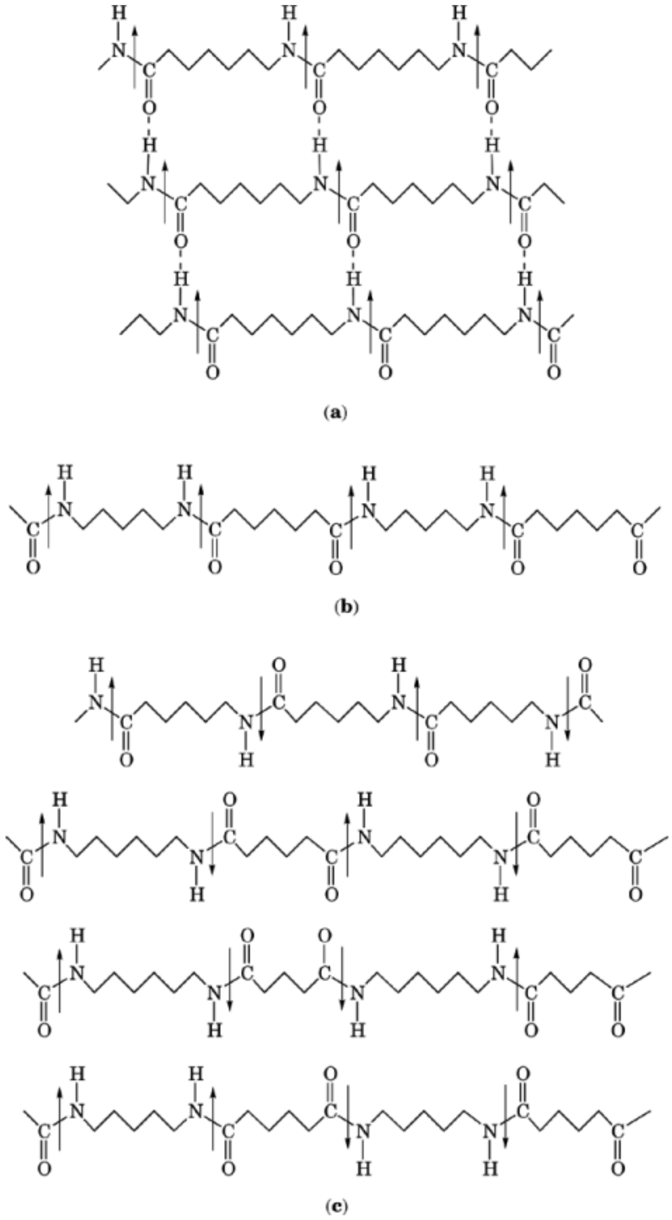


Fig. 3. Alignment of amide dipoles in polyamide crystals: (**a**) for a two-dimensional array of an odd nylon, nylon-7, (**b**) for a one-dimensional array of an odd–odd nylon, nylon-5,7; (**c**) for one-dimensional arrays of polyamides containing even segments: an even nylon, nylon-6; an even–even nylon, nylon-6,6; an even–odd nylon, nylon-6,5; and an odd–even nylon, nylon-5,6 (31).

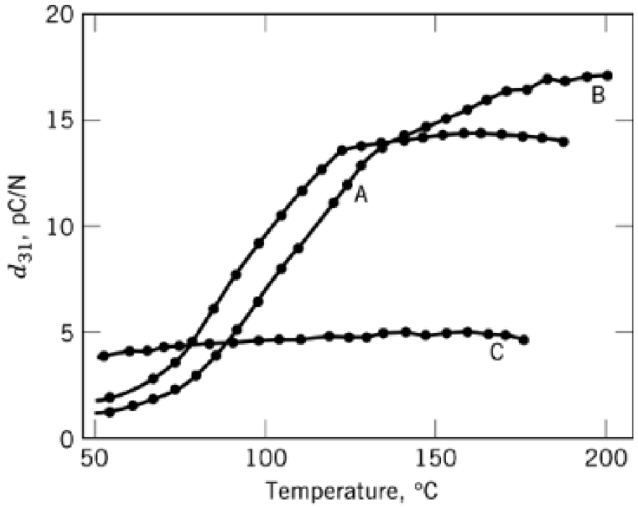
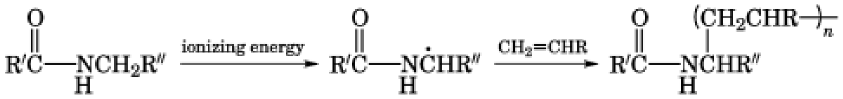


Fig. 4. The effect of temperature on the piezoelectric strain constant, d_{31}, for A, nylon-11; B, nylon-7; and C, poly(vinylidene fluoride) (PVF_2) films (35).

5.2.4. Grafting

Grafting is the process of chemically bonding additional polymeric units, usually not polyamides, to the nylon polymer chain. This is most often initiated by reaction of the grafting substrate directly with the polyamide backbone, but grafting can also be achieved by introducing non-amide reactive sites into the polymer chain, through the incorporation of reactive comonomers during polymerization. In general, the polyamides are relatively inert chemically, and a source of high energy sufficient to create free-radical sites is necessary to initiate the grafting reaction, eg, α-particles, electrons from linear accelerators, γ-rays from ^{60}Co, x-rays, glow discharges, or uv radiation. The predominant reactive intermediate is believed to be the alkyl free radical formed by the removal of the α-hydrogen adjacent to the amide nitrogen (69). The reaction with vinyl monomers is typically as follows:



$$R'\overset{\overset{O}{\|}}{C}\!-\!\underset{H}{N}CH_2R'' \xrightarrow{\text{ionizing energy}} R'\overset{\overset{O}{\|}}{C}\!-\!\underset{H}{N}\dot{C}HR'' \xrightarrow{CH_2{=}CHR} R'\overset{\overset{O}{\|}}{C}\!-\!\underset{H}{N}\overset{\overset{(CH_2CHR\!\!-\!)_n}{|}}{C}HR''$$

Grafting can also occur in the amide nitrogen, either through an anionic-type mechanism which is believed to operate when ethylene oxide [75-21-8] and similar copolymers are grafted to polyamides, or through a polycondensation mechanism when secondary amides are formed as graft copolymers (70).

Grafting can be used to change the surface properties of the final polyamide article, especially film or fiber; its hydrophilic, antistatic, frictional, or other characteristics are altered. Also, grafting can be made to occur in the bulk polymer; this alters, for example, the mechanical (toughening) or optical (delustering) properties of the polyamide. Although there is a substantial amount of work published both in the open and patent literature that discusses grafting onto polyamides (70–74), this technology does not appear to be practiced by the primary polyamide manufacturers to any great extent and is probably reserved for specialty end use applications, where the resulting performance changes warrant the added cost of materials and processing.

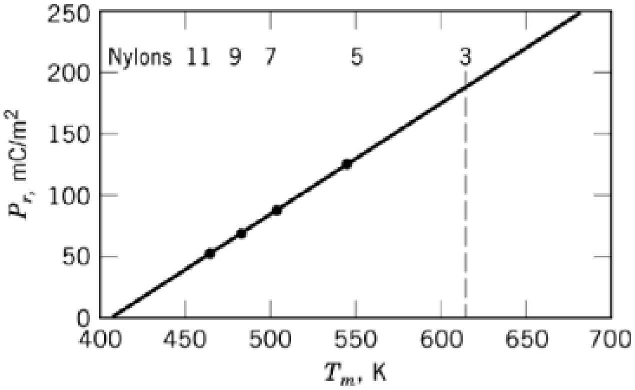


Fig. 5. The dependence of remanent polarization, P_r, on the melting point, T_m, in odd nylons (40).

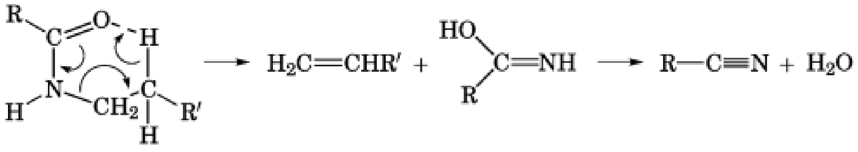
5.3. Degradation of Polyamides

5.3.1. Hydrolysis

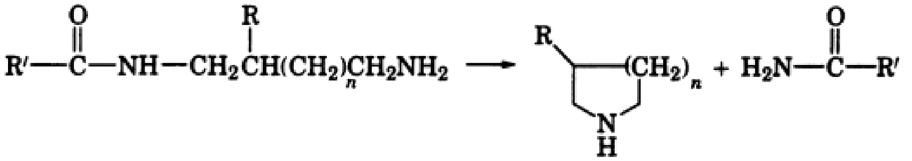
Hydrolysis (eq. **5**) is the reverse of the amidation reaction. As a consequence, if the water is not removed from the reaction media, the polyamidation reaction eventually approaches equilibrium and the ultimate molecular weight of the polymer is limited (75). In many polymerization processes, a vacuum is applied to the polymer melt and the molecular weight can continue to grow. Nonetheless, hydrolysis is important in determining the stability of the final polymer after it has been quenched and dried. Because the equilibrium moisture content of polyamides at room temperature at any practical relative humidity is almost always greater than the equilibrium water content in the melt, polyamides must be dried to avoid a significant decrease in molecular weight when they are remelted. Reduction of molecular weight via hydrolysis can also occur when polyamides are in use, particularly in a high humidity environment or when they are placed in direct contact with water. The hydrolysis reaction is generally slow at room temperature, but it is accelerated at higher temperatures and when catalyzed by acids or bases. An example is the rapid loss of strength in tire cord that occurs as water comes in contact with nylon fiber in a tire carcass. The hydrolysis reaction can be used to advantage in the determination of the composition of polyamides. Most aliphatic polyamides can be completely hydrolyzed by heating in 8 *N* HCl for 16 h at about 110°C. The solution is then neutralized and the monomers are extracted or dried, derivatized, and analyzed by gas chromatography (gc) or high performance liquid chromatography (hplc) for the relative amounts of their constituent monomers (76).

5.3.2. Thermal Degradation

The degradation that occurs in the absence of oxygen affects all polyamides at a sufficiently high temperature and is usually significant above 300°C. Thermooxidation reactions often occur simultaneously owing to the presence of small amounts of air, which can lead to a confusion of the two processes. The general thermal decomposition reaction in polyamides, which is the cleavage of the amide bond to eventually form an olefin and a nitrile, results in chain cleavage and thus a loss in molecular weight.

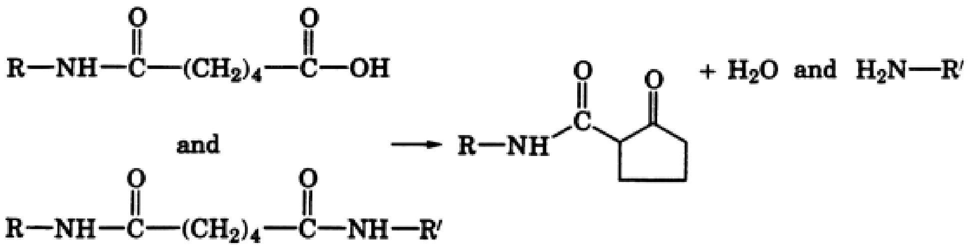


However, if there is a lower energy decomposition pathway available, then an alternative degradation reaction dominates. There is a growing body of evidence to suggest that cyclization reactions to form small stable ring compounds are one such decomposition pathway, especially for polyamides containing monomers with four to six carbon atoms (77, 78) (eq. **7**). The first example of this is the formation of cyclic amines, which is the principal decomposition pathway in nylon-4,6 (in eq. **7**, $n = 1$ and $R = H$) (79); this has also been observed in MPMD-containing polyamides (in eq. **7**, $n = 2$, $R = CH_3$) (80), as well as in nylon-6,6 (in eq. **7**, $n = 3$, $R = H$).

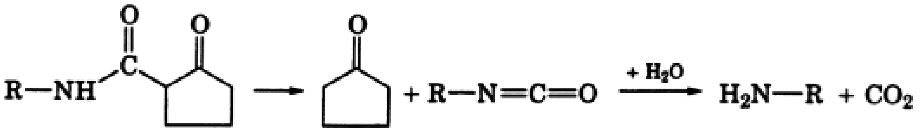


(7)

Another example of a cyclic product is the formation of cyclopentanone [120-92-3] as a thermal decomposition product in nylon-6,6 (81, 82). The following mechanism (eqs. **8** and **9**) accounts not only for the formation of the cycloketone but also for the increase in amine ends, the decrease in acid ends, and the evolution of CO_2 that is observed in the thermal decomposition of nylon-6,6 (82).

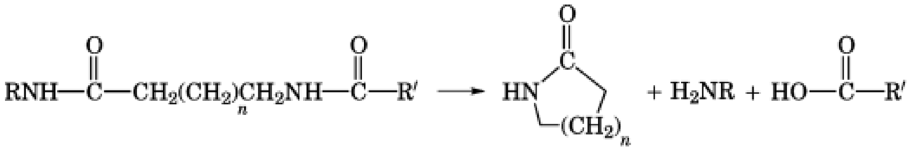


(8)

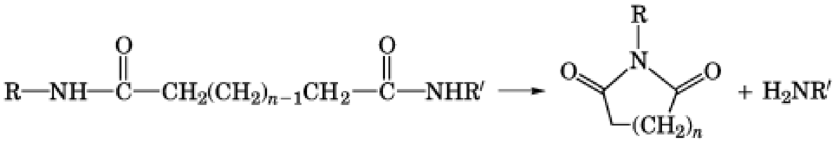


(9)

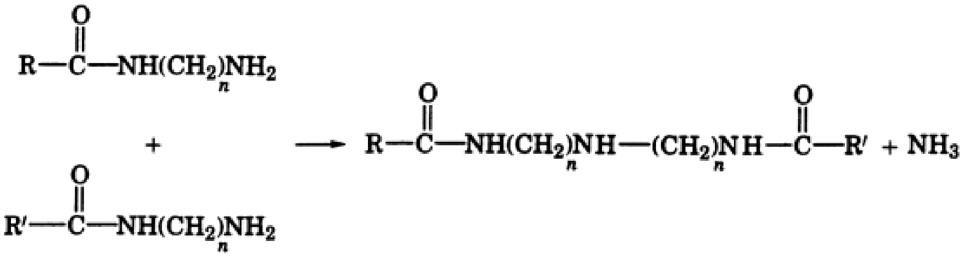
In type AB polyamides the reequilibration reaction leading to production of the starting lactam can be viewed as the decomposition of the polyamides into cyclic products (83); $n = 1$, 2, and 3 for nylon-4, nylon-5, and nylon-6, respectively.



