

I. Polyamides

I.1. Introduction

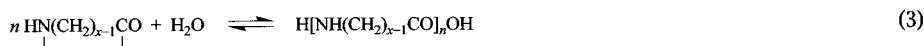
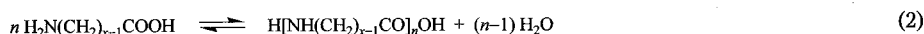
Polyamides are, literally, polymers that contain an amide group, $-\text{CONH}-$, as a recurring part of the chain. The polyamides known as “nylons” exclude (1) the proteinaceous polyaminoacids, (2) the relatively low-melting “polyamide resins” used in inks, adhesives, and coatings (\rightarrow Other Synthetic Resins) and (3) the wholly aromatic “aramids” used to make high-performance fibers. Rate and equilibrium constants, thermal and oxidative stability, resistance to hydrolysis and solvents, and other chemical behavior depend on the specific polymer, but the basic chemistry discussed herein applies to all of these polyamides.

1.1.1. History

The year 1929 saw the publication of the original papers of CAROTHERS [1], [2] on polycondensation which gave incontrovertible evidence to the Staudinger thesis [3] that polymers are high molecular mass species and not aggregated entities. CAROTHERS' classic review of polymerization and definition of terminology still valid today appeared in 1931 [4]. Development of techniques to achieve molecular masses in excess of 10 000 led to realization of the potential for fiber formation. This was the genesis of the effort by the DuPont company which yielded "nylon": the first semicrystalline polymer, the first synthetic fiber, and the first engineering thermoplastic. The term "nylon" is generic and is equivalent to "polyamide" in the limited sense defined above. Synthesis of poly(hexamethylene adipamide), the original "nylon", in a DuPont laboratory in 1935 provided a material whose properties were judged to be appropriate for apparel use and culminated in its commercial introduction in 1938. The other principal polyamide or nylon, polycaprolactam, was first made in an IG Farben laboratory by SCHLACK in 1938. The history of these nylons and those made from 11-aminoundecanoic acid and dodecanolactam were reviewed in 1986 [5]–[7]. Although use as a fiber dominated the interest in nylon from the outset, application as a plastic for a variety of purposes such as brush filaments, wire coating, coil forms, and gears occurred very soon thereafter. The use of nylons as plastics has steadily increased versus that of fibers. In the United States it has gone from 7 % in 1965 to 11 % in 1978 and 22 % in 1988; in Western Europe, from 24 % in 1978 to 47 % in 1988. Economic aspects are reviewed in Chapter 1.9. The focus of this article is on the polyamides used as plastics.

1.1.2. Nomenclature

The nylons (polyamides) under discussion here are most often made from (1) diamines and dibasic acids, (2) ω -amino acids, or (3) lactams¹:



- 1) The constitutional repeating units (CRUs) shown for polymers in equations (1) and (3) are incorrectly oriented according to IUPAC and CAS rules (see → Polymer Nomenclature for more information). The correct orientation for (3) is $\text{HOOC}-(\text{CH}_2)_{x-1}-[\text{NH}-\text{CO}-(\text{CH}_2)_{x-1}]_n-\text{NH}_2$; the correct orientation for (1) depends upon the values of x and y , i.e. upon the carbon chain lengths of the diamine and the dicarboxylic acid comonomers used to prepare the polyamide.

Table 1. Commercial polyamides or nylons

Common name	xy or x *	CAS name, CAS registry no.
Poly(tetramethylene adipamide)	46	poly[imino(1,4-dioxo-1,4-butanediyl)imino-1,6-hexanediyl] [24936-71-8]
Poly(hexamethylene adipamide)	66	poly[imino(1,6-dioxo-1,6-hexanediyl)imino-1,6-hexanediyl] [32131-17-2]
Poly(hexamethylene azelaamide)	69	poly[imino-1,6-hexanediylimino(1,9-dioxo-1,9-nonanediyl)] [28757-63-3]
Poly(hexamethylene sebacamide)	610	poly[imino-1,6-hexanediylimino(1,10-dioxo-1,10-decanediyl)] [9008-66-6]
Poly(hexamethylene dodecanoamide)	612	poly[imino-1,6-hexanediylimino(1,12-dioxo-1,12-dodecanediyl)] [24936-74-1]
Poly(dodecamethylene dodecanoamide)	1212	dodecanedioic acid, polymer with 1,12-dodecanediamine [36497-34-4]
Poly(<i>m</i> -xylylene adipamide)	MXD 6	poly[iminomethylene-1,3-phenylene-methyleneimino(1,6-dioxo-1,6-hexanediyl)] [25805-74-7]
Poly(trimethylhexamethylene terephthalamide)	TMDT	1,4-benzenedicarboxylic acid, polymer with 2,2,4-trimethyl-1,6-hexanediamine and 2,4,4-trimethyl-1,6-hexanediamine [25497-66-9]
Poly(11-aminoundecanoamide)	11	poly[imino(1-oxo-1,11-undecanediyl)] [25035-04-5]
Polycaprolactam or polycaproamide	6	poly[imino(1-oxo-1,6-hexanediyl)] [25038-54-4]
Polydodecanolactam or polylauro lactam or polydodecanoamide	12	poly[imino(1-oxo-1,12-dodecanediyl)] [24937-16-4]

