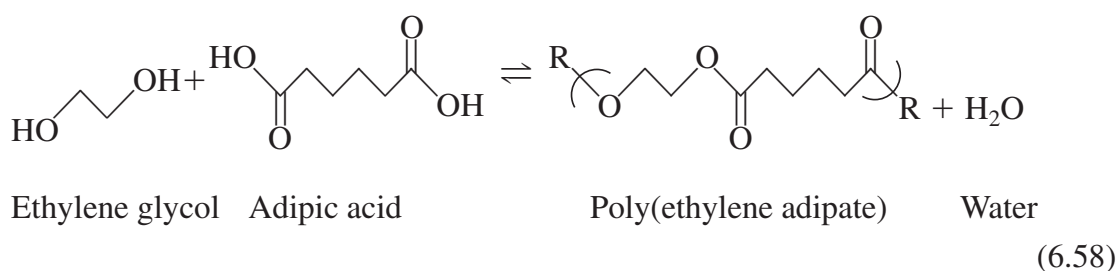


6.6 POLYESTERS

Carothers and his research group at Dupont began to investigate the formation of polymers from the reaction of aliphatic diacids with diols, generally adipic acid and ethylene glycol (derived from the reaction of ethylene oxide with water, it is the major ingredient in most antifreezes), in search of materials that would give them fibers. They were only able to form syrupy mixtures. This is because unlike reactions with diamines (Sec. 6.7), the equilibrium reaction greatly disfavors ester formation. Further, the ability to have almost equal amounts of functional groups is easily achieved with the amines through formation of salts with the amines as shown in (6.59) but diols do not form such salts. The critical need to have the reactants present in equal molar amounts for equilibrium determined reactions is clearly seen in Eq. (6.29). Carothers' group understood the principle of "driving" an equilibrium reaction so sought to remove water thus forcing the reaction toward ester formation. For this they developed a so-called "molecular still," which was simply heating the mixture and applying a vacuum coupled with a "cold-finger" that allowed evacuated water to condense and be removed from the reaction system. Since the fractional conversion (p) was only 0.95 the average chain length of these polyesters was less than 20.



The Dupont research turned from the synthesis of polyesters to tackle, more successfully, the synthesis of the first synthetic fiber material, nylon, which approached, and in some cases exceeded, the physical properties of natural analogs (see the next section).

The initial experience with polyesters was put to use in the nylon venture. Today, we know that Carothers would of had greater success in producing high molecular weight material had his group employed transesterification, ring opening (of the “diol” derived moiety), or the reaction of diols with acyl dichlorides (Schotten-Baumann reaction) or anhydrides. These techniques then compose the major techniques employed in the synthesis of polyesters. Each of these reactions involve the nucleophilic addition to the carbonyl group as shown in Sec. 6.5 and are illustrated in reactions (6.59)–(6.63). Focusing on the carbonyl-containing reactant, polyester formation employing direct esterification (reaction between an acid and alcohol) and transesterification is relatively slow with each mechanistic step reversible. Reaction rates are increased through the use of acid catalysts that coordinate the carbonyl oxygen enhancing the electrophilic nature of the carbonyl carbon. Weakly basic catalysts are often employed in transesterification reactions probably to increase the nucleophilicity of the alcohol through formation of an alkoxide ion. Reaction with anhydrides and acid chlorides are more rapid and can occur in an essentially nonreversible fashion. But anhydrides and acid chlorides are considered so-called “high energy” reactants, since they often involve additional energy requiring steps in their production and thus are less suitable for large scale production of materials. The activity energies for direct esterification and transesterification are on the order of 30 kcal/mole (120 kJ/mole), while the activation energies for anhydride and acid chloride reaction with alcohols are on the order of 15–20 kcal/mole (60 to 80 kJ/mole).

The initial polyester formation actually occurred much earlier and is attributed to Gay Lussac and Pelouze in 1833 and Berzelius in 1847. These polyesters are called glyptals and alkyds, and they are useful as coatings materials and not for fiber production. While these reactions had low fractional conversions, they formed high molecular weight materials because they had functionalities (that is number of reactive groups on a single reactant) greater than 2 resulting in crosslinking.