Finally, when polyamides containing four or five carbon diacids, ie, succinic acid [110-15-6] and glutaric acid [110-94-1], respectively, are heated, they form cyclic imides that cap the amine ends and prevent high molecular weights from being achieved (84). For nylon-*x*,4, $n = 1$ and for nylon-*x*,5, $n = 2$.

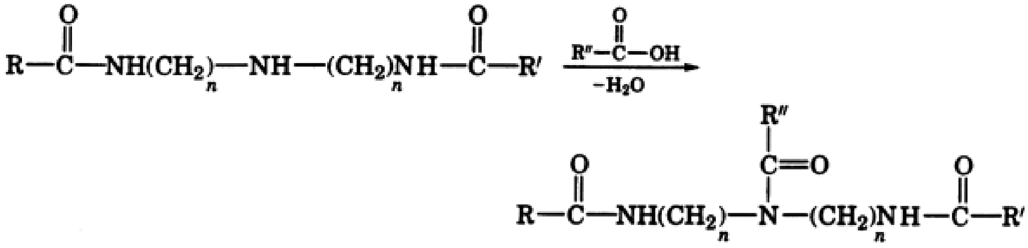


Other noncyclic reactions are observed, especially in polyamides of longer carbon chain monomers; for example, the linear analogue to the cyclic amine reaction is diamine coupling (eq. **10**) to form secondary amines that can act as branch points (eq. **11**).



$$R{-}\overset{O}{\overset{\|}{C}}{-}NH(CH_2)_nNH_2 + R'{-}\overset{O}{\overset{\|}{C}}{-}NH(CH_2)_nNH_2 \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}NH(CH_2)_nNH{-}(CH_2)_nNH{-}\overset{O}{\overset{\|}{C}}{-}R' + NH_3$$

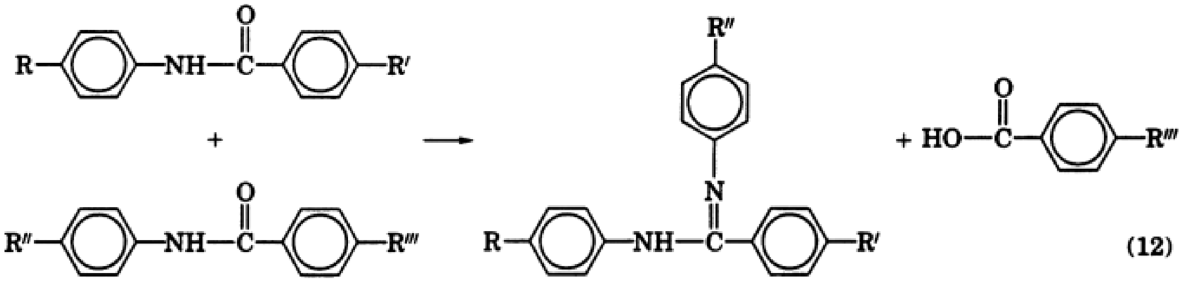
(10)



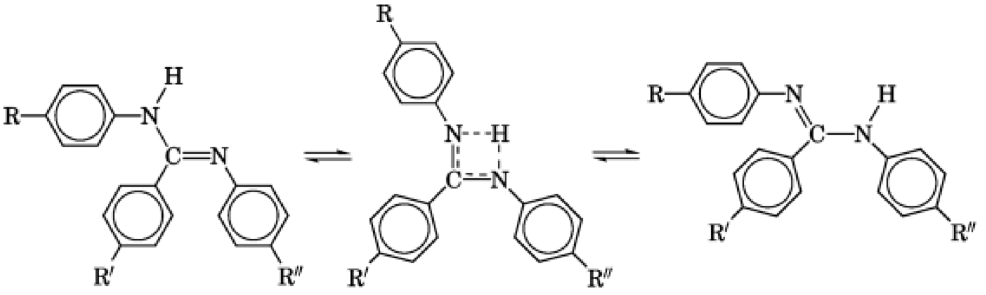
$$R{-}\overset{O}{\overset{\|}{C}}{-}NH(CH_2)_n{-}NH{-}(CH_2)_nNH{-}\overset{O}{\overset{\|}{C}}{-}R' \xrightarrow[-H_2O]{R''-\overset{O}{\overset{\|}{C}}-OH} R{-}\overset{O}{\overset{\|}{C}}{-}NH(CH_2)_n{-}\overset{\overset{R''}{|}}{\overset{C=O}{\overset{|}{N}}}{-}(CH_2)_nNH{-}\overset{O}{\overset{\|}{C}}{-}R'$$

(11)

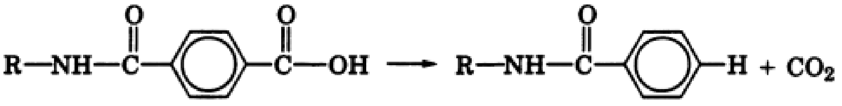
In nylon-6,6, the secondary amine so formed, bis-hexamethylenetriamine [143-23-7] (BHMT) has been thought by some to be the source of cross-linking and gelation in this polyamide (84–86). However, nylon-6,10 and nylon-6,12 do not exhibit such gelation behavior, and the branching reaction in nylon-6,6 is generally believed to be associated with the presence of adipic acid [124-04-9]. Although other branch sites have been postulated (87), the nature of the specific chemical steps leading to the formation of gel in nylon-6,6 remains an open question. Several patents have appeared that claim to inhibit the gel formation in nylon-6,6, but no mechanistic details are given (86, 88, 89). Another type of branching reaction which has been found in aromatic polyamides is amidine formation (eq. **12**) (90).



Such structures are stabilized by having the imine bond conjugated between two aromatic rings and the possibility of tautomerism between two equivalent structures:



Decarbonylation of the acid ends is another reaction (eq. **13**) that can occur during the thermal decomposition of polyamides, especially above 300°C. This reaction, which forms an unreactive end and thus limits the ultimate molecular weight that is attainable, is particularly troublesome during the processing of polyamides containing a high ratio of terephthalic acid; these polyamides generally have a high melting point and require high processing temperatures.



(13)

5.3.3. Thermooxidation

This is an autoxidation process that occurs in all polyamides. It is significantly accelerated at elevated temperatures and can lead to carbonization of the polymer, but it also occurs during ambient temperature storage unless the polymer is protected with an antioxidant or the storage temperature is reduced. The principal effects of thermooxidation are a loss in molecular weight, increase in acid ends, decrease in amine ends, and the generation of color. Thermooxidation is the primary source of color generation in aliphatic polyamides; this is sometimes attributed incorrectly to thermal degradation. Aliphatic polyamides should be protected from air during thermal processing and in high temperature applications if the negative effects of oxidation are to be avoided. Blanketing the polymer with inert gas or the addition of antioxidants (qv) are two techniques providing good protection.

Figure 6 presents the first steps in the generally accepted mechanism for thermooxidation (and photooxidation). Isotopic labeling studies have demonstrated that the position alpha to the amide nitrogen is the predominant site for oxygen attack (91), and the corresponding alkyl radical has been observed using electron-spin resonance (esr) in polyamides exposed to ionizing radiation (92). The effectiveness of free-radical trapping agents and peroxide decomposers used as additives to inhibit oxidation in polyamides gives strong support to the remaining steps in the mechanism, which are essentially the same as those that have been thoroughly investigated for polyolefins. However, this mechanism does not account for any of the primary deleterious effects of thermooxidation in polyamides mentioned above.

It is usually postulated that the final product in the accepted mechanism, the alkoxyl radical 6, cleaves (eqs. **14** and **15**) before or after hydrogen abstraction, and that this accounts for the drop in molecular weight of the

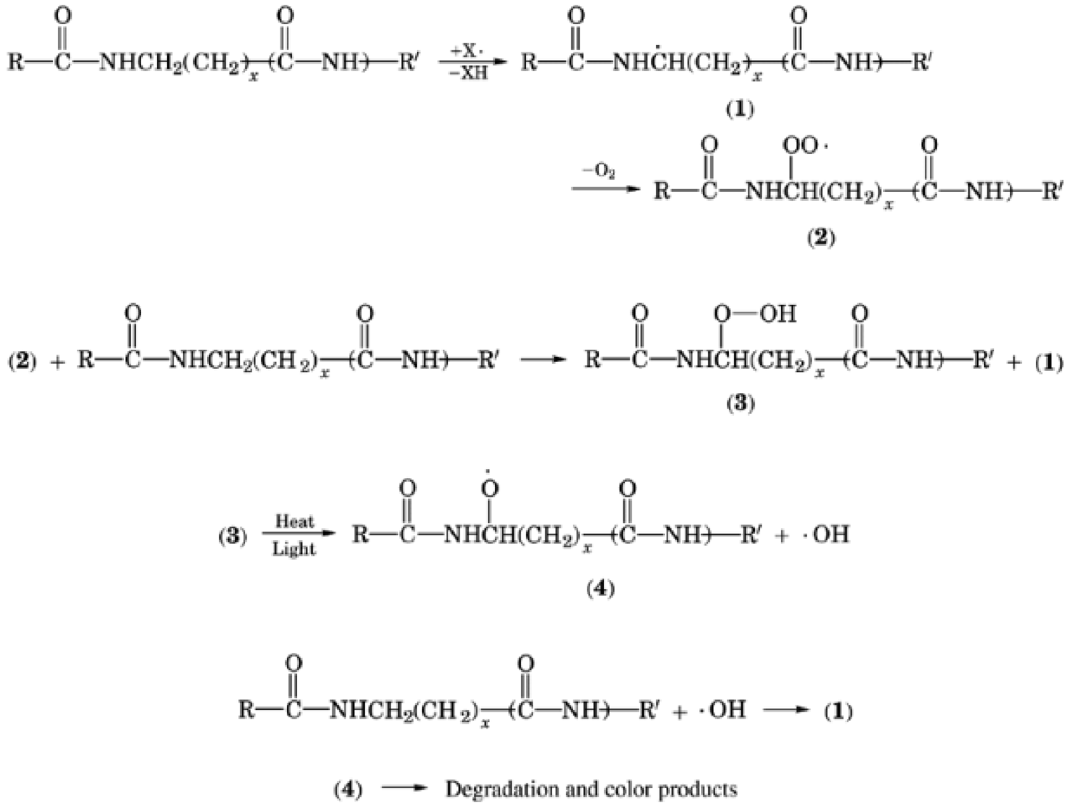
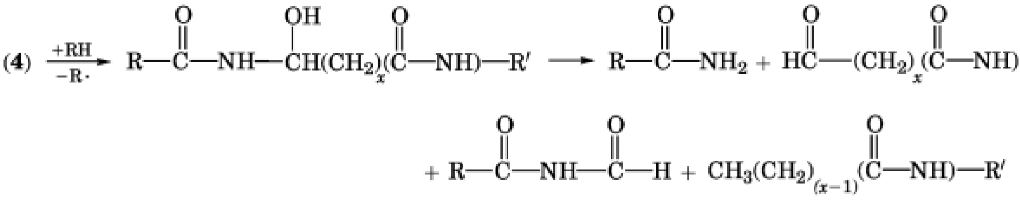
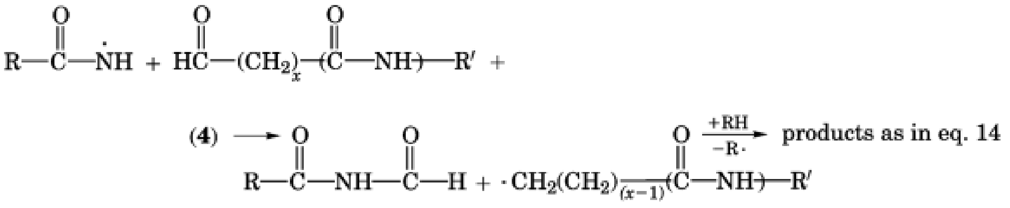


Fig. 6. The initial degradation pathway for thermooxidation and photooxidation. The free radical X is generated by the effect of heat or light on impurities, additives, and polymer.

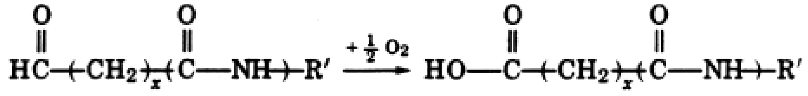


(14)



(15)

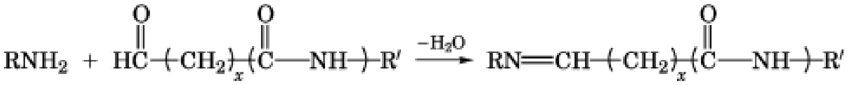
polymer. When the site of the alkyl radical is located beta or gamma to the amide nitrogen with a lower probability, as the isotopic labeling indicates, then a homologous series of products is formed. The carbonyl absorption of the aldehydes (93) and the alkyl amines formed after hydrolysis of the polymer (94) have been observed in nylon-6,6. It is also likely that further oxidation of the aldehydes leads to the increase in acid ends (eq. **16**). The condensation reaction between



$$\mathrm{H\overset{O}{\overset{\|}{C}}{-}(CH_2)_x{-}(\overset{O}{\overset{\|}{C}}{-}NH){-}R'} \xrightarrow{+\frac{1}{2}\mathrm{O_2}} \mathrm{HO{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_x{-}(\overset{O}{\overset{\|}{C}}{-}NH){-}R'} \qquad (16)$$

the acid and amine ends is probably the primary pathway for the reduction of the amine ends, particularly when the temperature is elevated.