* xy and x refer to the number of carbon atoms according to Equations (1)–(3).

Equation (3) represents the hydrolytic polymerization of a lactam. It is described in detail in Section 1.2.2.

Where two types of reactive monomer are required, the polymerization is said to be an AABB type; where one suffices, an AB type. A and B stand for the functional groups -NH_2 and -COOH , respectively. In current practice AABB and AB may describe products that do not involve polymerization via amine and acid ends but can be visualized as if so made. This is realistic because the same equilibria in the presence of water or other solvolytic agents will apply.

Useful molecular mass requires better than 99 % reaction and places a high demand on purity of the reactants. Stoichiometry is also critical for AABB types. The AABB types are regarded as homopolymers because of the absolute need for alternation of both reactants to form a polymeric chain which includes both moieties in the repeating structure (see Chap. 1.2). This is consistent with IUPAC recommendations [8]. Copolymers result from simultaneous polymerization of AABB and AB types or use of more than one AA, BB, or AB type. They are common and were used as early as 1940 [6].

The polyamides (PA) or nylons are identified by numbers corresponding to the number of carbon atoms in the monomers (diamine first for the AABB type).

Table 1 provides a list of the common names of the commercial nylon homopolymers, their numerical designations, their CAS registry numbers, and their CAS names. The systematic IUPAC naming of polyamides [9] is awkward and is rarely encountered in the commercial literature. The CAS names are largely in accord with IUPAC practice, but examination of Table 1 reveals some inconsistencies. Many of the IUPAC recommendations for nomenclature are conveniently assembled in a polymer

Table 2. Monomers for polyamides

Common and (CAS) name	CAS registry no.	x or y *	Source
Adipic acid (hexanedioic acid)	[124-04-9]	6	benzene, toluene
Azelaic acid (nonanedioic acid)	[123-99-9]	9	oleic acid
Sebacic acid (decanedioic acid)	[111-20-6]	10	castor oil
Dodecanedioic acid	[693-23-2]	12	butadiene
Dimer acid (fatty acids, dimers)	[61788-89-4]	36	oleic and linoleic acids
Isophthalic acid (1,3-benzenedicarboxylic acid)	[121-91-5]	1	<i>m</i> -xylene
Terephthalic acid (1,4-benzenedicarboxylic acid)	[100-21-0]	T	<i>p</i> -xylene
Tetramethylenediamine, 1,4-diaminobutane (1,4-butanediamine)	[110-60-1]	4	acrylonitrile and HCN
Hexamethylenediamine, 1,6-diaminohexane (1,6-hexanediamine)	[124-09-4]	6	butadiene, propene
4,4'-Diaminodicyclohexylmethane (cyclohexanamine, 4,4'-methylenebis-)	[1761-71-3]	PACM	aniline and formaldehyde
<i>m</i> -Xylylenediamine (1,3-benzenedimethanamine)	[1477-55-0]	MXD	<i>m</i> -xylene
Trimethylhexamethylenediamine (mix of 1,6-hexanediamine, 2,2,4-trimethyl and 2,4,4-isomer)	2,2,4-[3236-53-1] 2,4,4-[3236-54-2]	TMD	acetone
Dodecamethylenediamine, 1,12-diaminododecane (1,12-dodecanediamine)	[2783-17-7]	12	butadiene
11-Aminoundecanoic acid (undecanoic acid, 11-amino-)	[2432-99-7]	11	castor oil
ϵ -Caprolactam (2 <i>H</i> -azepin-2-one, hexahydro)	[105-60-2]	6	benzene, toluene
Lauro lactam, dodecanolactam, (azocyclotride- cane-2-one)	[947-04-6]	12	butadiene

* x, y = number of carbon atoms according to Equations (1)–(3).

handbook [10] wherein, however, older versions of the IUPAC names for PA 66 and 6 are used [11]: poly(iminoadipoyl-iminohexamethylene) and poly[imino(1-oxohexamethylene)].