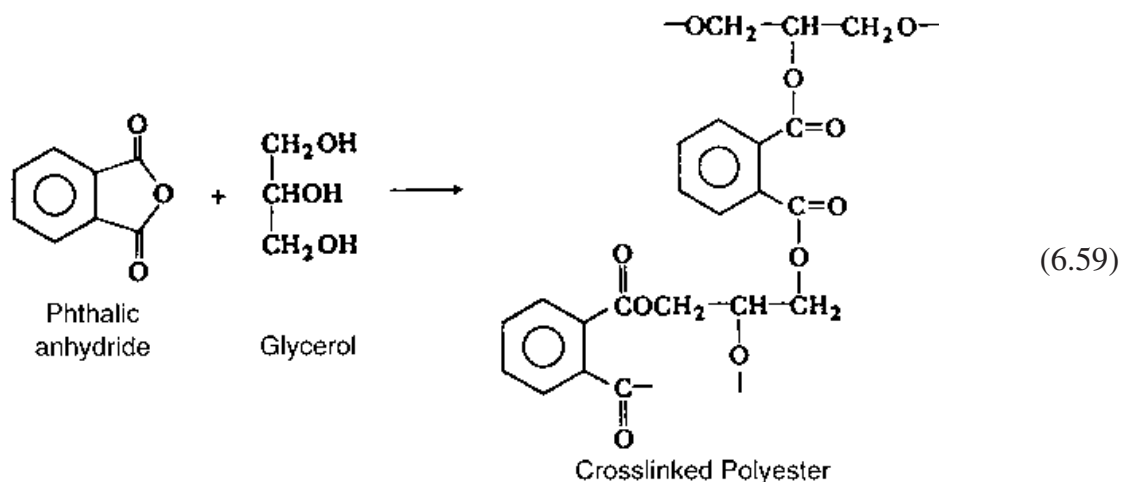
When the average functionality is greater than 2 crosslinking occurs. Utilization of the modified Carothers equation (6.51) gives large numbers approaching infinity for the average DP as the product of p and f approaches 2. Thus, for the reaction of 0.99 mol of difunctional phthalic anhydride with 0.99 mol of ethylene glycol and 0.01 mol of trifunctional glycerol,

$$f = \frac{0.99 \text{ mol} \times 2 + 0.99 \text{ mol} \times 2 + 0.01 \text{ mol} \times 3}{1.99 \text{ mol}} = 2.02$$

Substitution of $r = 2.02$ and $p = 0.95$ into Eq. (6.51) gives an average DP of 25. For $p = 0.97$, the average DP is 50; for $p = 0.99$, the average DP increases to 10,000. This march toward infinity as the product of pf approaches 2 is consistent with the formation of high molecular weight crosslinked products.

In the statistical approach to the requirements for incipient gelation, one introduces a branching coefficient α , which is defined as the probability that a reactant with a value for f of greater than 2.0 is connected to a linear chain segment or to another multifunctional reactant or branch point. The critical value for incipient gelation (α_c) is the probability that one or more of the $f - 1$ chain segments on the branch unit will be connected to another branch unit, i.e., $\alpha_c = (f - 1)^{-1}$ or $1/(f - 1)$. Thus, when $f = 2.2$, $\alpha_c = 0.83$.

Glyptal polyesters were produced in 1901 by heating glycerol and phthalic anhydride. Since the secondary hydroxyl is less active than the terminal primary hydroxyls in glycerol, the first product formed at conversions of less than about 70% is a linear polymer. A crosslinked product is produced by further heating:

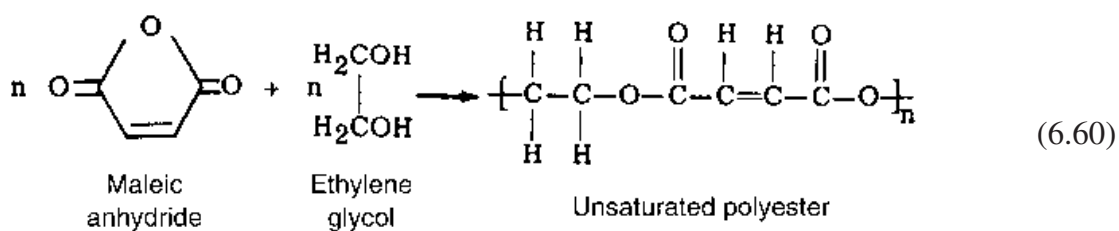


Alkyds were synthesized by Kienle in the 1920s from trifunctional alcohols and dicarboxylic acids. Unsaturated oils called drying oils were transesterified with the phthalic anhydride in the reaction so that an unsaturated polyester was obtained.