No definitive evidence has appeared that identifies the source of the color generated during thermooxidation (95). However, two laboratories have postulated that the reactions leading to the formation of the color chromophores are aldol-type reactions, either via the reaction of aldehydes directly (96) or via imines (95, 97) formed by the condensation of the aldehyde with an amine end, which could also contribute to the loss of amine ends:

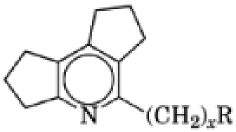


$$\mathrm{RNH_2} + \mathrm{H\overset{O}{\overset{\|}{C}}{-}(CH_2)_x{-}(\overset{O}{\overset{\|}{C}}{-}NH){-}R'} \xrightarrow{-\mathrm{H_2O}} \mathrm{RN{=}CH{-}(CH_2)_x{-}(\overset{O}{\overset{\|}{C}}{-}NH){-}R'}$$

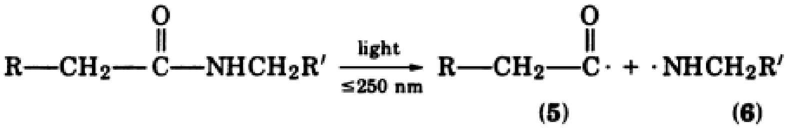
These polyaldol–condensation reactions lead to a system of conjugated double bonds that, when the number of bonds is sufficient, can account for absorption at visible wavelengths, ie, yellow color. However, the color chromophores can also be formed via further reaction of these species, such as continued oxidation, cyclization, etc. Primarily because of the tendency of nylons to yellow and because of long-term strength loss, antioxidants are commonly used in commercial polymers. The copper halide system, the combination of a soluble copper(II) salt with sodium or potassium iodide, is probably the most frequently used antioxidant in polyamides (98). The mechanism for stabilization by copper halides has been reviewed and a new function for the metal ion as a peroxide decomposer has been postulated (99), as well as its accepted role as a radical scavenger (100). What is particularly attractive about this mechanism is that it offers an explanation as to why the copper halide system works so well in polyamides, whereas copper ions promote severe thermooxidation in polyolefins. In polyamides there is always a carbonyl oxygen available to coordinate the copper in a stable, six-membered ring when the hydroperoxide is formed in its most probable position, alpha to the amide nitrogen. In polyolefins, the possibility of coordination seldom occurs, and the copper ion is free to act in its usual role as an oxidation catalyst. Other antioxidants are also used in polyamides, eg, phenols, hypophosphites, and phosphites. However, the high processing temperatures, presence of moisture, and the acid–base functionality associated with polyamides significantly limit the number and type of stabilizers that can be used in polyamides. For example, most hindered amines, which have been used with great success when combined with other antioxidants for the thermo- and photostabilization of polypropylene, are thermally unstable above 200°C (101), and therefore cannot be used in a melt process for most polyamides.

5.3.4. Photodegradative Processes

Polymers can undergo two types of photodegradative processes; one in the presence of oxygen, photooxidation, and one in its absence, photodegradation. Additive-free, noncontaminated nylons appear to have only one significant chromophore in the uv-visible region, a strong, $\log \epsilon \geq 4.0$, at approximately 185 nm, which is assigned to the $\pi \longrightarrow \pi^*$ transition of the amide group. There may also be a much weaker $n \longrightarrow \pi^*$ at slightly longer wavelengths, but its presence is usually masked by absorption resulting from thermooxidative impurities or the carbonyl absorption of the acid ends. The strongly forbidden ground singlet state to first excited triplet state absorption, $S_0 \longrightarrow T_1$, can lie as low as 285 nm, based on low temperature phosphorescence excitation–emission spectra of model alkyl-bis(hexanamides) (102). A weak, predominantly continuum absorption by the thermooxidative degradation products occurs from about 235 to at least 400 nm, where they are the primary source of yellow color in polyamides. Thermal degradation products can also show a continuum-like absorption in this region; however, nylon-6,6 shows a weak but discernible absorption peak at 290 nm (103) which has been assigned to the following chromophore (104):



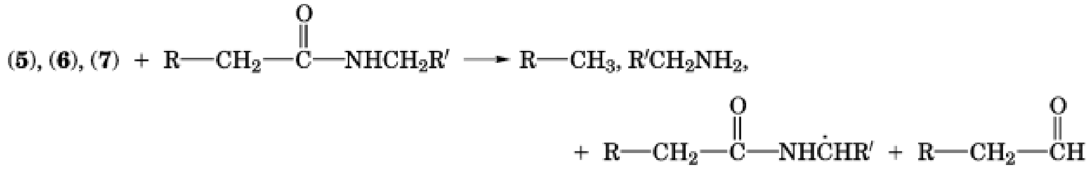
The mechanism for photodegradation at short wavelengths is generally believed to be initiated by the photolytic cleavage of the amide bond (eq. **17**), which has the lowest bond strength in aliphatic polyamides (220 kJ/mol (53 kcal/mol))



$$\mathrm{R{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}NHCH_2R'} \xrightarrow[\leq 250\ \mathrm{nm}]{\text{light}} \underset{(\mathbf{5})}{\mathrm{R{-}CH_2{-}\overset{O}{\overset{\|}{C}}\cdot}} + \underset{(\mathbf{6})}{\mathrm{\cdot NHCH_2R'}} \qquad (\mathbf{17})$$

$$(5) \longrightarrow \mathrm{R{-}CH_2 + CO}$$

(7)



$$(\mathbf{5}), (\mathbf{6}), (\mathbf{7}) + \mathrm{R{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}NHCH_2R'} \longrightarrow \mathrm{R{-}CH_3,\ R'CH_2NH_2,} + \mathrm{R{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}NH\dot{C}HR'} + \mathrm{R{-}CH_2{-}\overset{O}{\overset{\|}{C}}H}$$

(105, 106). The product radicals are then consumed by recombination or by the reaction with oxygen (Fig. 6) when the sample is exposed to air.

The initial steps in the mechanism for photooxidation are generally accepted as being the same as for thermooxidation. This is supported by the facts that similar degradation products have been detected and the effectiveness of similar stabilizers, especially the copper halide system. Although there are some claims that the initial formation of free radicals at wavelengths above 300 nm is the result of the photolytic cleavage of the amide bond, an extrapolation of the logarithm of the molar extinction coefficient for the amide absorption of model amide compounds (107) to 300 nm suggests that the value of the coefficient would be on the order of 0.01 to 0.001, and thus would not be a significant source of radicals even if the quantum yield were high. A more likely source is the photolysis of additives or impurities, such as degradation products like hydroperoxides. Iron(III) halides have been suggested as a likely source of photoinitiated radicals in polyamides (108) at wavelengths above 310 nm, and iron has been shown to have significant negative impact on the photostability of nylon (109). The additive anatase titanium dioxide [1317-70-0], commonly used as a delustrant in fibers, has long been recognized as a potent photodegradant that can, however, be stabilized with the use of manganese(II) compounds (110, 111). Dyes and pigments can also act as either prodegradants or as stabilizers, presumably as a result of their propensity to produce free radicals or to act as excited-state quenchers, respectively (112–114).

The generation of color during photooxidation, known as photoyellowing, has long been recognized as a source of color in nylon-6,6 and nylon-6 (115). This effect has been shown to occur in all aliphatic polyamides

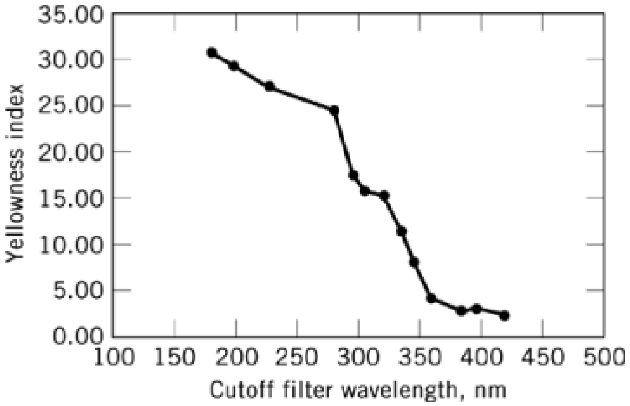


Fig. 7. Photoyellowing of nylon-12 as a function of wavelength.

at wavelengths between 320 and 350 nm (116) (Fig. 7). The chemical nature of the yellow chromophore has not been identified.

5.3.5. Bio-, Environmental, and Mechanical Degradation

Pressure on industry to reduce or remove plastic materials from waste streams is increasing. One approach to meeting this expectation is to manufacture plastic materials that degrade in the environment (117, 118) (see Polymers, environmentally degradable). Unfortunately, polyamides, like almost all synthetic polymers, are not directly biodegradable. However, if the polymeric material is reduced to low molecular weight oligomers, then many can be metabolized by microorganisms. Polyamide materials can be fragmented and then reduced in molecular weight by a process of mechanical destruction, photooxidation, and hydrolysis. This process can occur in a managed waste treatment facility, but it is expensive. An alternative approach has been to incorporate naturally occurring amino acids into polyamide polymer chains to provide sites for enzymatic attack. Numerous articles describing research in this area have appeared (119–123), but it has not been commercially successful, owing to cost and the fact that at high amino acid content most of the desirable properties of synthetic polyamides are lost and at low content the polymers are not sufficiently biodegradable.

Polyamides, like other macromolecules, degrade as a result of mechanical stress either in the melt phase, in solution, or in the solid state (124). Degradation in the fluid state is usually detected via a change in viscosity or molecular weight distribution (125). However, in the solid state it is possible to observe the free radicals formed as a result of polymer chains breaking under the applied stress. If the polymer is protected from oxygen, then alkyl radicals can be observed (126). However, if the sample is exposed to air then the radicals react with oxygen in a manner similar to thermo- and photooxidation. These reactions lead to the formation of microcracks, embrittlement, and fracture, which can eventually result in failure of the fiber, film, or plastic article.

6. Principal Commercial Nylons: Nylon-6,6 and Nylon-6

6.1. Nylon-6,6

Nylon-6,6 [32131-17-2] is a tough, translucent white, semicrystalline, high melting ($T_m = 265\ ^\circ\mathrm{C}$) material. The common physical properties are shown in Table 9, and principal producers worldwide in Table 10, for nylon-6,6 and other commercial polyamides.

Table 9. Physical Constants of Commercial Aliphatic Polyamide Homopolymers[a]

Property	Nylon-6,6	Nylon-6	Nylon-4,6[b]	Nylon-6,9[b]	Nylon-6,10	Nylon-6,12[b]	Nylon-11[b]	Nylon-12
melting point, °C	255	220	295	210	220[b]	212	185	175
at equilibrium		231						
crystalline	270	260						
specific gravity	1.14[b]	1.13[b]	1.18	1.07	1.07[b]	1.06	1.05	1.01[b]
density, g/cm^3								
crystalline[c]								
α	1.22–1.24 T	1.21–1.24 M						
β	1.248 T							
γ		1.13 H						
γ		1.17 M						
amorphous								
γ		1.09						
α		1.11						
heat of fusion, kJ/kg[d]			104.6					
crystalline form ΔH_m	196	190			215			95
α-crystalline form ΔH_m		240–260						
amorphous, annealed 8 h at 50°C		45						45
entropy of fusion, J/(moK)[d]								
crystalline	83–86	44–47.5			110–114			
heat capacity, J/(moK)[d]								
crystalline, 20°C	374	204			502			354
specific heat, J/(g·K)[d]	1.67	1.67	2.09	1.67		1.67		
heat of crystallization, kJ/kg[d]	−54	−46.5						
heat of combustion, kJ/kg[d]	−31.4	−31.4						
coefficient of thermal expansion								
linear at 20°C, m/m/K × 10^5	7–10	7–10	16	15	8–10	9	8.5	11
volume at 20°C, m^3/m^3/K × 10^4	2.8	2.7			3.8			2.9
thermal conductivity, W/(m·K)								
crystalline (wet) at 30°C	0.43	0.43	0.29					
amorphous (wet) at 30°C	0.36	0.36			0.35			
melt at ~250°C	0.15	0.21						
moldings	0.23	0.23			0.23	0.22		0.25
dielectric strength, kV/mm								
dry	120	100	26.5	23	100		30	90
dry at 100°C	40	40						25
humid	80	60	16		60			
volume resistivity, Ω·cm								
dry as molded	1×10^{15}	1×10^{15}	5×10^{14}		1×10^{15}	10^{15}	10^{14}	10^{15}
50% rh at 20°C	3×10^{11}	2×10^{11}	2×10^{9}		2×10^{12}	10^{13}		10^{14}
dry at 100°C	3×10^{9}	3×10^{9}			5×10^{8}			10^{9}
50% rh at 100°C	4×10^{7}							
dielectric constant								
100 Hz (dry)	3.6	3.5	3.83		3.2	4.0		4.0
10^6 Hz (dry)	3.2	3.3	3.55		3.0	3.5		
100 Hz (50% rh)	7.5	10.9	11.0		6.5	6		>20
10^6 Hz (50% rh)	3.7	3.8	4.5		3.5	4		
dissipation factor								
100 Hz (dry)	0.0085	0.0065	0.012		0.010	0.02		0.07

Table 9. *Continued*

Property	Nylon-6,6	Nylon-6	Nylon-4,6[b]	Nylon-6,9[b]	Nylon-6,10	Nylon-6,12[b]	Nylon-11[b]	Nylon-12
10^6 Hz (dry)	0.025	0.024	0.026		0.021	0.02		
100 Hz (50% rh)	0.110	0.145	0.35		0.200	0.15		>0.500
10^6 Hz (50% rh)	0.070	0.092	0.12		0.080	0.1		
refractive index (n^{D}) single crystals								
α(calc)	1.475				1.475			
β(calc)	1.565				1.525			
γ(obs)	1.58				1.565			
moldings	1.53	1.53			1.53			

[a] All data from Ref. 127 unless indicated otherwise.

[b] From trade literature.

[c] T = triclinic; M = monoclinic; and H = hexagonoal.

[d] To convert J to cal, divide by 4.184.