As shown in Table 1, it is sometimes necessary to use letters instead of numbers for certain monomers. The diamine TMD is a mixture of 2,2,4- and 2,4,4-trimethylhexamethylenediamine and yields head-to-head, head-to-tail isomerism in its polymer with, for example, terephthalic acid (T). Thus PA TMDT is, in fact, a copolymer. Another special case is PACM which is a mix of *cis-cis*, *cis-trans*, and *trans-trans* isomers. The crystallinity of the derived polymer and associated properties depend largely on the percentage of *trans-trans* isomer.

Pronunciation is in accord with the monomers so that 66 is six-six not sixty six, 612 is six-twelve, 11 is eleven, etc. Other nylons of commercial interest exist and will be discussed below where appropriate.

The monomers used in polyamide homopolymers and copolymers are listed in Table 2; *p*- and *m*-phenylenediamines could be added but are specific to the high-performance fibers. Included is dimer acid although its use is largely in the low-melting adhesive and ink resins.

I.4.2. PA 66

The first step is preparation of pure, balanced salt in aqueous solution. Stoichiometric equivalence is determined by pH measurement. Some excess diamine is normally added to compensate for losses due to its relative volatility. The equivalence pH for the aliphatic salts approximates 7.6 [111], [112]. Charcoal decolorization of the salt solution is required unless the diamine has been carefully refined and, in particular, is free of *cis*-1,2-diaminocyclohexane [113]. Purging a charcoal bed with inert gas increases its life [114]. Treatment with diacid followed by removal of acid with diamine before use with salt solution avoids initial losses in molecular mass [115]. A two-stage, recycling method of salt preparation is used in a continuous process [116]. Two-step addition to diamine with intermediate evaporation of water yields a concentrated salt solution [117]. Ways of mixing molten acid and diamine have been patented [118]–[120]. To avoid precipitation when stored at about 25 °C a 50 % aqueous salt solution is normally prepared.

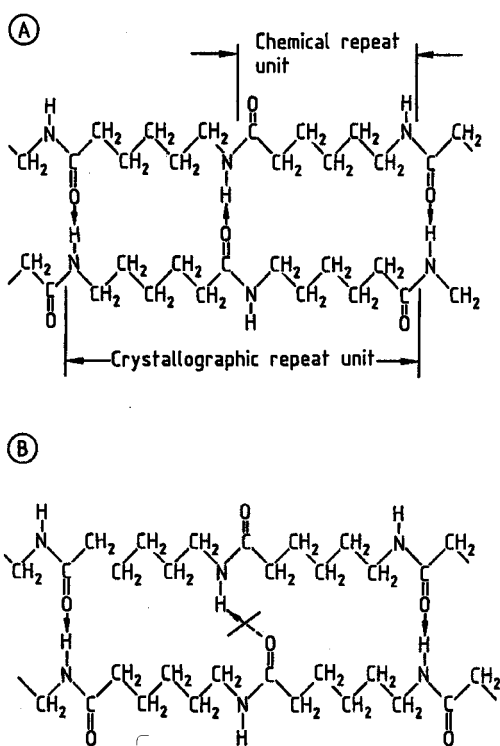


Figure 14. Schematic of a hydrogen bonded sheet of PA 6 with antiparallel (A) and parallel (B) orientation of amide groups

1.5. Properties

The utility of nylons rests upon their combination of properties and upon their susceptibility to modification. Key properties are resistance to oils and solvents; toughness; fatigue and abrasion resistance; low friction and creep; stability at elevated temperatures; fire resistance; drawability; good appearance and good processability.