The extent of crosslinking or “drying” of these alkyds in the presence of a soluble lead or cobalt catalyst or drier was dependent on the amount of unsaturated oil present. The terms short oil, medium oil, and long oil alkyd are used to signify the “oil length” obtained by use of 30–50%, 50–65%, and 65–80% of unsaturated oil, respectively.

The term alkyd is sometimes used to describe all polyesters produced from the condensation of a polybasic acid and a polyhydric alcohol. Thus, the terms nonoil and oil-free alkyds have been used to distinguish between the principal types of polyesters. The terms saturated and unsaturated polyesters are also widely used. The chain reaction mechanism of the curing of these unsaturated polymers will be discussed in Chapter 15.

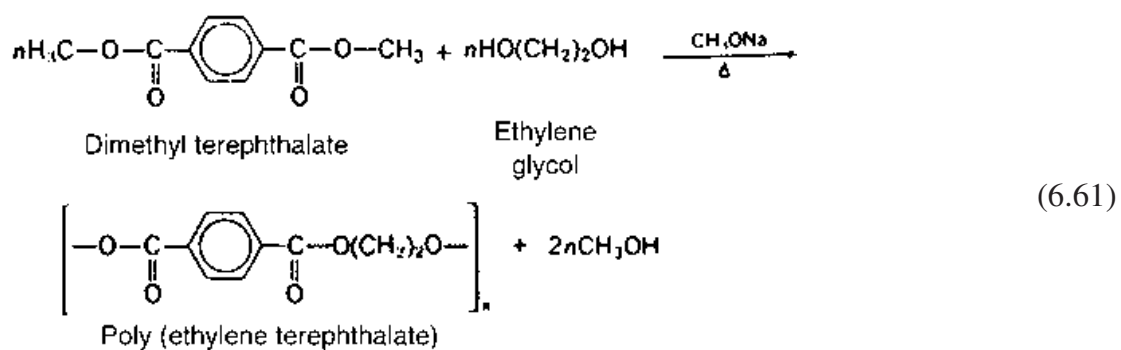
Another type of unsaturated polyester is produced by the condensation of ethylene glycol with phthalic anhydride and maleic anhydride [Eq. (6.60)]. These polyesters may be dissolved in styrene and used as crosslinking resins for the production of fibrous glass–reinforced plastics.



Aromatic polyesters had been successfully synthesized from reaction of ethylene glycol and various aromatic diacids but commercialization awaited a ready inexpensive source of aromatic diacids. An inexpensive process was discovered for the separation of the various xylene isomers by crystallization. The availability of inexpensive xylene isomers allowed the formation of terephthalic acid through the air oxidation of the p-xylene isomer. In 1953, Dupont produced polyester fibers from melt spinning, but it was not until the 1970s that Dupont’s polyester fibers became commercially available.

Expanding on the work of Carothers and Hill on polyesters, in England Whinfield and Dickson overcame the problems of Carothers and coworkers by employing an ester interchange reaction between ethylene glycol and the methyl ester of terephthalic acid forming the polyester poly(ethylene terephthalate) with the first plant coming on line in

1953. This classic reaction producing Dacron, Kodel, and Terylene fibers and Dacron fibers is shown below.



Polyester fibers [poly(ethylene terephthalate), PET, Fig. 6.8], which are now the world's leading synthetic fibers, are produced at an annual rate of over 1.5 million tons in the United States. Thicker oriented films or sheets are used in the manufacture of containers for carbonated drinks.

