POLYAMIDES

1. Introduction

Polyamides, often also referred to as nylons, are high polymers that 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.

\[
\begin{align*}
\text{AB} & : \quad \text{C} = \text{N} - \text{R} \\
\text{AABB} & : \quad \text{C} = \text{N} - \text{R} - \text{N} - \text{R}
\end{align*}
\]

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 \(\omega\)-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. Some common terms used with polyamides are nylon, aramid, and polyphthalamide (PPA) (1).

Nylon is defined by the U.S. Federal Trade Commission as any polyamide having less than 85% of the amide groups directly connected to two aromatic groups. This definition is specifically for a fiber, but is conveniently extended.

Aramid is a polyamide having 85% or more of the amide groups directly connected to two aromatic groups.

Polyphthalamide (PPA) as a polyamide in which the residues of terephthalic acid or isophthalic acid or a combination of the two comprise at least 55 mol% of the dicarboxylic acid portion of the repeating units in the polymer chain. PPAs are considered nylons.

2. Nomenclature

The nomenclature 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-hexanediolamine [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 (2,3) 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 polyamides is as follows: nylon-\(x\) becomes poly[imino-R_{0}imino(1,\(y\)-dioxo-R_{00})]. When \(x < y\), then the name is poly[imino(1,\(y\)-dioxo-R_{"})imino-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, the IUPAC name is poly[imino-R' imino(1,\(y\)-dioxo-R'_{")}]. When \(x < y\), 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 (4). 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
### Table 1. Codes for Common Polyamide Monomers

<table>
<thead>
<tr>
<th>Abbreviation or code</th>
<th>Chemical name</th>
<th>CAS Registry Number</th>
<th>Structure</th>
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<td>[100-21-0]</td>
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<td>[1141-38-4]</td>
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<td>MPD</td>
<td>m-phenylenediamine</td>
<td>[108-45-2]</td>
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<td>p-phenylenediamine</td>
<td>[106-50-3]</td>
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<td>MXD</td>
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<td>[1477-55-0]</td>
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<td>Pip</td>
<td>piperazine</td>
<td>[110-85-0]</td>
<td><img src="image" alt="Structure of piperazine" /></td>
</tr>
<tr>
<td>MPMD or D</td>
<td>2-methylpentamethylenediamine or Dytek A*</td>
<td>[15520-10-2]</td>
<td><img src="image" alt="Structure of 2-methylpentamethylenediamine or Dytek A*" /></td>
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<tr>
<td>TMD or 6-3</td>
<td>mixture of 2,2,4- and 2,4,4-trimethylexamethylenediamine</td>
<td>[3236-53-1] [3236-54-2]</td>
<td><img src="image" alt="Structure of mixture of 2,2,4- and 2,4,4-trimethylexamethylenediamine" /> and <img src="image" alt="Structure of mixture of 2,2,4- and 2,4,4-trimethylexamethylenediamine" /></td>
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</table>

*Registered trademark of Du Pont Co.*
<table>
<thead>
<tr>
<th>x or y&lt;sup&gt;b&lt;/sup&gt;</th>
<th>R, R', or R&lt;sup&gt;0b&lt;/sup&gt;</th>
<th>(\omega)-Amino acid replaces 1-oxo-R</th>
<th>Diamine radical replaces R&lt;sup&gt;0&lt;/sup&gt;</th>
<th>Diacid radical replaces 1,(y)-dioxo-R&lt;sup&gt;0&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1-methanediyl</td>
<td>1-oxomethylene</td>
<td>methylene</td>
<td>c</td>
</tr>
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<td>2</td>
<td>1,2-ethanediyl</td>
<td>1-oxoethylene</td>
<td>ethylene</td>
<td>oxalyl</td>
</tr>
<tr>
<td>3</td>
<td>1,3-propanediyl</td>
<td>1-oxotrimethylene</td>
<td>propylene, trimethylene</td>
<td>malonyl&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>4</td>
<td>1,4-butanediyl</td>
<td>1-oxotetramethylene</td>
<td>tetramethylene</td>
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<td>1,5-pentanediyl</td>
<td>1-oxopentamethylene</td>
<td>pentamethylene</td>
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</tr>
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<td>hexamethylene</td>
<td>adipoyl</td>
</tr>
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<td>1,7-heptanediyl</td>
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<td>heptamethylene</td>
<td>heptanedioyl, pimeloyl</td>
</tr>
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<td>8</td>
<td>1,8-octanediyl</td>
<td>1-oxooctamethylene</td>
<td>octamethylene</td>
<td>octanediyl, suberoyl</td>
</tr>
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<td>9</td>
<td>1,9-nonanediyl</td>
<td>1-oxononamethylene</td>
<td>nonamethylene</td>
<td>nonanediyl, azelaoyl</td>
</tr>
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<td>10</td>
<td>1,10-decanediyl</td>
<td>1-oxodecamethylene</td>
<td>decamethylene</td>
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</tr>
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<td>11</td>
<td>1,11-undecanediyl</td>
<td>1-oxoundecamethylene</td>
<td>undecamethylene</td>
<td>undecanediyl</td>
</tr>
<tr>
<td>12</td>
<td>1,12-dodecanediyl</td>
<td>1-oxododecamethylene</td>
<td>dodecamethylene</td>
<td>dodecanediyl</td>
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<td>1-oxotridecamethylene</td>
<td>tridecamethylene</td>
<td>tridecanediyl</td>
</tr>
</tbody>
</table>