This introductory section, however, is concerned with those features of neat polyamides which determine their properties and account for differences between individual nylons. The most distinguishing feature is the amide group which is responsible for strong hydrogen bonding between adjacent chains. Melting point increases with increasing ratio of CONH groups to CH_2 groups in the chain and the increased opportunity for hydrogen bonding but not regularly because, whether the number of CH_2 groups between the CONH groups is odd or even is important as well as the ratio of CH_2 to CONH. The odd number of CH_2 groups between the amide groups in PA 6 allows complete hydrogen bonding when the amides in adjacent chains have an opposed or antiparallel orientation but not when they have the same or parallel orientation (Fig. 14). Changing from a parallel to an antiparallel array requires inverting the entire molecular chain in this odd-numbered case, but only a one-segment lateral movement is needed if there is an even number of CH_2 groups, as in the case of PA 66 with its intervening number of 4 and 6 CH_2 groups. It is believed that this

Table 5. Glass transition temperatures (T_g , °C) of polyamides at various relative humidities (R.H.) *

PA	Dry				50 % R.H.		100 % R.H.	
	A	B	C	D	C	D	C	D
46	102	78	78					
66	82	65	80, 78, 66	48	35	15	-15	-37
6 (extracted)	56	65	75, 65	41	20	3	-22	-32
610	56	46	67, 70	42	40	10		
612	52	40	60	45	40	20	20	
11	36	29	53	43				
12	29	25	54	42			42	
MXD 6	71		68					
TMDT			150					

* A) Estimated from melting temperatures using $T_g = (2/3) T_m$ [163]; B) Calculated from group contributions [164]; C) Dynamic measurements with torsion pendulum [102], [165]–[167]; D) Static measurements by differential thermal analysis or inflection point in curve of modulus of elasticity as a function of temperature [13], [168].

odd/even feature accounts for the lower melting point and percent crystallinity of PA 6 versus PA 66. It is the reason in general why PA-odd and PA-odd/even have lower melting points than comparable or similar PA-even/even such as PA 6 versus PA 7.

Increasing crystallinity results in higher stiffness, density, tensile and yield stress, chemical and abrasion resistance, and better dimensional stability. It decreases elongation, impact resistance, thermal expansion and permeability. Crystallinity is responsible for the development of microscopically observable structures, known as spherulites, which scatter light and make nylons opalescent unless very thin. The transparent nylons are amorphous and are made so by appropriate copolymerization involving at least in part aromatic or cycloaliphatic AB, AA, or BB monomers in order to have acceptable stiffness.

Orientation [5, p. 300] contributes importantly to properties not only in film, fiber, and strapping but also in injection-molded articles. The resulting anisotropy means that properties vary with the direction of stress and must be considered in rationalizing resin behavior.

Water absorption is characteristic of nylons. Unless compensated for by increased crystallinity, a higher proportion of amide groups leads to higher water adsorption. Increased water content has an effect analogous to that of increased temperature, i.e., enhanced segmental mobility with, for example, concomitant loss in stiffness and tensile strength, gain in toughness, and growth in dimensions (elongation). At very low temperatures, however, water stiffens the nylon. Thus, the brittleness temperature (ASTM D 746) of PA 66 is -80°C if dry and -65°C if conditioned to 50 % relative humidity. Properties are frequently reported in the “dry”, as-molded condition corresponding to about 0.2 % water or less, and after equilibration to a specified relative humidity such as 50 or 65 %, and occasionally to 100 %. The greatest change occurs in the vicinity of the glass transition temperature (T_g) so that a useful aid in understanding behavior is a knowledge of the effect of humidity on T_g . This is complicated because of variation with the method of calculation or measurement (Table 5), but it is generally

true that nylons with fewer CONH groups and lower water adsorption have a lower dry T_g but show less change of T_g with relative humidity [13], [102], [163]–[168].

1.5.1. Properties of Unmodified Polyamides

A problem common to most polymers is the lack of adequate and comparable data. Nylons are no exception, but it is hoped that current efforts to correct this situation will succeed. A limited comparison of unmodified nylon resins is provided in Table 6. Even these data are not unambiguous because the molecular masses are not specified. The table is self evident and reflects the differences in amide group concentration and crystallinity discussed above.

Little change in sensitivity to aliphatic hydrocarbons occurs with a change in PA-type, but aromatic hydrocarbons are more strongly absorbed by polyamides with fewer amide groups. For example, PA 66 and PA 6 absorb 1% toluene; PA 610, PA 3, and PA 11 absorb 6.8%.