Table 10. Producers[a] of Polyamides by Region

Producer	Manufacturing facilities[b]	Principal polymer types
	North and South America	
AlliedSignal	U.S. Eur	6 and amorphous
Amoco	U.S.	6,T/6,I/6,6 and 6,T/6,6
Cookson Fibers	U.S.	6 and 6,6 fibers
Du Pont	NA, Eur, A/P, SA	6,6; 6,12; 6,T/D,T; aramids; 6; and amorphous
Fairway Filamentos[c]	SA	6,6
Hoechst-Celanese	U.S.	6,6 resins
Mohawk	U.S.	6 carpet fibers
Monsanto	U.S., A/P	6,6; 6,9; and 6,10
Shaw Industries	U.S.	6 carpet fibers
	Europe, Middle East, and Africa	
Akzo	Eur, U.S., SA, India	6; 6,6; and aramid
Aqualon	Italy	6
BASF	Eur, NA	6,6; 6; 6,10; and 6,T/6
Bayer	Eur	6 and amorphous
Beaulieu	Eur, U.S., Africa	6 carpet fiber
Chimvolorno (Grodno)	Belarus	6
DSM	Netherlands	6; 6,6; 4,6; and 6/12
Elf Atochem	France	11; 12; 6; 6,6; and amorphous
EMS	Switzerland, U.S.	6; 12; and amorphous
Hüls	Germany	6/12; 12; and TMD,T
Nilit	Israel	6,6
Radici	Italy	6 and 6,6
Rhône-Poulenc	Eur, SA, A/P	6,6; 6; and 6,10
RP-Snia Joint Ventures	Eur	6
SANS	South Africa	6,6
Snia	Italy	6 films
Stilon	Poland	6
	Asia/Pacific	
Asahi	A/P	6,6 and 6
Chung Shing	Taiwan	6
Formosa Chem. & Fiber Co.	Taiwan	6,6 and 6
Hualon	Taiwan	6
Kanebo	Japan	6

Table 10. *Continued*

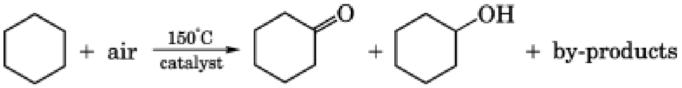
Producer	Manufacturing facilities[b]	Principal polymer types
Kohap	Korea	6
Kolon	Korea	6,6
Liaoyiang	China	6,6
Mitsubishi Gas	Japan	MXD/6
Mitsui	Japan	6,T/6,I and 6,T/6,6
PT Branta Mulia	Indonesia	6,6 fiber
Shen Ma (Pingdingshan)	China	6,6
Shri Ram	India	6
Tae Kwang	Korea	6,6
Teijin	Japan	aramids
Teijin–Du Pont joint venture	Japan	6 to 6,6[d]
Tong Yang	Korea	6
Toray	A/P	6; 6,6; 6,10; and 12
Toray–Du Pont joint venture	Japan	aramid
Toyobo	Japan	6
Ube	Japan	6; 6,6; and 12
Unitika	Japan	6

[a] There are many smaller facilities producing nylon-6,6 and especially nylon-6.
[b] United States (U.S.), Europe (Eur), North America (NA), South America (SA), and Asia/Pacific (A/P).
[c] Joint venture of Hoechst-Rhodia.
[d] The polymer base is being converted from nylon-6 to nylon-6,6.

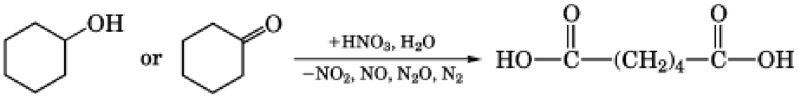
6.1.1. Ingredients

Nylon-6,6 is made from the reaction of adipic acid [124-04-9] and hexamethylenediamine [124-09-4]. The manufacture of intermediates for polyamides is extremely important; not only is the quality of the polymer, such as color, degree of polymerization, and linearity, strongly dependent on the ingredient quality, but also the economic success of the producer is often determined by the yields and cost of manufacture of the ingredients.

Adipic acid(qv) has a wide variety of commercial uses besides the manufacture of nylon-6,6, and thus is a common industrial chemical. Many routes to its manufacture have been developed over the years but most processes in commercial use proceed through a two-step oxidation of cyclohexane [110-83-8] or one of its derivatives. In the first step, cyclohexane is oxidized with air at elevated temperatures usually in the presence of a suitable catalyst to produce a mixture of cyclohexanone [108-94-1] and cyclohexanol [108-93-0], commonly abbreviated KA (ketone–alcohol) or KA oil:



In the second step, KA is further oxidized by nitric acid [7697-37-2] to adipic acid, which is separated, purified usually through crystallization, and dried (see Adipic acid).



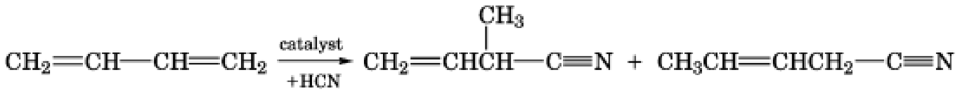
Virtually all the hexamethylenediamine manufactured is used captively in the production of nylon-6,6, with a small amount being used to produce diisocyanates. It is produced via the reduction of adiponitrile

[111-69-3] (ADN):

$$N\equiv C(CH_2)_4C\equiv N + 4\,H_2 \xrightarrow{\text{catalyst}} H_2N(CH_2)_6NH_2$$

The highly exothermic reduction reaction is generally carried out in either a high or low pressure process (128). In the high pressure process, an iron or cobalt catalyst is used at 20–35 MPa (3000–5000 psi) and a temperature of 100–150°C. The low pressure process uses a Raney nickel catalyst containing iron or chromium activated by sodium or potassium hydroxide in solution and operates at a pressure of 2–3.5 MPa (300–500 psi) and a temperature of 60–100°C (Raney is a registered trademark of W. R. Grace Co.). Although the temperature and pressure ranges are substantially reduced in the low pressure process and thus the capital investment is also reduced, the productivity is lower and the catalyst costs are higher than for the high pressure processes.

There are three commercial routes to ADN in use. The first method, direct hydrocyanation of 1,3-butadiene [106-99-0], has replaced an older process, cyanation via reaction of sodium cyanide with 1,4-dichlorobutane [110-56-5] owing to the lower cost and fewer waste products of the new process. During the initial steps of the direct hydrocyanation process, a mixture of two isomers is generated, but the branched isomer is readily converted to the linear 3-pentenenitrile [4635-87-4].



$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[+HCN]{\text{catalyst}} CH_2{=}CH\overset{CH_3}{\overset{|}{C}}H{-}C\equiv N + CH_3CH{=}CHCH_2{-}C\equiv N$$

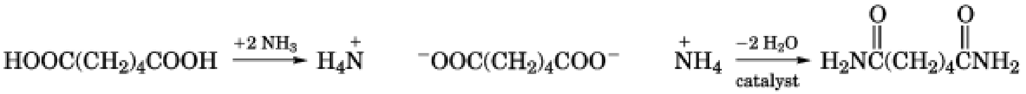
In the final step the dinitrile is formed from the anti-Markovnikov addition of hydrogen cyanide [74-90-8] at atmospheric pressure and 30–150°C in the liquid phase with a Ni(0) catalyst. The principal by-product, 2-methylglutaronitrile[4553-62-2], when hydrogenated using a process similar to that for the conversion of ADN to hexamethylenediamine, produces 2-methyl-1,5-pentanediamine or 2-methylpentamethylenediamine [15520-10-2] (MPMD), which is also used in the manufacture of polyamides as a comonomer.

In the second method to produce ADN, known as electrohydrodimerization, two moles of acrylonitrile [107-13-1] are combined and hydrogenated in an electrochemical cell where the two half-cells are separated by a membrane.

$$2\,CH_2{=}CH{-}C\equiv N \xrightarrow{+2\,e^-} 2\,CH_2{=}CH{-}C\equiv \overset{\cdot}{N}^- \xrightarrow[-2\,OH^-]{+2\,H_2O} N\equiv C(CH_2)_4C\equiv N$$

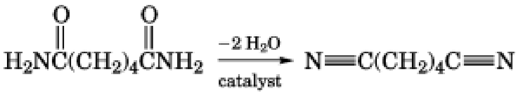
In the second-generation process a membrane is not needed to separate the two half-cell reactions; instead, a finely divided, two-phase emulsion consisting of an organic phase containing acrylonitrile is used, and ADN is suspended in the aqueous phase containing Na_2HPO_4 [13708-85-5], a tetraalkylammonium salt, and acrylonitrile (qv). The electrodes can be graphite and magnetite, or, more recently, cadmium and iron (129, 130).

In the third method adipic acid is converted to ADN via dehydroamination with NH_3 in the gas (131) or liquid phase (132); a dehydration catalyst, usually phosphoric acid, is used.



$$HOOC(CH_2)_4COOH \xrightarrow{+2\,NH_3} H_4\overset{+}{N}\quad {}^-OOC(CH_2)_4COO^-\quad \overset{+}{N}H_4 \xrightarrow[\text{catalyst}]{-2\,H_2O} H_2N\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}NH_2$$

The diamide intermediate is dehydrated to form the dinitrile.



$$H_2N\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow[\text{catalyst}]{-2\,H_2O} N{\equiv}C(CH_2)_4C{\equiv}N$$

This same method, followed by hydrogenation, is also used to produce the C-12 and C-13 diamines from the corresponding diacids in the production of nylon-12,12 and nylon-13,13.

6.1.2. Polymer Production

Three processes are used to produce nylon-6,6. Two of these start with nylon-6,6 salt, a combination of adipic acid and hexamethylenediamine in water; they are the batch or autoclave process and the continuous polymerization process. The third, the solid-phase polymerization process, starts with low molecular weight pellets usually made via the autoclave process, and continues to build the molecular weight of the polymer in a heated inert gas, the temperature of which never reaches the melting point of the polymer.

Nylon-6,6 salt, hexamethylenediammonium adipate [3323-53-3], is made by adding adipic acid to a solution of hexamethylenediamine in water (133). The diamine is usually stored at approximately 85% concentration in water to keep it in the liquid state for ease of handling and blanketed with an inert gas, N_2, to prevent oxidation and color formation. The diamine is diluted further before reaction so that the final concentration of salt is about 50%. To this solution a slight excess of diacid is added and thoroughly dissolved and neutralized; then, in a second reactor, the remaining diamine is added to reach the desired stoichiometric balance. The end point is determined very accurately via pH measurement on a diluted sample. In the past the salt solution was then filtered through activated charcoal to remove color and impurities, but in the 1990s the quality of the starting materials and the degree of process control have eliminated the need for this step. This salt solution is held under inert gas until it is sent to the polymerization process. The dilution of the ingredients and exothermic heat of reaction (110 kJ/mol (26.4 kcal/mol)) (134) generate substantial heat, which can be recovered and used in other steps in the process.

If dry salt is to be isolated from solution, it can be precipitated by the addition of methanol [67-56-1], washed, filtered, and dried, since its solubility in alcohol is low (0.4% at 25°C) (135). An alternative method has been developed to produce dry salt in a continuous process using a saturated nylon-6,6 salt solution from which the solid salt can be precipitated by adjusting the temperature and concentration (136). Adipic acid is dissolved in a recycled, saturated aqueous solution of nylon salt at approximately 60°C under nitrogen. When diamine is added as an 85% aqueous solution, additional salt is formed, most of which precipitates out of solution, and the temperature rises. The mixture is cooled, which precipitates the maximum amount of salt. This is separated by centrifuging the slurry; the isolated salt is then washed and dried. The mother liquor is reheated and recycled. Dry salt is quite stable; it can be used to transport ingredients for nylon-6,6 over long distances, and does not require an inert atmosphere to prevent degradation. However, it is never used internally for the production of nylon-6,6, because the pure diacid–diamine or salt solution has a lower manufacturing cost.

In the first step of the autoclave process, the salt solution is concentrated to about 75% by boiling in a vessel commonly referred to as an evaporator. The heat contained in the steam generated in this step can be recovered in a heat exchanger and used elsewhere in the process. After the salt is concentrated, it is fed into an autoclave, which is a large and sometimes stirred pressure vessel, where the polymerization takes place. Often additives, such as TiO_2, stabilizers, etc, are injected at this point in the process. During the polymerization, the temperature and pressure are adjusted to control the loss of diamine and to release steam (137). In the first step of the autoclave cycle the vessel is closed and the temperature is raised, which allows the pressure to increase to 1.75 MPa (250 psig). During this step, most of the diamine and diacid react to form oligomers. After the boiling mass is held at pressure for a time sufficient for the reaction to come to equilibrium (138), the excess steam is vented and the polymerization reaction proceeds to build molecular weight. As a result of the equilibrium between the bound and unbound diamine, some free diamine is lost with the exiting steam owing to its low boiling point, but it can be recovered and recycled. In the final step, the temperature is raised to 275°C while the pressure is held at atmospheric pressure. The polymerization then approaches equilibrium. An additional vacuum finishing step can be added if still higher molecular weight polymer is desired; however, this process step can lead to complications such as discoloration resulting from oxidation introduced from the atmosphere via vacuum leaks, thermal degradation from the longer time at high temperature, and difficulty in draining the polymer mass from the vessel owing to the higher viscosity achieved. After polymerization is completed, the polymer is drained from the autoclave through a die which forms a series of continuous polymer strands. These are fed into a casting machine that cools and solidifies the polymer in water, cuts it into small cylindrical pellets, and separates the pellets from the water. The pellets are then dried and stored for further processing or sale. The advantages of the autoclave process are relatively low capital investment, flexibility, and relatively simple operation. The disadvantages are low throughput, high labor costs, variation of polymer properties through the batch and from batch to batch, and difficulty in obtaining high molecular weight polymer.

The continuous polymerization (CP) process was invented to solve the limitations inherent in the batch process. The process makes use of several vessels through which the polymeric material flows while it grows in molecular weight (139–141). In a modern CP unit, nylon salt is introduced into the first vessel, which functions much like an evaporator to concentrate the salt solution. It is then fed into the bottom of a pressurized column reactor, where the initial polymerization reaction takes place. The column allows the steam that is produced as a by-product to be removed without the loss of hexamethylenediamine. After a suitable residence time, higher molecular weight polymer is produced and then pumped into the flasher, a vessel designed to lower the pressure of the polymer mass while steam escapes from the polymer. Flow through the flasher is quite complex because there are two phases with decreasing pressure and increasing temperature. From the flasher the polymer enters the separator at a pressure slightly above atmospheric and at a temperature of approximately 275°C. In the separator, water vapor is separated from the polymer, which has reached about 98% of reaction. The polymer is then pumped into the vacuum finisher, which maintains the pressure at about 40 kPa (300 mm Hg). The final degree of polymerization is completed in the finisher. The final polymer is pumped from the bottom of the finisher and sent directly to a spinning machine or to a die for pelletizing. Additives addition can be made at various points along the CP process such as in the initial salt, the flasher, or after the finisher. The advantages of the CP are high, continuous throughput, uniform polymer properties, and the ability to produce high molecular weight and low cost, high volume polymer. Its disadvantages are high capital investment and complex operation and maintenance.