<sup>a</sup>Not used in Chemical Abstracts, but appear in other references, eg, Ref. 4.

<sup>b</sup>In poly[imino(1-oxo-R)], poly[imino-R imino(1,\(y\)-dioxo-R<sup>0</sup>)], and poly[imino-(1,\(y\)-dioxo-R<sup>0</sup>)imino-R<sup>0</sup>], as explained in text.

<sup>c</sup>Polymer names based on carboxylic acid and diamines are considered polyureas.

<sup>d</sup>The systematic name of a small radical can replace the trivial name, eg, propanedioyl for malonyl.
provides appropriate methods for designating end groups, copolymers, and nonlinear polymers (2,5).

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 containing Registry Numbers, 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.

3. 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 (6). 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] (7). 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 (8). At this time he and his co-workers also made other polyamides from dibasic acids and aliphatic diamines (9); 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 (10). In less than one year, DuPont scientists and engineers built the first commercial plant in Seaford, Delaware, which began production in 1939.
<table>
<thead>
<tr>
<th>Type AB</th>
<th>CAS Registry Numbers for Source-Based Monomers</th>
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<td>Type AABB</td>
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<td>isophthalic, C₁₀H₈O₄</td>
<td>[67937-43-3]</td>
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</table>
8 POLYAMIDES

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 (11). 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 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.

4. Physical Properties

4.1. Crystallinity. Linear polyamide homopolymers consist of crystalline and amorphous phases and are termed semicrystalline. Crystallinity enhances yield strength, hardness abrasion resistance, tensile strength, elastic and shear modulus, and probably resistance to thermooxidation (12), 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. 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 1 shows the unit cell for nylon-6,6, and Table 5 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

Table 5. Lattice Constants for Some Polyamides

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<tr>
<th>Polyamide</th>
<th>Crystal system</th>
<th>Lengths, nm</th>
<th>Angles, °</th>
<th>Zb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a   b    c</td>
<td>α</td>
<td>β</td>
</tr>
<tr>
<td>nylon-6,6</td>
<td>α-triclinic</td>
<td>0.49</td>
<td>0.54 1.72</td>
<td>48.5</td>
</tr>
<tr>
<td>nylon-6</td>
<td>α-monoclinic</td>
<td>0.956</td>
<td>0.801</td>
<td>1.724</td>
</tr>
<tr>
<td></td>
<td>γ-monoclinic</td>
<td>0.914</td>
<td>0.484</td>
<td>1.668</td>
</tr>
<tr>
<td>nylon-6,10</td>
<td>α-triclinic</td>
<td>0.495</td>
<td>0.54 2.24</td>
<td>49</td>
</tr>
<tr>
<td>nylon-12</td>
<td>α-monoclinic</td>
<td>0.479</td>
<td>3.19</td>
<td>0.958</td>
</tr>
</tbody>
</table>

a Refs. 13–15.
bZ = number of chemical repeat units per unit cell.
size in polyamides has been determined by wide-angle x-ray scattering (waxs) (16) and small-angle x-ray scattering (saxs). 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 (17) and from the melt (18). It is generally accepted that such lamellar structures are present as crystallites in isotropic samples (19), 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 (20), and extensive crystallographic data are also available (21).