1.5.2. Additives for and Modification of Polyamides

Additives are materials used in small amounts (less than 5 wt% and usually less than 1 wt%) to affect processing, properties, or appearance. Processing additives include coloration inhibitors, lubricants, mold-release agents, nucleating agents, and viscosity thickeners or reducers. They have little or no effect on properties except in the instance of nucleating agents which increase the rate of crystallization and the degree of crystallinity. Enhanced crystallization may be desired not only to shorten molding cycles but also to modify mechanical properties. Additives used to alter properties or appearance are antioxidants, antistatic agents, biodegradative agents, biopreservatives, blowing agents, colorants, fragrances, and stabilizers against hydrolysis, thermal degradation, or UV degradation.

Modifiers are used in larger amounts, usually more than 5 wt%, in order to achieve desired changes in properties. Examples are mineral fillers, glass or carbon fibers, lubricants to improve wear and friction, plasticizers, fire retardants, electrically conductive materials, and other polymers to toughen or otherwise affect the nylon.

Alternative techniques of modification include copolymerization, adjusting molecular mass and posttreatments such as annealing, conditioning to some moisture level, dyeing, metallizing, painting, irradiation, or chemical reaction, e.g., alkoxyalkylation.

A broad discussion of additives is given in [13]. The emphasis here is on the more important modifiers and alternative techniques. Selection is necessary in light of the fact that the industry offers over 1500 compositions (grades); that number includes the inevitable duplications from different suppliers.

Table 8. Pattern of nylon consumption in the United States [200] and Western Europe [201] in 1988

Class	Percentage use in	
	United States	Western Europe
Appliances and power tools	3.0	
Building		6
Consumer products	6.1	
Electrical and electronic applications	7.7	20
Export	13.7	
Extrusion markets	25.8	23
Furniture/household		5
Industrial equipment	7.7	
Machinery		8
Miscellaneous	9.6	6
Transportation	26.4	32
Total percent	100.0	100
Total production, t/a	261 000	320 000

1.7. Uses

Nylons are used in many and diverse ways. They are found in appliances, business equipment, consumer products, electrical/electronic devices, furniture, hardware, machinery, packaging, and transportation. This diversity makes classification and analysis difficult as shown in Table 8 which compares the pattern of consumption in the United States [200] with that in Western Europe [216].

Transportation is the largest market for nylons. Unreinforced resins are used in electrical connectors, wire jackets, windshield wiper and speedometer gears, and emission canisters. The softer nylons are used in fuel lines, air brake hoses, and spline shaft coatings. Glass reinforced nylons are found in engine fans, radiator headers and grilles, brake and power steering fluid reservoirs, valve covers, wheel caps, air brake contacts and head-rest shells. Applications for nylons combining tougheners and reinforcement include brackets, steering wheels, and accelerator and clutch pedals. Mineral-filled resins are used in wheel caps, radiator grilles, and mirror housings. Nylons containing both glass fibers and minerals are used in exterior parts such as fender extensions. Toughened nylons are found in stone shields and trim clips.

Electrical and electronic applications comprise a major market for nylons, albeit more so in Western Europe than in the United States. Flame-retardant materials are particularly important in this area. Uses include color-coded components, plugs, connectors, coil forms, wiring devices, terminal blocks, antenna mounting devices, and harness ties. A review of nylon in electrical power engineering and electronics has already been cited [192]. Wire and cable jacketing is used mostly over primary insulation because of the solvent, wear and abrasion resistance of nylons. Relays, fittings, and contact makers constitute a partial list of applications in telecommunications.

Industrial applications are attracted to the excellent fatigue resistance and repeated impact strength of nylons. Examples are hammer handles and moving machine parts. The mechanical strength accounts for use in gears, bearings, antifriction parts, snap fits, and detents. Food- and textile-processing equipment, pumps, valves, agricultural and printing devices, and business and vending machines comprise a partial list of other industrial uses.