An alternative route to high molecular weight polymer is the solid-phase polymerization (SPP) process (142). There are two basic types of SPP process: batch and continuous. The batch process is little more than a rotary dryer operating at a higher temperature under a flowing atmosphere of controlled-moisture inert gas. In the continuous SPP process, pellets are introduced into a holding vessel where they are slowly heated to about 100°C under nitrogen. In this step, most of the atmospheric oxygen absorbed by the pellets during formation and storage is removed, and the pellets are dried to a uniform, initial moisture level. The pellets are then fed into the SPP vessel, which is a large, vertical plug-flow reactor with a counterflow of hot nitrogen gas. The moisture level is adjusted in the hot gas to control the final moisture level in the pellets and the rate of polymerization. Typical reactor conditions are a temperature of 150–200°C and a holdup time of 6–24 h. The finished pellets are removed at the bottom of the reactor and can be sent directly to an extruder for spinning or compounding, or to a cooler and then packaged or stored for future sale. An important component of an SPP reactor, whether batch or continuous, is the gas recycle loop. Because large quantities of nitrogen are needed, recycling the gas is essential. As the gas leaves the top of the reactor it contains added moisture and organic materials, mostly cyclic oligomers, which must be removed before the gas is reused. After the gas is scrubbed, the moisture level must be readjusted and the gas reheated to the level required in the process.

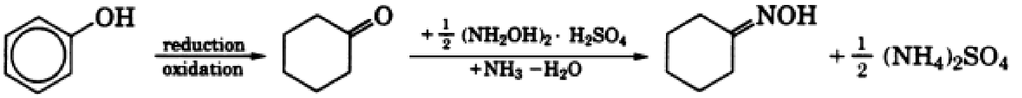
The SPP process has the advantage of being able to produce polymer of very high molecular weight without increasing the thermal degradation of the polymer. Although this is useful for nylon-6,6, it can be essential for other types of polyamides that cannot be processed in the melt phase owing to thermal degradation, eg, many aromatic-containing polyamides. Unfortunately, this is done at the cost of long holdup times in the continuous process or a slow processing step in batch processing. In addition, thermooxidative damage is always increased in the polymer along with the accompanying increase in yellow color, because oxygen can never be completely excluded from the reactor at a practical cost. Another disadvantage is the additional capital investment above that needed for autoclaves or CP units.

6.2. Nylon-6

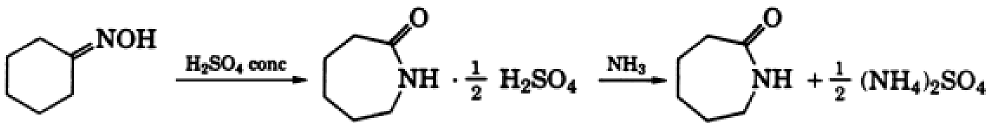
Nylon-6 [25038-54-4] was first made in 1899 by heating 6-aminohexanoic acid (143), but its commercially feasible synthesis from caprolactam was discovered by Paul Schlack at I. G. Farbenindustrie in 1938. Like nylon-6,6, it is a tough, white translucent, semicrystalline solid, but melts at a lower temperature ($T_m = 230$°C. The physical properties and primary producers of nylon-6 are listed in Tables 9 and 10, respectively.

6.2.1. Ingredients

Nylon-6 is produced commercially from caprolactam [105-60-2], which is the most important lactam industrially. All industrial production processes for caprolactam are multistep and produce ammonium sulfate [7783-20-2] or other by-products. Approximately 95% of the world's caprolactam is produced from cyclohexanone oxime [100-64-1] via the Beckmann rearrangement (144). The starting material for cyclohexanone can be cyclohexane, phenol [108-95-2] (eq. **18**), or benzene [71-43-2]. Then, through a series of reductions (for the aromatic starting materials) and oxidations, cyclohexanone is formed. This cyclic ketone then reacts with a hydroxylamine salt, usually the sulfate, to form the oxime and ammonium sulfate. The oxime is rearranged in concentrated sulfuric acid, and the resulting lactam sulfate salt is hydrolyzed to form caprolactam and more ammonium sulfate (eq. **19**).



(18)



(19)

An additional mole of ammonium sulfate per mole of final lactam is generated during the manufacture of hydroxylamine sulfate [10039-54-0] via the Raschig process, which converts ammonia, air, water, carbon dioxide, and sulfur dioxide to the hydroxylamine salt. Thus, a minimum of two moles of ammonium sulfate is produced per mole of lactam, but commercial processes can approach twice that amount. The DSM/Stamicarbon HPO process, which uses hydroxylamine phosphate [19098-16-9] in a recycled phosphate buffer, can reduce the amount to less than two moles per mole of lactam. Ammonium sulfate is sold as a fertilizer. However, because H_2SO_4 is released and acidifies the soil as the salt decomposes, it is a low grade fertilizer, and contributes only marginally to the economics of the process (145, 146) (see Caprolactam).

6.2.2. Polymer Production

Commercially the ring-opening polymerization of caprolactam to nylon-6 is accomplished by both the hydrolytic and anionic mechanisms. However, the hydrolytic process is by far the most predominantly used method because it is easier to control and better adapted for large-scale production. Like nylon-6,6, the polymerization process for nylon-6 via the hydrolytic mechanism can be batch or continuous; however, the processes for the two polymers are significantly different. The hydrolytic process for nylon-6 contains the following steps: caprolactam and additives addition, hydrolysis, addition, condensation, pelletizing (for remelt processing), leaching/extraction of monomers, drying, and packaging (for pellet sales) (147). Caprolactam is usually handled as a molten liquid because its melting point is 69°C and it can be melted with hot water. Increasingly caprolactam is being shipped as a molten liquid vs a dried solid for ease of handling. When delivered as a solid, it is melted and fed into the first step of the process as a liquid.

Batch processing of nylon-6 is generally used only for the production of specialty polymers such as very high molecular weight polymer or master batch polymers for special additives. In a typical modern batch process (147–150), the caprolactam is mixed in a holding tank with the desired additives and then charged to an autoclave with a small amount (2–4%) of water. During the two-stage polymerization cycle, the temperature is raised from 80 to 260°C. In the first stage, water is held in the reactor, the pressure rises, and the hydrolysis and addition steps occur. After a predetermined time the pressure is releasedand the final condensation reaction step occurs. The molecular weight of the polymer can be increased by means of a vacuum finishing step, if desired. The entire process can take three to five hours. The final polymer is then drained, often with a forcing pressure of inert gas, through a die to form ribbons of polymer, which are then cooled in water and cut into pellets. Because nylon-6 has such a high monomer and oligomer content, 10–12% by weight, in the cast pellets, which would significantly reduce the quality of the final fiber or resin products, it must be extracted. This is usually done in hot water under pressure at 105–120°C for 8–20 h. Most of the caprolactam and higher oligomers that are released with the steam from the autoclave or extracted from the pellets in hot water are then recycled. The pellets must be carefully dried because excess water decreases the molecular weight of the polymer during subsequent melt processing. The final polymer processed through water extraction and drying can have an oligomer level of $<0.2\%$ and a moisture level of $<0.05\%$. A low level of total oligomers is necessary because on remelting and further processing, the oligomers' content will increase owing to the reestablishment of the equilibrium distribution of molecular species that occurs for all condensation polymers (151). Because the approach to equilibrium progresses at a moderate rate, it is possible to utilize extracted nylon-6 in a remelt process without increasing the oligomer concentration above 2–3% and thus avoiding any significant drop in final properties.

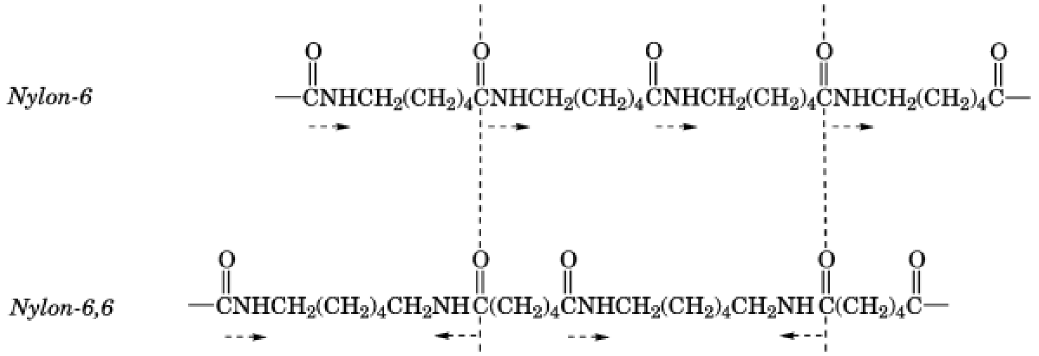
In the continuous polymerization process for nylon-6 the three steps of polymerization can be made to take place in a series of connected vessels or in a single long, vertical, tubular reactor, sometimes referred to as the VK tube (147–150, 152). There are many variations and proprietary reactor designs for the continuous process. However, the purpose of the various configurations is the same as in the batch process; first, to provide water-rich reaction media to accelerate hydrolysis and the initial coupling of the monomers; and then to provide a low water environment for the polycondensation reaction to approach equilibrium. The polymer can be cast and cut into pellets in a continuous pelletizing and drying operation similar to the batch process. However, a continuous, vacuum-stripping step can be applied to remove much of the caprolactam while the nylon-6 is still in the melt; the polymer can then be spun directly into fiber or cast into resin. The oligomer content in this case is 2–3%; and, when this level of oligomers is acceptable, the advantage of the lower cost for vacuum stripping can be attained by eliminating the water quench, extraction, drying, and remelt steps.

In order to attain higher molecular weight polymer, nylon-6 can also be polymerized in the solid phase in a manner similar to that used for nylon-6,6. The same advantages and disadvantages arise in the case of nylon-6, except that one additional difficulty occurs for nylon-6 from the presence of residual caprolactam. Since the temperature range of the SPP process is 140–170°C, the residual lactam is a liquid or vapor in the reactor. As a liquid it can collect on the surface of the pellets and reactor walls, which causes the pellets to stick together or to the walls, thus impeding their uniform flow through the SPP reactor. More vapor-phase oligomers can collect in the gas recycle loop.

Anionic polymerization is also used in commercial processing, but not for fiber production. By casting the rapidly polymerizing polymer or using reaction injection molding (RIM), stock or custom-shaped bulk polymer items can be fabricated directly (153). The stock shapes can be readily machined to the desired finished item; or, in the case of large production runs, the RIM process can produce directly the finished shape in a mold. However, much after-processing is required in the RIM-cast articles. In a typical casting process, sodium lactamide is generally used as the catalyst, and either hexamethylene diisocyanate [822-06-0] (HDI) or imidodicarbonic diamide [4035-89-6], a biuret derivative of HDI, is used as the activator. Anionic polymerization is essentially a direct monomer-to-finished item process. Two streams of caprolactam, one containing the catalyst and the other containing the activator, are mixed and then fed into a heated mold. The rate of reaction and the process temperatures are adjusted to reduce the buildup of internal stresses as the polymer reacts and cools. The finished parts can be annealed at 100–120°C for 8 h to further relieve the stresses. Anionic polymerization is usually practiced commercially below the melting point of nylon-6, at approximately 160°C. An interesting consequence of this is that the concentration of residual caprolactam is only about 2% in the final nylon-6; this is significantly below what would be expected from the extrapolated concentration as a function of temperature in the melt, ie ~7% (154). Thus, the oligomers do not need to be extracted from the bulk plastic articles, which makes this process economically feasible. Another interesting feature of anionic polymerization is its ability to produce block copolymers. Because of the two ingredient streams and the low processing temperature, it is possible to blend and react caprolactam with a prepolymer, such as modified polyols, and randomization is avoided. Thus, block copolymer plastics can be produced that might be impossible in the melt at 250°C. Random copolyamides can also be made by blending and reacting capro- and laurolactams to make nylon-6-*co*-nylon-12.

6.3. Comparison of Nylon-6,6 and Nylon-6

Nylon-6,6 and nylon-6 have competed successfully in the marketplace since their respective commercial introductions in 1939 and 1941, and in the 1990s share, about equally, 90% of the total polyamide market. Their chemical and physical properties are almost identical, as the similarity of their chemical structure might suggest: the amide functions are oriented in the same direction along the polymer chain for nylon-6, but are alternating in direction for nylon-6,6.



$$\text{—}\overset{\overset{\displaystyle O}{\|}}{C}NHCH_2(CH_2)_4\overset{\overset{\displaystyle O}{\|}}{C}NHCH_2(CH_2)_4\overset{\overset{\displaystyle O}{\|}}{C}NHCH_2(CH_2)_4\overset{\overset{\displaystyle O}{\|}}{C}NHCH_2(CH_2)_4\overset{\overset{\displaystyle O}{\|}}{C}\text{—}$$

$$\text{—}\overset{\overset{\displaystyle O}{\|}}{C}NHCH_2(CH_2)_4CH_2NH\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_4\overset{\overset{\displaystyle O}{\|}}{C}NHCH_2(CH_2)_4CH_2NH\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_4\overset{\overset{\displaystyle O}{\|}}{C}\text{—}$$

Table 9 shows the similarity of properties; however, a few differences between the two polyamides do exist: in melting point, in ingredients preparation, and in polymer manufacturing. The melting point of nylon-6,6 is about 40°C higher than that for nylon-6. This is an advantage for nylon-6,6 in those end uses where high temperature performance is required, such as under-the-hood applications for automobiles, high speed thermal processing of fibers and films, and high temperature fatigue resistance in industrial tire cords (qv). On the other hand, the lower processing temperatures for nylon-6 result in slightly lower energy costs and could potentially permit the use of some additives which would decompose at the higher temperatures necessary for processing nylon-6,6. Nylon-6 appears to have a definite advantage in ingredients preparation because it requires the capital investment and handling costs for only one monomer, whereas nylon-6,6 requires the same for two monomers. However, the added cost of ammonium sulfate production, handling, and sales increases the cost of caprolactam production. Also hexamethylenediamine is increasingly being made from three- or four-carbon petroleum-based hydrocarbons vs higher cost six-carbon feedstocks for caprolactam (and adipic acid). In general, the nylon-6,6 ingredients are made in very large plants by a few producers, which allows for substantial economy-of-scale. This has an unexpected consequence for the relative growth of the two polymers. Although caprolactam and adipic acid are commodity chemicals, hexamethylenediamine is not, since almost its entire world production is consumed internally to produce nylon-6,6. Thus nylon-6 can be made from its monomer, purchased on the open market without the investment in an ingredients facility, whereas nylon-6,6 cannot. This probably accounts for the growth of nylon-6 in such developing areas as Asia/Pacific.