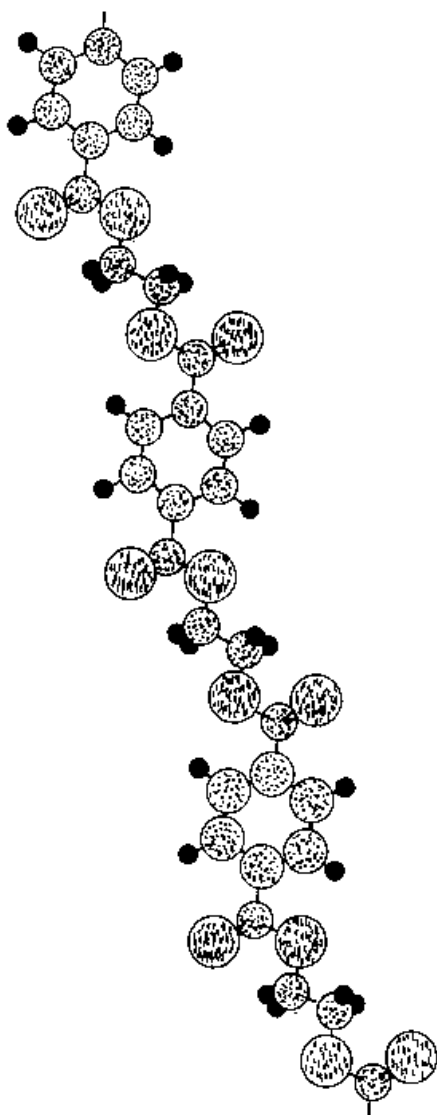


Figure 6.8 Ball-and-stick model of poly(ethylene terephthalate).

PET is generally produced using a two-step process. Dimethyl terephthalate is heated with ethylene glycol giving a mixture of oligomers including dihydroxyethyl terephthalate. The mixture is then heated to over 250°C under vacuum in the presence of a catalyst to give the final product.

Fibers are produced if the product is pushed through a small hole. As the polyester emerges from the hole, tension is applied assisting the polymer chains to align, giving a material with added strength. Crystallization of polyester resin can be achieved through heating to about 190°C followed by slow cooling. Rapid cooling, called *quenching*, produces more amorphous material from which transparent film can be produced.

Film strength is increased through application of heat and pulling of the film. Biaxially oriented PET film is one of the strongest films available. It is used as magnetic film in X-ray and other photographic applications, and in such food applications as food packaging including the boil-in-a-bag foods. Thicker films are used in the manufacture of many of the carbonated single-drink bottles because PET can be injection-molded and because it has low carbon dioxide permeability.

The addition of antinucleating agents permits the injection molding of PET (Rynite). Injection-moldable glycol-modified polyesters (PETG, Kodar) have been produced by partial replacement of the ethylene glycol by cyclohexanol dimethylol.

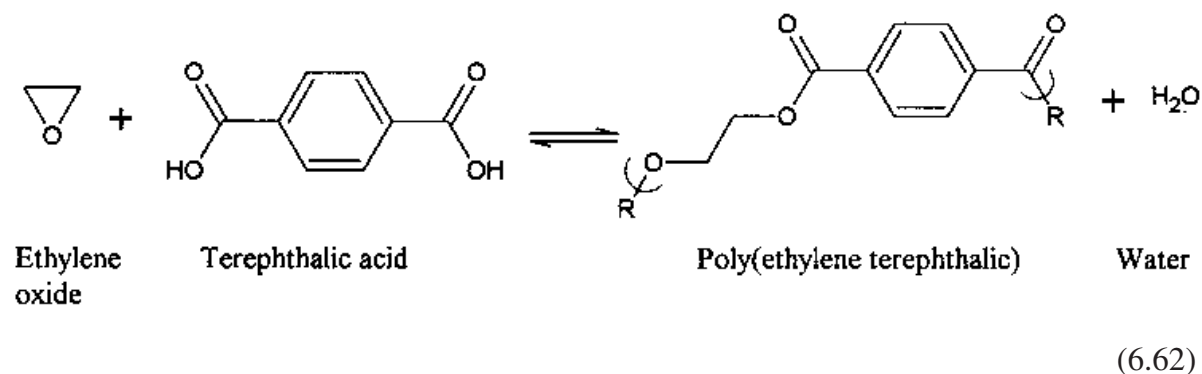
Moldability of aryl polyesters has also been improved by the use of poly(butylene terephthalate) (PBT) instead of PET or by the use of blends of PET and PBT. PBT under the trade names Celanex, Valox, Gafite, and Versel is being produced at an annual rate of 25 thousand tons. Copolymers of carbonate and aryl esters, acrylics and aryl esters, and imide and aryl esters as well as physical blends of polyesters and other polymers are available. These aryl polyesters are being used for bicycle wheels, springs, and blow-molded containers.

A new high-impact blend of PBT and polybutene (Valox CT) is also available. The melt viscosity of blends of PET and nylon-66 has been reduced by the addition of poly(vinyl alcohol). Self-reinforcing PET has been produced by the addition of p-hydroxybenzoic acid, which forms liquid crystals in the composite.