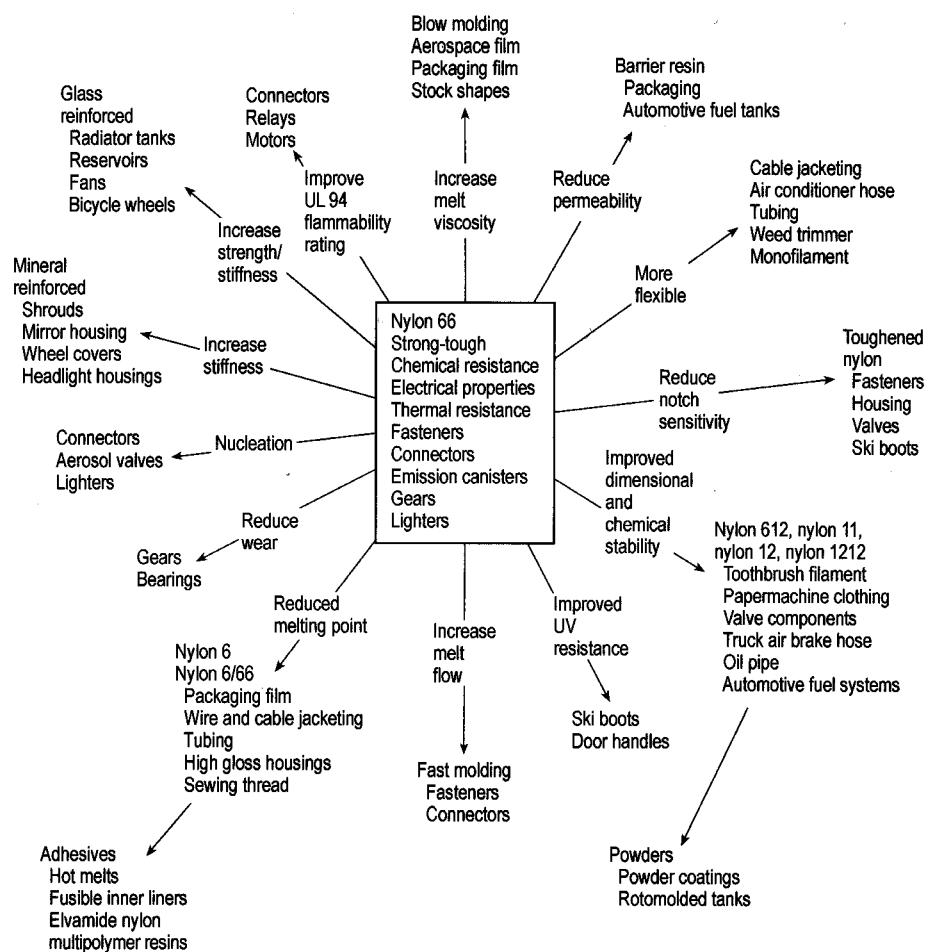
Consumer products exploit the toughness of nylons in ski boots, ice and roller skate supports, racquet equipment, and bicycle wheels. Kitchen utensils, toys, photographic equipment, brush bristles, fishing line, sewing thread, and lawn and garden equipment show that the breadth of utility of nylon also includes consumer products.

Appliances and power tools make use of the impact strength of nylons. Glass-reinforced resins, which combine stiffness at high temperatures with toughness and grease resistance, are used in handles, housings, and parts in contact with hot metal. Sewing machines, laundry equipment and dishwashers are examples of other appliances that have utilized nylons.

Film applications have grown in importance because of the use of nylons in co-extruded, composite films for food packaging. It is used also in cook-in bags and pouches. A relatively recent development involves dispersion of nylon platelets in a polyolefin matrix to combine both hydrocarbon and moisture barrier properties in blow molded containers [217], [218].

New developments continue to characterize nylon technology. The soft polymer-modified, anionically polymerized caprolactam has been used via RIM to make machine housings, grain buckets, and fuel tanks [219]. New blow molding compositions are extending utility in this area [220]. One example is the nylon platelet dispersion cited above. The new PA 46, PA 1212, and MXD 6 can be expected to find their places in the market [221]–[223]. Products with improved processing characteristics, high- and low-temperature performance, and new property profiles obtained via the use of new modifications and combinations thereof are continually appearing [224], [225]. A PA 6 with reduced moisture sensitivity has been recently claimed [222]. The use of block copolymers as thermoplastic elastomers has been cited [199].

The susceptibility of nylon to change and, if desired, to obtain diametrically opposite results is shown in Figure 16 which also gives examples of the applications involved. Nylons with qualified approval in the United States in 1989 for processing, handling and/or packaging food are PA 66, 66/610, 66/6 T, 610, 612, MXD 6, 6 I/6 T, 12/AI (A = bis(4-amino-3-methylcyclohexyl)-methane [6864-37-5]), 6, 6/66, 6/12, 6/69, and 11 [226].



Ecological Aspects and Toxicology

Figure 16. Nylon readily tailored to market needs

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