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 1,1,3,3,3-hexafluoropropyl alcohol [920-66-1] (HFIP) and 2,2,2-trifluoroethanol [75-89-8] (TFE) (22). Mixtures of TFE and methylene chloride in a 3:1 ratio are recommended as effective nmr solvents (23). 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 (24). 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 (25). 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-pyrroldione [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 (26). 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 (27). 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] (28), 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 2a 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 2b. The $\alpha$-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, waxes 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 2c.

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 (31) (Fig. 3). 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 (32).

Organic plasticizers (33) and water (34), 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/m² for nylon-11 to 135 mC/m² for nylon-5. This effect has been extrapolated to approximately 180 mC/m² for nylon-3 (35) (Fig. 4). 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 (27,36). In addition, remanent

Fig. 2. 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 (26).
polarizations have been measured for a series of polyamides containing \( m \)-xylylenediamine (37) and for those containing 1,3-bis(aminomethyl)cyclohexane (38). Pyroelectricity has been observed in nylon-11 (39) and nylon-5,7 (40).

5. Chemical Properties

5.1. Preparation. 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
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produce polyamides.

\[
\begin{align*}
n \text{H}_2\text{N} & \text{R} \text{C} \text{O} \text{H} \quad \text{H}_2\text{N} \text{R} + \text{C} \text{N} \text{H} \text{R} \text{C} \text{O} \text{H} + (n-1)\text{H}_2\text{O} \\
(n) & \quad (n) \\
\end{align*}
\]

\[
\begin{align*}
n \text{H}_2\text{N} & \text{R} \text{NH}_2 + n \text{HO} \text{C} \text{R} \text{C} \text{O} \text{H} \quad \text{H}_2\text{N} \text{R} \text{NH} + \text{C} \text{R} \text{NH} \text{R} \text{C} \text{O} \text{H} + (2n - 1)\text{H}_2\text{O} \\
(n) & \quad (n) \\
\end{align*}
\]

The 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 number average molecular weight is approximately equal for both, since the monomer, hexamethyleneadipamide, for nylon-6,6 has twice the unit weight as the monomer, \( \varepsilon \)-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:

\[
\begin{align*}
\text{H}_2\text{N} & \text{R} \text{NH} + \text{C} \text{R} \text{NH} \quad \text{H}_2\text{N} \text{R} \text{NH} + \text{C} \text{R} \text{NH} + (n-1)\text{H}_2\text{O} \\
(n) & \quad (n) \\
\end{align*}
\]

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 for type AABB and 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 (41). 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.

**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 (42). The basic reaction in the presence of a base, B:, is as follows:

\[
\begin{align*}
n \text{H}_2\text{N} \text{R} \text{N} \text{H}_2 + n \text{Cl} \text{C} \text{R} \text{C} \text{R} \text{Cl} & \rightarrow \text{H}_2\text{N} \text{R} \text{N} \text{C} \text{C} \text{R} \text{N} \text{H} \text{C} \text{R} \text{C} \text{R} \text{Cl} + (2n-1)\text{B:HCl}
\end{align*}
\]

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 (43). 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 (44). 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.

**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 can be formed in the reverse of the reaction just shown above.

\[
\begin{align*}
H_2N(CH_2)6C-OH + \text{NH}_3 & \rightarrow HO-C(CH_2)6NH-\text{C(CH_2)6NH}_2 \\
\text{HO-C(CH_2)6NH} + \text{C(CH_2)6NH}_2 & \rightarrow HO-C(CH_2)6NH+\text{C(CH_2)6NH}_2
\end{align*}
\]

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:

\[
\begin{align*}
\text{NH}_3 + \text{NaH} & \rightarrow \text{N}^+\text{Na}^+ + \text{H}_2
\end{align*}
\]

The lactamate then initiates a two-step reaction, which adds a molecule of the lactam to the polymer chain (45–47):

\[
\begin{align*}
\text{H} + \text{NH(CH}_2)_6\text{C} & \rightarrow \text{HO-C(CH}_2)_6\text{NH-\text{C(CH}_2)_6\text{NH}_2} \\
\text{H} + \text{HN(CH}_2)_6\text{C} & \rightarrow \text{HO-C(CH}_2)_6\text{NH+\text{C(CH}_2)_6\text{NH}_2}
\end{align*}
\]

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 (22,46,47). The complete reaction mechanism is complex and this approach has not as yet been used successfully in a commercial process.

**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 (48). In addition, many of the methods used to prepare simple amides are applicable to polyamides (49,50). Polyamides of aromatic diamines and aliphatic diacids can also be made by the reaction of the corresponding aromatic diisocyanate and diacids (51).