Finally, there are significant differences in polymer production. Nylon-6 requires the extraction of caprolactam and other oligomers, which increases the capital investment as well as operating costs in polymerization. On the other hand, nylon-6,6 is plagued with a propensity to branch and gel when exposed to the required higher processing temperatures for extended periods of time. Proper management of gel deposits in nylon-6,6 manufacturing and processing steps in order to maintain high polymer quality requires skill and experience, which undoubtedly adds to its overall costs. Finally, nylon-6,6 can be readily processed from ingredients to final polymer in 2 h, whereas nylon-6 takes 12–24 h.

The two polymers appear to be well balanced, and future competitive pressure will almost assuredly come not from each other, but rather from other polyamides and, even more likely, from other polymers, such as low cost polyolefins and polyesters or high performance engineering resins.

7. Other Aliphatic Nylons

7.1. Nylon-4,6

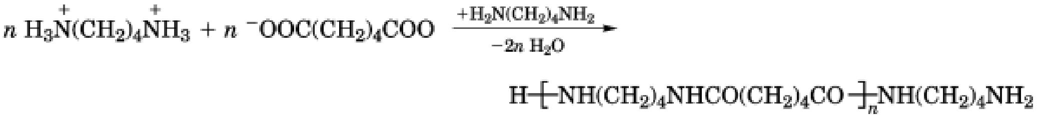
In the 1980s, Dutch State Mines (DSM) introduced a new commercial aliphatic polyamide, nylon-4,6 [50327-22-5] (155). This polymer was first studied by Carothers in the 1930s but was dropped, presumably the result of difficulties in obtaining a high molecular weight and the presence of substantial color formation resulting from degradation. In order to commercialize this polymer, DSM had to overcome this difficulty and the lack of a low cost supply of the diamine, tetramethylenediamine [110-18-9]. DSM developed a two-step process to produce the diamine, in the first of which acrylonitrile and HCN are combined, with triethylamine [121-44-8] (TEA) as the catalyst (156). The second step entails hydrogenation of the dinitrile, which is similar to the process used to produce hexamethylenediamine for nylon-6,6.

$$CH_2{=}CHC{\equiv}N + HCN \xrightarrow{TEA} N{\equiv}C(CH_2)_2C{\equiv}N \xrightarrow[+4\ H_2]{catalyst} H_2N(CH_2)_4NH_2$$

The second difficulty, degradation, required the development of a two-step polyamidation process following salt formation (157). During salt formation, tetramethylenediammonium adipate salt is formed in water solution at approximately 50% concentration or at a higher concentration in a suspension. As in nylon-6,6 manufacture, this salt solution, when diluted, permits easy adjustment of the stoichiometry of the reactants by means of pH measurement.

$$H_2N(CH_2)_4NH_2 + HOOC(CH_2)_4COOH \xrightarrow{H_2O} H_3\overset{+}{N}(CH_2)_4\overset{+}{N}H_3 + {}^{-}OOC(CH_2)_4COO^{-}$$

In the first step of the polymerization process, a prepolymer is prepared as a slurry in water. Excess diamine is added to control the degree of polymerization, eg, degree of polymerization = 6 – 14 (158). This prepolymerization step is conducted at approximately 200°C under autogenous pressure for less than 90 min.



$$n\,H_3\overset{+}{N}(CH_2)_4\overset{+}{N}H_3 + n\,{}^{-}OOC(CH_2)_4COO \xrightarrow[-2n\,H_2O]{+H_2N(CH_2)_4NH_2} H\left[NH(CH_2)_4NHCO(CH_2)_4CO\right]_n NH(CH_2)_4NH_2$$

The prepolymer is separated from the water by spray drying and then formed into cylindrical pellets of uniform size (159). At this point additives can be added to the porous pellets from solution or suspension. These pellets are then placed in a solid-phase condensation reactor where they are heated to 260°C for up to 4 h under nitrogen, with a small amount of water added. The pressure is maintained close to atmospheric pressure. At the end, $x > n$.

$$H\left[NH(CH_2)_4NHCO(CH_2)_4CO\right]_n NH(CH_2)_4NH_2 \longrightarrow H\left[NH(CH_2)_4NHCO(CH_2)_4CO\right]_x NH(CH_2)_4NH_2$$

The use of preformed pellets of uniform size is important because the rate of solid-phase polymerization and thus the uniformity of the degree of polymerization is dependent on particle size. This is especially important for nylon-4,6 because the polymer is not held in the melt long enough for transamidation to establish a uniform molecular weight distribution, owing to the sensitivity of nylon-4,6 to thermal degradation. The excess diamine is removed from the nitrogen stream and recycled. The pellets of high molecular weight nylon-4,6 exit the solid-phase reactor and are cooled and stored under nitrogen. Although this manufacturing process effectively minimizes any thermal degradation damage during polymer production, downstream melt-processing, such as injection molding or fiber spinning, requires increased care over what is necessary for nylon-6 or nylon-6,6, so as to avoid extended periods in the melt where further degradation damage could occur.

Nylon-4,6 has a high melting temperature ($T_m = 295°C$), high crystallinity, and a much faster crystallization rate, ie, four to eight times faster than that for nylon-6,6. As an unfilled plastic, nylon-4,6 has a high tensile strength, 80 MPa (12,000 psi), compared to 55–65 MPa (8250–9750 psi) for other polyamides; when filled with 30% glass, it has a heat deflection temperature of 285°C, vs 190–240°C for most other polyamides (160). Its dielectric properties have been well documented (161). All these properties make nylon-4,6 a good candidate for high temperature applications and end uses that require good resistance to impact and abrasion. Nylon-4,6 has been studied for fiber applications (162) and as tire cord it is claimed to be 30% better than nylon-6,6 in flat-spot index measurements, which is even better than polyester in this test (155). Besides its limited stability in the melt phase, its other significant drawback as an engineering plastic is its high moisture regain. Copolymers of nylon-4,6 with terephthalic acid, caprolactam, and nylon-6,10 have also been prepared (163–165).

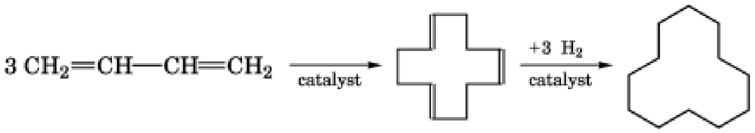
7.2. Nylon-6,9, Nylon-6,10, and Nylon-6,12

These related polyamides are produced in a process similar to that used for nylon-6,6, where a salt of hexamethylenediamine and the appropriate diacid is formed in water. The solution is heated in an autoclave until polymerization is complete. Processing times, pressures, and temperatures are adjusted for the slightly different melting points and viscosities of these polymers. Because of the lower melting points, ie, nylon-6,9 ($T_m = 210°C$), nylon-6,10 ($T_m = 220°C$), and nylon-6,12 ($T_m = 212°C$), and the perhaps greater chemical stability of the diacids, these polymers generally experience less thermal degradation in processing than nylon-6,6. They are generally used as engineering resins for specialty applications where reduced moisture regain and chemical resistance are important. Nylon-6,12 [24936-74-1] and its copolymers are also used in the manufacture of toothbrush bristles and fishing line.

The diacids for these polymers are prepared via different processes. Azelaic acid [123-99-9] for nylon-6,9 [28757-63-3] is generally produced from naturally occurring fatty acids via oxidative cleavage of a double bond in the 9-position, eg, from oleic acid [112-80-1]:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow{+2\ O_2} HOOC(CH_2)_7COOH + CH_3(CH_2)_7COOH$$

The by-product of this process, pelargonic acid [112-05-0], is also an item of commerce. The usual source of sebacic acid [111-20-6] for nylon-6,10 [9008-66-6] is also from a natural product, ricinoleic acid [141-22-0] (12-hydroxyoleic acid), isolated from castor oil [8001-79-4]. The acid reacts with excess sodium or potassium hydroxide at high temperatures (250–275°C) to produce sebacic acid and 2-octanol [123-96-6] (166) by cleavage at the 9,10-unsaturated position. The manufacture of dodecanedioic acid [693-23-2] for nylon-6,12 begins with the catalytic trimerization of butadiene to make cyclododecatriene [4904-61-4], followed by reduction to cyclododecane [294-62-2] (see Butadiene). The cyclododecane is oxidatively cleaved to dodecanedioic acid in a process similar to that used in adipic acid production.



7.3. Nylon-11

Nylon-11 [25035-04-5], made by the polycondensation of 11-aminoundecanoic acid [2432-99-7], was first prepared by Carothers in 1935 but was first produced commercially in 1955 in France under the trade name Rilsan (167); Rilsan is a registered trademark of Elf Atochem Company. The polymer is prepared in a continuous process using phosphoric or hypophosphoric acid as a catalyst under inert atmosphere at ambient pressure. The total extractable content is low (0.5%) compared to nylon-6 (168). The polymer is hydrophobic, with a low melt point ($T_m = 190°C$), and has excellent electrical insulating properties. The effect of formic acid on the swelling behavior of nylon-11 has been studied (169), and such a treatment is claimed to produce a hard elastic fiber (170).

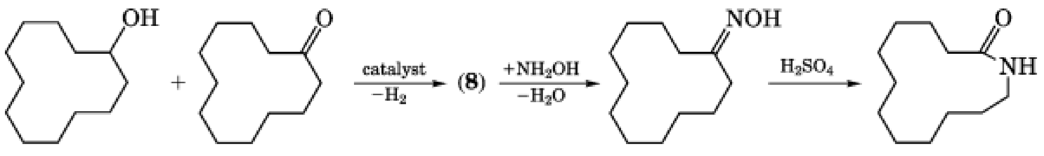
The starting amino acid for nylon-11 is produced from methyl ricinoleate [141-24-2], which is obtained from castor oil (qv). The methyl ricinoleate is pyrolized to methyl 10-undecylenate [25339-67-7] and heptanal [111-71-7]. The unsaturated ester is hydrolyzed and then converted to the amino acid by hydrobromination, followed by ammoniation and acidification. The ω-amino acid product is a soft paste containing water, which is dried in the first step of the polymerization process.

$$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOCH_3 \xrightarrow[-\text{heptanal}]{\Delta} CH_2{=}CH(CH_2)_8COOCH_3 \xrightarrow[-CH_3OH]{+H_2O}$$

$$CH_2{=}CH(CH_2)_8COOH \xrightarrow[\text{peroxide}]{+HBr} BrCH_2CH_2(CH_2)_8COOH \xrightarrow[-NH_4Br]{+2\ NH_3\ \text{acid}} H_2N(CH_2)_{10}COOH$$

7.4. Nylon-12

Laurolactam [947-04-6] is the usual commercial monomer for nylon-12 [24937-16-4] manufacture. Its production begins with the mixture of cyclododecanol and cyclododecanone which is formed in the production of dodecanedioic acid starting from butadiene. The mixture is then converted quantitatively to cyclododecanone via dehydrogenation of the alcohol at 230–245°C and atmospheric pressure. The conversion to the lactam by the rearrangement of the oxime is similar to that for caprolactam manufacture. There are several other, less widely used commercial routes to laurolactam (171).



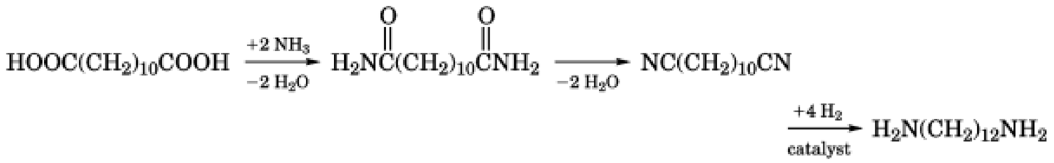
(8)

The mechanism for the production of nylon-12 from the lactam is similar to that for nylon. However, in the case of nylon-12, the ring opening is more difficult and the rate of polymerization is slower, at least in part owing to the lower solubility of the lactam in water. A catalyst such as an acid, amino acid, or nylon salt can serve as a ring-opening agent. Nylon-12 can also be produced via anionic polymerization, ie, polymerization using an anhydrous alkali catalyst. This process can be quite fast even at low temperatures, eg, a few minutes at 130°C.

The properties of nylon-12 compared to nylon-6 and nylon-6,6 include lower moisture regain, which gives it better electrical resistance and dimensional stability. It has a significantly lower melting point ($T_m = 178^\circ C$). The dielectric and dynamical mechanical properties have recently been studied in dry and water-saturated polymer (172, 173). When dry, it is less strong but retains its strength better in high relative humidity and subzero environments. It is less soluble in polar solvents, but more soluble in nonpolar ones. Because of these properties, it has found application in automotive, mechanical, and electrical parts; in food packaging (qv); and in other specialty polymer end uses.