Since PET has a melting point of 240°C, it is difficult to mold. However, PBT produced from butylene glycol has a melting point of 170°C and is more readily molded. It is a strong, highly crystalline engineering plastic.

Floppy disks and hard drives use magnetic material laid on thin flexible sheets made of PET or on stiffer sheets made from glass or aluminum. These sheets can be made quite thin, less than 10 nm.

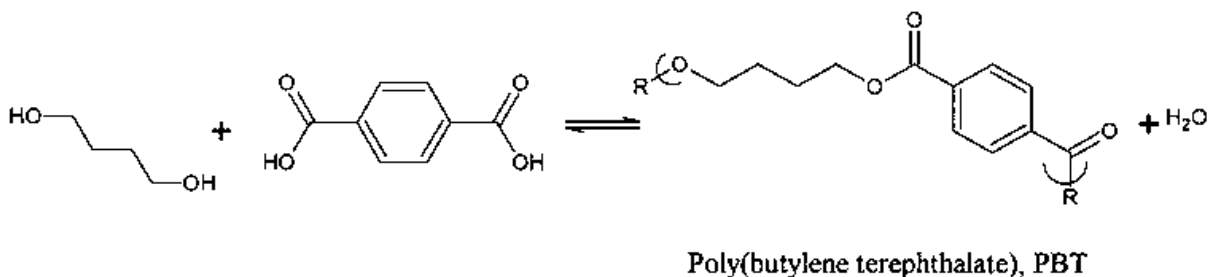
While PET is normally made as described in Eq. (6.61), it can also be made from the ring-opening reaction with ethylene glycol as shown below.



PET is difficult to mold because of its high melting point (T_m 240°C). PBT, because of the addition of two methylene units in the diol-derived portion, is lower melting with

a T_g of about 170°C. PET also crystallizes relatively slowly so that extra care must be exercised to insure that the PET-molded products are fully crystallized or the partial crystallized portions will be preferred sites for cracking, crazing, shrinkage, etc. Thus, nucleating agents and crystallization accelerators have been used to improve the crystallization rate. Postannealing has been used where appropriate.

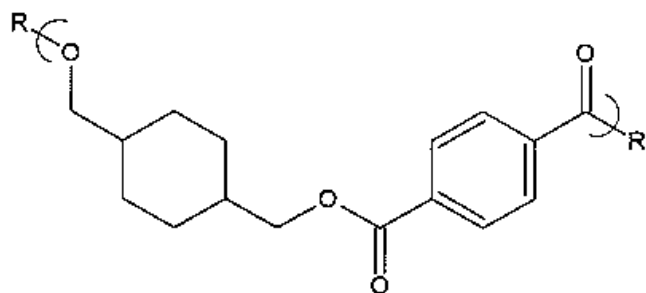
PET is now extensively used as bottling material for soft drinks because of its low carbon dioxide permeability. Carbon dioxide permeability decreases with increasing film thickness and crystallinity. To achieve the necessary crystallinity, partially crystalline PET is employed in the stretch blow molding process with the molding process carried out to promote further crystalline formation.



(6.63)

By comparison, PBT melts at a lower temperature and crystallizes more rapidly and is often employed as a molding compound. PBT offers a balance of properties between nylons and acetals with low moisture absorption, good fatigue resistance, good solvent resistance, extremely good self-lubrication, and good maintenance of physical properties even at relatively high use temperatures. Fiber-reinforced PBT molding compound is sold under the tradename Celanex. A PBT molding compound was first sold under the tradename Valox. Today, there are many PBT molding compounds available.

Poly(dihydroxymethylcyclohexyl terephthalate) was introduced by Eastman Kodak as Kodel in 1958. In comparison to PET and PBT, the insertion of the cyclohexyl moiety gives a more hydrophobic material as well as a more moldable product that can be injected molded. The sole raw material is again dimethyl terephthalate. Reduction of the dimethyl terephthalate gives the dialcohol cyclohexanedimethanol. (Notice the reoccurring theme of reusing or using in a modified form the same readily available and inexpensive materials.) This material, along with blends and mixtures, is often extruded into film and sheeting for packaging. Kodel-type materials are used to package hardware and other heavy items as well as blow molded to produce packaging for shampoos, liquid detergents, etc.