**5.2. Reactions of Polyamides.** Acidolysis, Aminolysis, and Alcoholyisis. When heated, polyamides react with monofunctional acids, amines, or alcohols, especially above the melt temperature, to undergo rapid loss of molecular weight (52,53), eg, as in acidolysis (eq. 3) with acetic acid [64-19-7]
or aminolysis (eq. 4) with an aliphatic amine:

$$\text{RCO} \quad \text{R}^{' \prime} \quad \text{NH} \quad \text{R}$$

$$\text{CH}_3\text{C} \quad \text{O} \quad \text{OH} \quad \text{RCO} \quad \text{R}^{' \prime} \quad \text{NH} \quad \text{R}$$

(3)

$$\text{R} \quad \text{C} \quad \text{NH} \quad \text{R}^{' \prime} \quad \text{+} \quad \text{CH}_3\text{(CH}_2\text{)}_x\text{NH}_2$$

$$\text{R}^{' \prime} \quad \text{NH}_2 \quad \text{+} \quad \text{CH}_3\text{(CH}_2\text{)}_x\text{NH} \quad \text{C} \quad \text{R}$$

(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 aminolysis.

$$\text{H}_2\text{N} \quad \text{C(CH}_2\text{)}_4\text{C} \quad \text{O} \quad \text{NH}_2 \quad \text{+} \quad \text{H}_2\text{N(CH}_2\text{)}_6\text{NH}_2$$

$$\text{H}_2\text{N} \quad \text{C(CH}_2\text{)}_4\text{C} \quad \text{O} \quad \text{NH}_2 \quad \text{+} \quad \text{H}_2\text{N(CH}_2\text{)}_6\text{NH}_2 \quad \text{+} \quad (2n-1)\text{NH}_3$$

(5)

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

Phosphoric acid [7664-38-2] and its derivatives are effective catalysts for this reaction (54). 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 (55). 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.

Ammonolysis. In a reaction closely related to aminolysis, ammonia [7664-41-7] reacts with polyamides, usually under pressure and at elevated temperatures (56).

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 (57). 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.
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.

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.

\[
\begin{align*}
R \rightleftharpoons C \rightleftharpoons NH \rightleftharpoons R' + R'' \rightleftharpoons C \rightleftharpoons NH \rightleftharpoons R'''' & \rightleftharpoons R \rightleftharpoons C \rightleftharpoons NH \rightleftharpoons R' + R'' \rightleftharpoons C \rightleftharpoons NH \rightleftharpoons R''''
\end{align*}
\]

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 (eq. 4) or acidolysis (eq. 3) (59). 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.

\[
\begin{align*}
R \rightleftharpoons C \rightleftharpoons NH \rightleftharpoons R' + H_2O & \rightleftharpoons R \rightleftharpoons C \rightleftharpoons OH + H_2N \rightleftharpoons R'
\end{align*}
\]

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

\[
\begin{align*}
R \rightleftharpoons C \rightleftharpoons OH + H_2N \rightleftharpoons R'' & \rightleftharpoons R \rightleftharpoons C \rightleftharpoons NH \rightleftharpoons R'''' + H_2O
\end{align*}
\]

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 (53,59).

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 (60). 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 (61). This
is often a convenient route to produce polyesteramides.

\[
\begin{align*}
O & \quad \quad O \\
R-C-NH-R' + R''-C-O-R''' & \rightarrow R-C-O-R'' + R''-C-NH-R'
\end{align*}
\]

Here, R and R' represent polyamide chain fragments, and R'' and R'''
represent polyester chain fragments of any length. Polymers are generally
more easily hydrolyzed than polyamides and thus are quite sensitive to the pre-
sence 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 copolymesters by transesterification (62).

**Grafting.** Grafting is the process of chemically bonding additional polyn-
meric 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 chemi-
cally, and a source of high energy sufficient to create free-radical sites is neces-
sary to initiate the grafting reaction, eg, \(\alpha\)-particles, electrons from linear
accelerators, \(\gamma\)-rays from \(x\)-rays, glow discharges, or uv radiation. The predomi-
nant reactive intermediate is believed to be the alkyl free radical formed by the
removal of the \(\alpha\)-hydrogen adjacent to the amide nitrogen (63). The reaction with
vinyl monomers is typically as follows:

\[
R'\text{CH2CHR•} + R''\text{CH2CHR•} \rightarrow (\text{CH2CHR}•)_n \text{CHR•}
\]

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 polycondensa-
tion mechanism when secondary amides are formed as graft copolymers
(64).