7.5. Nylon-12,12

Nylon-12,12 [36497-34-4], [36348-71-7] was introduced into the marketplace by Du Pont in the late 1980s (174). This polymer possesses very low moisture absorption, high dimensional stability, and excellent chemical resistance, with a moderately high melt point ($T_m = 185^\circ C$) (175). Its manufacture begins with the formation of dodecanedioic acid produced from the trimerization of butadiene in a process identical to that used in the manufacture of nylon-6,12. The other starting material, 1,12-dodecanediamine, is prepared in a two-step process that first converts the dodecanedioic acid to a diamide, and then continues to dehydrate the diamide to the dinitrile. In the second step, the dinitrile is then hydrogenated to the diamine with hydrogen in the presence of a suitable catalyst.



$$HOOC(CH_2)_{10}COOH \xrightarrow[-2\,H_2O]{+2\,NH_3} H_2N\overset{O}{\overset{\|}{C}}(CH_2)_{10}\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow[-2\,H_2O]{} NC(CH_2)_{10}CN$$

$$\xrightarrow[\text{catalyst}]{+4\,H_2} H_2N(CH_2)_{12}NH_2$$

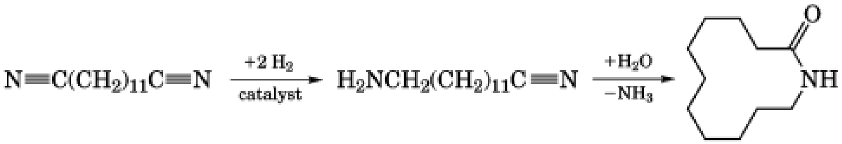
The polymerization process proceeds in a manner similar to that of other type AABB polyamides, such as nylon-6,6. The final resin had found application in automotive and other high performance end uses but was withdrawn from the market in 1994.

7.6. Nylon-13,13 and Nylon-13

The ingredients for nylon-13,13 [26796-68-9], [26796-70-3] and nylon-13 [14465-66-8], [26916-48-3] and their copolymers have become available in developmental quantities from a natural source, crambe and rapeseed oil (176). Erucic acid [112-86-7] is obtained in high yield approaching 50 wt % from the oil and oxidatively cleaved to produce the dicarboxylic acid, brassylic acid [505-55-2] and pelargonic acid:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH \longrightarrow HOOC(CH_2)_{11}COOH + CH_3(CH_2)_7COOH$$

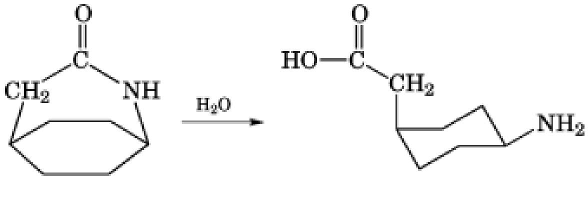
Then in a series of chemical transformations the diamine or lactam can be prepared from brassylic acid (177, 178). The diamine is formed as described above for the 12-carbon diamine, ie, diacid → diamide → dinitrile → diamine. The lactam is made from the dinitrile as follows.



The pelargonic acid by-product is already a useful item of commerce, making the overall process a commercial possibility. The 13-carbon polyamides appear to have many of the properties of nylon-11, nylon-12, or nylon-12,12: toughness, moisture resistance, dimensional stability, increased resistance to hydrolysis, moderate melt point, and melt processibility. Thus, these nylons could be useful in similar markets, eg, automotive parts, coatings, fibers, or films. Properties for nylon-13,13 are $T_g = 56°C$ and $T_m = 183°C$ (179).

8. Copolyamides and Mixed Aliphatic–Aromatic Polyamides

Copolymers of polyamides, when prepared in the melt or in solution or when held in the melt for a sufficient time, are usually fully randomized. Such random copolyamides generally show a decrease in melting point, slower rate and lower degree of crystallization, lower modulus, and a higher solubility than that of either homopolymer. The variation in melting point with a change in the relative composition of the two polymers shows a depression in melting point similar to the eutectic behavior observed for nonpolymeric compounds (180) (Fig. 8). However, there are select combinations of polyamides for which melting point increases monotonically with composition (Fig. 9). The monomers of these copolymers can replace each other isomorphically in their crystal lattices, and these copolymers are called isomorphic copolymers, ie, the monomers are sufficiently similar in their three-dimensional structure that they do not significantly distort the crystal lattice when one is replaced by the other. This effect was first observed in the nylon-6,6/6,*T* system (182) and in the nylon-6–poly(*endo*-ethylenecaprolactam) system (183).



endo-ethylenecaprolactam 4-aminocyclohexylacetic acid

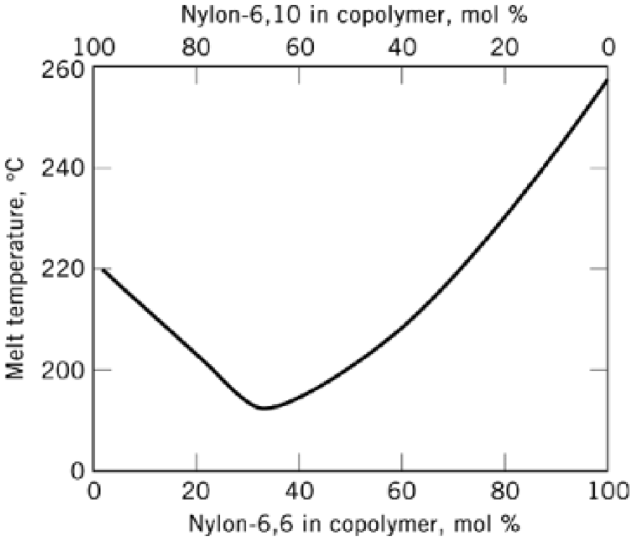


Fig. 8. Reduction in melting point for nylon-6,6/6,10 copolymers.

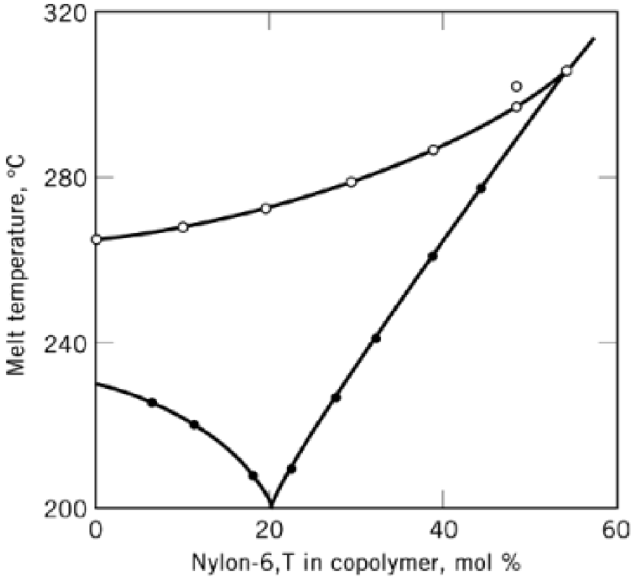


Fig. 9. Reduction in melting point for nylon-6,6/6,T (○) and nylon-6,10/6,T (●) copolymers (181).

Many combinations of diacids–diamines and amino acids are recognized as isomorphic pairs (184), for example, adipic acid and terephthalic acid or 6-aminohexanoic acid and 4-aminocyclohexylacetic acid. In the type AABB copolymers the effect is dependent on the structure of the other comonomer forming the polyamide; that is, adipic and terephthalic acids form an isomorphic pair with any of the linear, aliphatic C-6–C-12 diamines but not with *m*-xylylenediamine (185). It is also possible to form nonrandom combinations of two polymers, eg, physical mixtures or blends (Fig. 10), block copolymers, and strictly alternating (187, 188) or sequentially ordered copolymers (189), which show a variation in properties with composition differing from

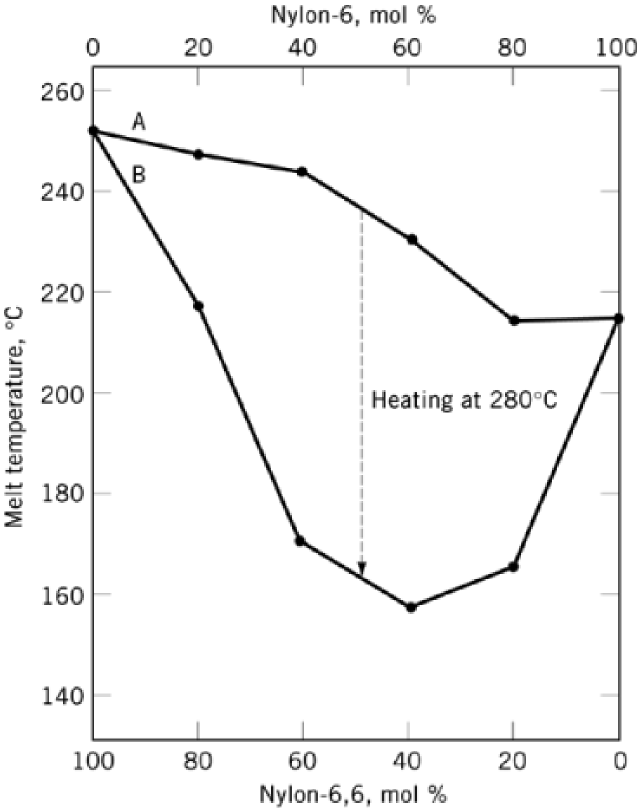


Fig. 10. Effect on melting point of varying composition of nylon-6,6 and nylon-6, where A represents a physical blend, and B, an equilibrated random copolymer (186).

those of the random copolymer. Such combinations require care in their preparation and processing to maintain their nonrandom structure, because transamidation introduces significant randomization in a short time above the melting point.

Because of the capacity to tailor select polymer properties by varying the ratio of two or more components, copolymers have found significant commercial application in several product areas. In fiber-spinning, ie, with copolymers such as nylon-6 in nylon-6,6 or the reverse, where the second component is present in low ($<10\%$) concentration, as well as in other comonomers with nylon-6,6 or nylon-6, the copolymers are often used to control the effect of spherulites by decreasing their number and probably their size and the rate of crystallization (190). At higher ratios, the semicrystalline polyamides become optically clear, amorphous polymers which find applications in packaging and barrier resins markets (191).

An emerging development is the introduction of high temperature polyamide resins for automotive, under-the-hood use and in some electrical end uses, such as cores for transformer windings. At first glance, nylon-6,T appears to be an excellent candidate, because it has a very high melting point (365°C) and its components, hexamethylenediamine and terephthalic acid, are low in cost and readily available. However, its high melting point requires even higher processing temperatures, which in turn lead to substantial thermal degradation. The attempt to produce copolymers with nylon-6 or nylon-6,6 in a melt process is thwarted by the formation of macroscopic portions of high melting blocks of nylon-6,T that can act as nucleating agents for spherulite (microscopic particles) formation, as particulate contamination (visible particles), and as nonmelting reactor

Table 11. High Temperature Polyamide Resins

Trade name[a]	Producer	Components	Melting point, °C
Amodel A-1000	Amoco	nylon-6,T/6,I/6,6	310
Super Amodel	Amoco	nylon-6,T/6,6	323
Ultramid T	BASF	nylon-6,T/6	295
Stanyl	DSM	nylon-4,6	295
Zytel HTN	Du Pont	nylon-6,T/D,T	300
Zytel 101	Du Pont	nylon-6,6	265
Arlen A	Mitsui	nylon-6,T/6,I	320
Arlen C	Mitsui	nylon-6,T/6,6	310

[a] Amodel is a registered trademark of Amoco Oil Co., Ultramid is a registered trademark of BASF, Stanyl is a registered trademark of DSM, Zytel is a registered trademark of Du Pont Co., Inc., and Arlen is a registered trademark of Mitsui Petrochemical Industries, Ltd.

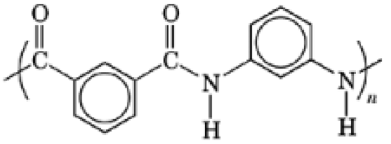
fouling (bulk material). In addition, when nylon-6,6 is blended with nylon-6,T, the required higher processing temperatures accelerate the rate of branching and gel formation to such an extent that the process is inoperable above 300°C. Since nylon-6,T and nylon-6,6 are isomorphic, they maintain a high degree of crystallinity in the copolymer, but when nylon-6 is used, its copolymer with nylon-6,T demonstrates the usual eutectic-like drop in melting point. Thus, a high ratio of nylon-6,T to nylon-6 is required to attain a significant increase in melting point. At high ratios, the copolymer can lose much of its crystallinity, but at a lower ratio it is still semicrystalline, and a satisfactory nylon-6,T/6 copolymer has been introduced by BASF. Amoco has introduced a proprietary process that allows the production of terephthalic acid-based copolymers which also contain isophthalic acid (192). These materials have been named polyphthalamides and show many desirable properties, such as a high melting point, high T_g, and low moisture regain (193).

Another approach to the production of high melting terephthalate-based copolyamides is first to make a low molecular weight prepolymer and then solid-phase the material to higher molecular weight; this process is similar in principle to that used in the manufacture of nylon-4,6. A variation of this process is used by Mitsui to produce its nylon-6,T/6,6 product, a copolymer of nylon-6,T and nylon-6,6 via a two-step process. First, an oligomer of the copolymer is made in an autoclave and spray-dried. The particles are then fed into an extruder, where the final copolymer is produced. A third approach, used by Du Pont, is to add a second diamine, 2-methylpentamethylenediamine (trade name Dytek A) rather than a second diacid to reduce the melting point (194, 195). This nylon-6,T/D,T copolymer is produced via an all-melt phase process in an autoclave. Although the resulting polymer has a high melt point, the process avoids the added cost of special process equipment and handling. Table 11 presents information on most of the high temperature resins that have been introduced into the marketplace; nylon-6,6 and nylon-4,6 are included for comparison.

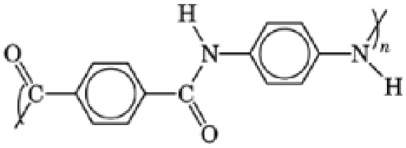
Two additional aromatic monomers have become commercially available for the production of polyamides: *m*-xylylenediamine and 2,6-naphthalenedicarboxylic acid. Mitsubishi Gas has introduced a nylon homopolymer, nylon-MXD,6, based on MXD and adipic acid under the trade name Reny (Reny is a registered trademark of Mitsubishi Gas Chemical Company, Inc.). Though the melting point of this polymer ($T_m = 243°C$) lies between those of nylon-6,6 and nylon-6, its glass-transition point is significantly higher, ie, $T_g = 102°C$ (dry), and it has lower water absorption (196). 2,6-Naphthalenedicarboxylic acid has been introduced by Amoco in development quantities for polyester and polyamide production. Several patents (197) and a publication (198) have appeared in regard to poly(hexamethylene naphthalamide) and nylon-6,N [26401-12-7] and its copolymers, but no commercial polymer has been introduced. The naphthalate aromatic system absorbs uv radiation at a longer wavelength than the terephthalate or isophthalate systems, which suggests that polymers containing the naphthalate segment would offer better uv protection for materials packaged in films containing nylon-6,N (199). If the concentration of aromatic chromophores is high enough in the polymer, it can increase the uv lifetime of the fiber, film, or plastic part itself (197) by absorbing the radiation at the surface of the polymer.