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 poly-
mer; this alters, for example, the mechanical (toughening) or optical (deluster-
ing) 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 (64–68), 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.

5.3. Degradation of Polyamides. 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 (69). 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 \( 8 \, N \) 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 (70).

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 (71,72) (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 \( R = H \)) (73); this has also been observed in MPMD-containing polyamides (in eq. 7, \( n = 2 \), \( R = CH_3 \)) (74), as well as in nylon-6,6 (in eq. 7, \( n = 3 \), \( R = H \)).

\[
\begin{align*}
\text{R'} & \quad \text{C} - \text{NH} - \text{CH}_2\text{CH(CH}_2\text{CH}_2\text{NH}_2 & \quad \text{R} \\
& \quad \text{R} & \quad \text{R} \\
& \quad \text{O} & \quad \text{O} \\
\end{align*}
\]

Another example of a cyclic product is the formation of cyclopentanone [120-92-3] as a thermal decomposition product in nylon-6,6 (75,76). 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 (76).

![Image of chemical reactions]

In type AB polyamides the re-equilibration reaction leading to production of the starting lactam can be viewed as the decomposition of the polyamides into cyclic products (77); $n = 1, 2,$ and 3 for nylon-4, nylon-5, and nylon-6, respectively.

![Image of chemical reactions]

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 (78). For nylon-$x$, $n = 1$ and for nylon-$x,5$, $n = 2$.

![Image of chemical reactions]

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).
In nylon-6,6, the secondary amine so formed, bis-hexamethylenetetramine [143-23-7] (BHMT) has been thought by some to be the source of cross-linking and gelation in this polyamide (78–80). 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 (81), 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 (80,82,83). Another type of branching reaction which has been found in aromatic polyamides is amidine formation (eq. 12) (84).

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.

\[
\begin{align*}
R-NH-C=O & \rightleftharpoons R-NH-C=O + CO_2 \\
(13)
\end{align*}
\]

**Thermooxidation.** This is an autooxidation 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 are two techniques providing good protection.

Figure 5 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 (85), and the corresponding alkyl radical has been observed using electron-spin resonance (esr) in polyamides exposed to ionizing radiation (86). 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 alkoxy radical (4), cleaves (eqs. 14 and 15) before or after hydrogen abstraction, and that this accounts for the drop in molecular weight of the polymer.

\[
+RH \quad \begin{array}{c}
R' \quad \vdash || \quad NH \quad \vdash || \quad CH(CH_2)_x(C = NH) - R' \\
\end{array} \quad \begin{array}{c}
R \quad \vdash || \quad NH \quad \vdash || \quad H + CH(CH_2)_{(x-1)}(C = NH) - R' \\
\end{array} \quad \begin{array}{c}
R \quad \vdash || \quad OH \quad \vdash || \quad O \\
\end{array} \quad \begin{array}{c}
R \quad \vdash || \quad OH \quad \vdash || \quad O \\
\end{array} \quad \begin{array}{c}
R \quad \vdash || \quad OH \quad \vdash || \quad O \\
\end{array} \\
(14)
\]
Fig. 5. The initial degradation pathway for thermooxidation and photooxidation. The free radical is generated by the effect of heat or light on impurities, additives, and 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 (87) and the alkyl amines formed after hydrolysis of the polymer (88) 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 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 (89). 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 (90) or via imines (89,91) formed by the condensation of the aldehyde with an amine end, which could also contribute to the loss of amine ends:

\[
\begin{align*}
\text{RNH}_2 + \text{HC} &\xrightarrow{\text{O}_2} \text{HO} - \text{C} \xrightarrow{\text{CH}_2} \text{C} - \text{NH} \xrightarrow{\text{R'}} \\
\text{R} &\xrightarrow{\text{CNH}} \text{R'}
\end{align*}
\]

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, i.e., 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 nylon 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 (92). 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 (93), as well as its accepted role as a radical scavenger (94). 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 (95), and therefore cannot be used in a melt process for most polyamides.