9. Aromatic Polyamides

Polyamides that contain 85% or greater of the amide bonds attached to aromatic rings are classified as aramids. These aromatic polyamides have been the subject of numerous reviews (200–206) and a book (207) since 1985; and although this area of research has been very active including the development of many chemical variations (202), commercially it is still dominated by those meta- and para-aramids sold as fibrous materials under the trade names for *m*-aramids, predominately poly(*m*-phenyleneisophthalamide) [24938-60-1]: Apial, Nomex, and Tejiconex; and for *p*-aramids, predominately poly(*p*-phenyleneterephthalamide) [24938-64-5]: Kevlar, Technora, and Twaron (Apial is a registered trademark of Unitika, Ltd.; Nomex and Kevlar are registered trademarks of Du Pont Company, Inc.; Tejiconex and Technora are registered trademarks of Teijin Ltd.; and Twaron is a registered trademark of Akzo, NV) (see High performance fibers).



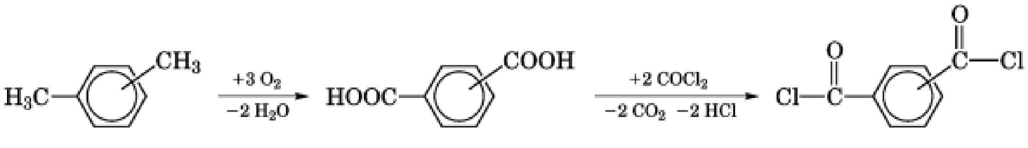
poly(*m*-phenyleneisophthalamide)



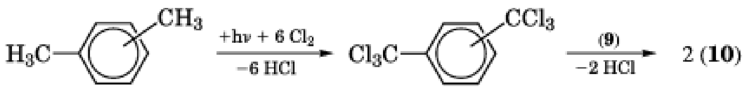
poly(*p*-phenyleneterephthalamide)

The aramids were first introduced into the marketplace by Du Pont in 1961 with the commercialization of Nomex fiber, which is used in flame-resistant fabrics and as an industrial fiber, such as in powerhouse filtration systems. Nomex has also been processed into a variety of papers, in which form it is used primarily as electrical insulation. The *p*-aramids were also first introduced commercially by Du Pont as Kevlar fiber in 1972. They possess outstanding tensile strength and modulus and are stronger than fiber glass or steel on a performance-per-weight basis. They can be heat-treated to improve these properties even further. Their end uses include tire cord, industrial fibers, and plastic reinforcement. The *p*-aramids are also being sold as pulp for vehicle brake linings and in woven and nonwoven blends, with *m*-aramids as fire-blocking materials for aircraft seating and other end uses.

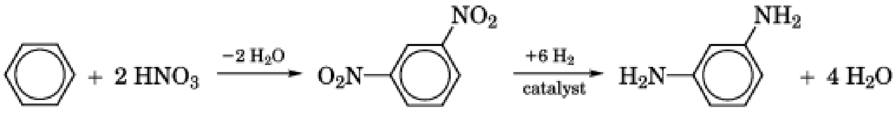
The diacid components for the manufacture of poly(*m*-phenyleneisophthalamide) and poly(*p*-phenyleneterephthalamide) are produced by one of two processes. In the first, the diacid chlorides are produced by the oxidation of *m*-xylene [108-38-3] or *p*-xylene [106-42-3] followed by the reaction of the diacids with phosgene [75-44-5]. In the second, process *m*- or *p*-xylene reacts with chlorine initiated by ultraviolet light to form the *m*- or *p*-hexachloroxylene. This then reacts with the respective aromatic dicarboxylic acid to form the diacid chloride.



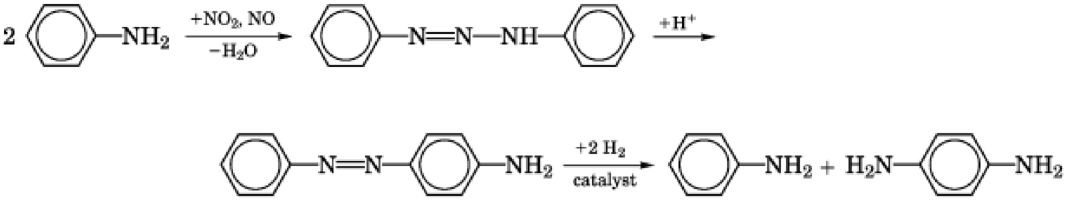
(9) (10)



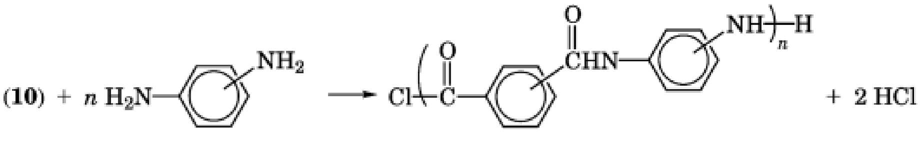
The synthesis of *m*-phenylenediamine [108-45-2] is also straightforward; it proceeds via the formation of *m*-dinitrobenzene [99-65-0] by the nitration of benzene, followed by hydrogenation to the diamine.



However, the production of the *p*-phenylenediamine [106-50-3] intermediate is more complex, because it involves the diazotization and coupling of aniline [65-53-3]. Aniline reacts with nitrogen oxides, produced via the oxidation of ammonia, to form 1,3-diphenyltriazene [136-35-6] in the process used by Du Pont (208, 209) (see Amines, aromatic–aniline and its derivatives). In the Akzo process a metal nitrite salt and acid in water is used (210). The triazene rearranges in the presence of acid and an excess of aniline to form predominately the *p*-aminoazobenzene [60-09-3] and a small amount of the ortho isomer, *o*-aminoazobenzene [2835-58-7]. The mixture of isomers is catalytically reduced to the respective diamines, and they are then separated from the aniline, which is recycled (208, 209). The *o*-phenylenediamine [95-54-5] is used in the manufacture of herbicides (see Amines, aromatic–phenylenediamines).



The aramids are formed in the low temperature reaction, *-10* to 60°C, of equimolar amounts of the diacid chloride and the diamine in an amide solvent, typically dimethyl acetamide (DMAc) or *N*-methyl-2-pyrrolidinone (NMP) and usually with a small amount of an alkali or alkaline-earth hydroxide and a metal salt, such as LiOH [1310-65-2], LiCl, $Ca(OH)_2$ [1305-62-0], or $CaCl_2$ added to increase the solubility of the polymer and neutralize the hydrochloric acid generated in the reaction.



The *m*-aramids are fully soluble at a moderate concentration in the solvent and are usually spun directly from the solution in a dry or wet spinning process, washed in water to remove excess solvent, and dried. High molecular weight poly(phenyleneterephthalamide), the polymer used to form Kevlar and Twaron aramid fiber, has a lower solubility in the amide solvents and is not typically spun directly into fiber. Rather it is precipitated from its polymerization solvent by the addition of water, neutralized, filtered, dried, and then redissolved in concentrated sulfuric acid. The acid solution is then spun through a spinnerette into a water bath after it passes through a short gap in the air that is essential to the process (211). The *p*-aramids form a liquid crystalline solution in the concentrated acid (212) and the spinning process further orients

Table 12. Properties of Commercial Aramid Fibers Compared to Nylon-6,6[a]

Fiber type	Density, g/cm^3	Strength, GPa[b]	Elongation, %	Modulus, GPa[b]	Maximum use temperature, °C
Kevlar 29	1.43	2.9	3.6	70	250
Kevlar 49	1.45	2.9	2.8	135	250
Kevlar 119	1.44	3.1	4.4	55	250
Kevlar 129	1.45	3.4	3.3	99	250
Kevlar 149	1.47	2.3	1.5	143	250
Technora	1.39	3.3	4.3	70	250
Nomex	1.38	0.6	22	17	250
Nylon-6,6[c]	1.14	1.0	18	5.5	<150

[a] From Ref. 207.
[b] To convert GPa to gram-force per denier (gpd), multiply by 11.33/density.
[c] Du Pont Type 728 industrial strength fiber.

the stiff, rod-like polymer molecules. This high degree of orientation, which is maintained in the washed, neutralized, and dried fiber, is responsible for the extraordinary properties of these fibers. Technora aramid fiber, a poly(phenyleneterephthalamide) copolymer, is soluble in NMP or DMAc solutions with $CaCl_2$ or LiCl. It is spun from an isotropic solution, then drawn 10 times to generate its high orientation. The aramids do not appear to be sold as bulk polymer, but only as yarn or staple fiber, paper, pulp, or fabrics. Some of the basic properties of aramid fibers appear in Table 12.

10. Health and Environment Aspects

10.1. Health

As is the case for almost all commercial polymers, there appears to be no significant recognized health hazard for additive-free polyamides in their normal fiber, film, or bulk plastic end uses, and the same also appears to apply to their higher oligomers (213, 214). However, the manufacturer's or supplier's Material Safety Data Sheet (MSDS) should always be consulted for the following reasons: (*1*) many commercial products contain additives which could significantly alter the health risks associated with the use of polyamides; (*2*) polyamides comprise an active area of research and changes in recognized levels of safety can occur; and (*3*) some potential end uses exceed the range of the manufacturer's intended applications for a given product. During incomplete combustion, polyamides can emit toxic products such as carbon monoxide [630-08-0], hydrogen cyanide, and NO_x, as well as other less hazardous products (213, 214).

The usual starting materials for type AABB polyamides, diamines, and diacids or diacid chlorides, are hazardous materials because they are moderate-to-strong bases, acids, or highly reactive chemicals, respectively. However, there is rarely any detectable starting material in type AABB polyamides. The common starting materials for type AB polyamides, lactams, or aminoacids are generally less hazardous but can be present in the final products. The most significant case is the relatively high concentration of caprolactam in nylon-6. Although caprolactam can be an eye, skin, and respiratory irritant, this is rarely a problem in the final product where the concentrations are kept low ($<2-3\%$) and the lactam is well below its melting point. Mechanical and thermal processing can generate higher levels of caprolactam in the air from nylon-6 or its copolymers and create dust from most polyamides, which can act as irritants and which are usually monitored and corrected in the workplace.

10.2. Environmental Aspects

In general, the polymerization processes for nylon-6,6 and nylon-6 generate little waste. However, because of economic advantages and governmental regulations, there has been a substantial increase in recycling of the starting materials for polyamides, especially hexamethylenediamine, caprolactam, and water; and of the energy, most often as steam. The hexamethylenediamine and caprolactam are usually emitted as vapors during the polymerization process along with steam and can be condensed, purified, and reused. The caprolactam extracted from the finished polymer, usually in aqueous solution, is also recycled in a similar manner.

During intermediates production, the generation of waste is greater; but again, significant success has been made in isolating, purifying, and selling the by-products, which previously were burned for their fuel value, in this instance as specialty chemicals into other industries. Waste streams whose contaminants are too low in concentration or in value to warrant separation are increasingly being remediated via biotreatment, rather than by more controversial methods such as burning or deep-well disposal. It has been recognized that the nitric acid oxidation of cyclohexanone–cyclohexanol mixture to adipic acid is a significant source of N_2O [10024-97-2] production worldwide (215). Nitrous oxide is potentially a contributor to the greenhouse effect and contributes to catalytic ozone depletion. In 1991 an interindustry consortium was formed to share information on N_2O abatement (216, 217). There are three potential, commercially viable routes to solving this problem: (*1*) thermal combustion of N_2O in a reducing flame to produce nitrogen and carbon dioxide; (*2*) controlled partial oxidation of N_2O to NO [10102-43-9], then dissolution in H_2O to form nitric acid; and (*3*) catalytic decomposition of N_2O into nitrogen and oxygen. Du Pont has patented the third method and is making it available for implementation around the world between 1996 and 1998 to eliminate this source of nitrous oxide (218).

Polymer recycle has been practiced as part of the manufacturing process for nylon-6,6 (219) and nylon-6 (220) almost from the beginning of the industry. Acid hydrolysis by Du Pont and base hydrolysis by BASF and Rhône-Poulenc of relatively pure nylon-6,6 waste streams, followed by separation of ingredients, purification, and reuse, has been practiced for many years. Also, phosphoric acid-catalyzed hydrolysis and steam distillation of caprolactam from pure nylon-6 is still used by BASF, Rhône-Poulenc, and SNIA. However, it is the challenge of recycling post-consumer waste that has generated the greatest activity since 1990. Stimulated by more stringent governmental regulations for recycling plastic packaging and automotive plastic components in Germany and the growing landfill problem in the United States, the nylon industry has developed several technologies to address the issue of recycling post-consumer waste. One of the greatest economic challenges is the collection and separation of nylon from other wastes, including other polymers. The ultimate solution to this problem may await the development of a cost-effective waste handling infrastructure for all recycled materials, at which point relatively pure, high volume, low cost, post-consumer nylon will become available. Recycled nylon carpets constitute the largest single supply of potentially recyclable nylon. A patent has appeared for the preparation of a thermoplastic composite by remelting all the components of a nylon carpet and forming it into bulk plastic parts (221). Unfortunately, because of the thermo- and photooxidative products formed in nylon during manufacture and use, and the thermal degradation and thermooxidative products formed during further melt processing, any direct remelt processing of nylon results in a low grade product, even with the use of currently available thermal stabilizers. Other approaches have focused on depolymerization and separation of the ingredients. Several patents and articles have appeared regarding the recovery of caprolactam from post-consumer waste nylon-6 via hydrolysis (222) or polymer pyrolysis (223), and the recovery of polymer via solvent dissolution of nylon-6 from nonpolyamide contamination (224); however, these technologies are limited to waste streams that contain nylon-6 as the only polyamide. In particular, nylon-6,6 significantly interferes with these processes. Several technologies have appeared which attempt to separate nylon-6,6 and nylon-6, and convert them simultaneously to useful monomers (225, 226). The most promising technology to date appears to be the ammonolysis of nylon-6,6–nylon-6 mixtures, which converts all three ingredients to hexamethylenediamine (227, 228).

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