**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 ε ≥ 4.0, at approximately 185 nm, which is assigned to the π–π* transition of the amide group. There may also be a much weaker n–π* 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, $S_0 - T_1$, can lie as low as 285 nm, based on low temperature phosphorescence excitation–emission spectra of model alkyl-bis(hexanamides) (96). 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 (97) which has been assigned to the following chromophore (98):

$$\text{N} (\text{CH}_2)_x \text{R}$$

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)] (99,100). The product radicals are then consumed by recombination or by the reaction with oxygen (Fig. 6) when the sample is exposed to air.

$$\begin{align*}
\text{(5)} \rightarrow \text{R} - \text{CH}_2 + \text{CO} \\
\text{(6)} \rightarrow \text{R} - \text{CH}_2 - \text{C} - \text{NHCH}_2\text{R'}
\end{align*}$$

$$\begin{align*}
\text{(5)}, (6), (7) + \text{R} - \text{CH}_2 - \text{C} - \text{NHCH}_2\text{R'} & \rightarrow \text{R} - \text{CH}_2, \text{R'} \text{CH}_2\text{NH}_2, \\
& + \text{R} - \text{CH}_2 - \text{C} - \text{NHCH} \text{'R'} + \text{R} - \text{CH}_2 - \text{CH}
\end{align*}$$

**Fig. 6.** Photo-yellowing of nylon-12 as a function of wavelength.
The initial steps in the mechanism for photo-oxidation are generally accepted as being the same as for thermo-oxidation. 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 (101) 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 (102) at wavelengths above 310 nm, and iron has been shown to have significant negative impact on the photostability of nylon (103). The additive anatase titanium dioxide [1317-70-0], commonly used as a delustrant in fibers, has long been recognized as a potent photodegrader that can, however, be stabilized with the use of manganese(II) compounds (104,105). 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 (106–108).

The generation of color during photo-oxidation, known as photo-yellowing, has long been recognized as a source of color in nylon-6,6 and nylon-6 (109). This effect has been shown to occur in all aliphatic polyamides at wavelengths between 320 and 350 nm (110) (Fig. 6). The chemical nature of the yellow chromophore has not been identified.

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 (111,112). 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 (113–117), 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.

A recent patent describes a method for extracting nylon from waste materials by contacting the nylon-containing material with an alkanol-containing solvent at elevated temperature and at a pressure higher than the equilibrium pressure of the alkanol-containing solvent at the elevated temperature. This dissolves the nylon in the alkanol-containing solvent, which can then be later recovered by precipitation (118).
Polyamides, like other macromolecules, degrade as a result of mechanical stress either in the melt phase, in solution, or in the solid state (119). Degradation in the fluid state is usually detected via a change in viscosity or molecular weight distribution (120). 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 (121,122). 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. Economic Aspects

Nylon accounts for 8.9% of all the synthetic fiber/filament produced globally. It is the second largest category after polyester. Total world consumption of nylon resins is forecast to increase at an average rate of about 4%. In 2008 and 2009, the world economic crisis impacted markets globally. The value of the industry was $15.22 \times 10^9$ in 2007 and eroded in 2008 by 8%. While production volume declined 8.9%, prices gained little over 1% globally. In Japan, consumption of engineering plastics such as nylon resins decreased by more than 40% during 2008-2009. However, some countries such as China recovered in 2009 and consumption is increasing rapidly. Good growth was expected in 2010 in such sectors as automotive parts, industrial/machinery, electrical/electronics and film.

Increased use of reprocessed nylon fiber to make nylon resin compounds has extended the range of nylon resin applications. Nylon 6 is less likely to crystallize and can be recycled many more times than nylon 6,6. Nylon 6,6 resins have been increasingly used in automotive under-the-hood applications, including intake manifolds. Nylon 6 and nylon 6,6 are used to reduce weight and flexibility of design. Growth in Europe and the United States is forecast to be 3.8% and 1.6% respectively during the years 2009-2014. China will see a high average annual growth of 7.5 (123).

Nylon fibers are used in a wide variety of applications including apparel, home furnishings, and industrial end uses. As of mid-2008, the ten largest producers accounted for almost 38% of the world’s capacity. INVISTA has 13% of the world’s nylon fiber capacity, with fiber production facilities in North America, Central and South America, Western Europe, and Asia. The next largest producers are Shaw Industries and Solutia with about 5% of world capacity (124). The global nylon carpet yarn suffered from the steepest decline in production and fell by 9% to 824,000 t in 2008. The fall was mostly in the United States. The real estate crisis is one of the factors for poor carpet volumes. Similar developments were seen in Europe and Canada. In addition to lower consumer spending lose of exports to the Middle East were also a factor (125).

The global market for aramid fibers is essentially dominated by Teijin and DuPont. Demand for aramid fibers was down 20% for the year from the 2008