(6.64)

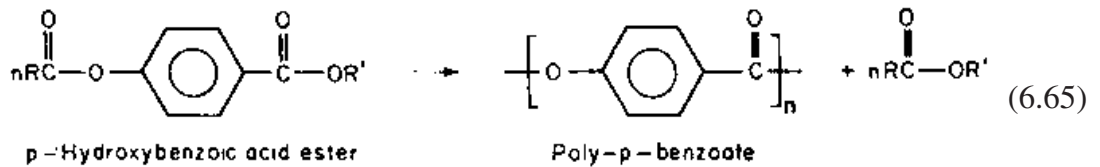
Poly(dihydroxymethylcyclohexyl terephthalate)

The hard-soft block copolymer approach (Sec. 9.4) employed to produce segmental polyurethanes has also been used with polyesters with the hard block formed from 1,4-

butadienediol and terephthalic acid while the soft block is provided from oligomeric (approximate molecular weight of 2000 Daltons) poly(tetramethylene glycol) and is sold under the trade name of Hytrel.

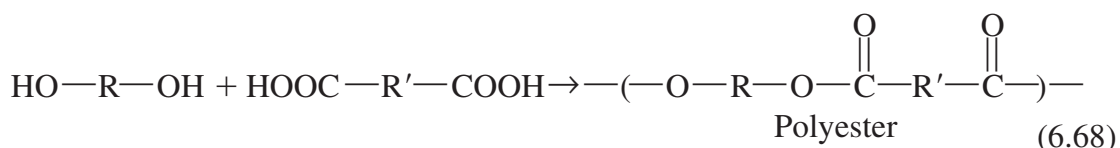
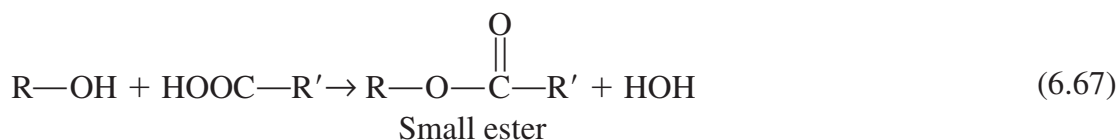
Along with nylons, polyester fibers approach and exceed common natural fibers such as cotton and wool in heat stability, wash-and-wear properties, and wrinkle resistance. Blended textiles from polyester and cotton and wool also can be made to be permanent press and wrinkle resistant. The fibers are typically formed from melt or solvent spinning (Chapter 17). Chemical and physical modification are often employed to produce differing fiber appearances from the same basic fiber material. Self-crimping textiles are made by combining materials with differing shrinkage properties. Different shaped dyes produce materials with varying contours and properties, including hollow fibers.

Several “wholly” aromatic polyesters are available. As expected, they are more difficult to process, stiffer, and less soluble, but are employed because of their good high thermal performance. Ekonol is the homopolymer formed from p-hydroxybenzoic acid. Ekonol has a T_g in excess of 500°C . It is highly crystalline and offers good strength.



6.7 SYNTHETIC POLYAMIDES

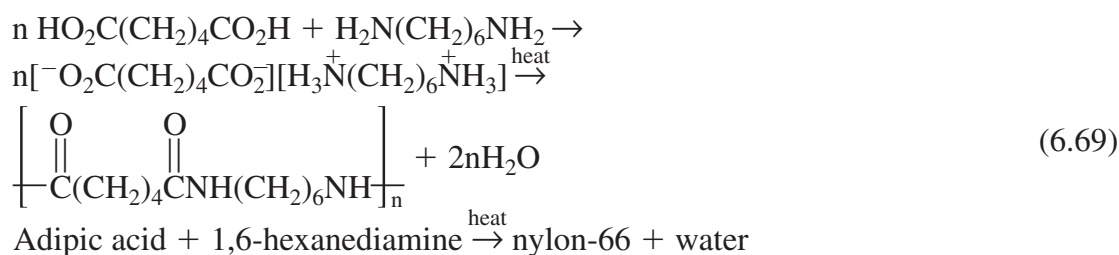
Wallace Hume Carothers was brought to Dupont because his fellow researchers at Harvard and the University of Illinois called him the best synthetic chemist they knew. He started a program aimed at understanding the composition of natural polymers such as silk, cellulose, and rubber. Many of his efforts related to condensation polymers was based on his belief that if a monofunctional reactant reacted in a certain manner forming a small molecule, similar reactions except employing reactants with two reactive groups would form polymers.



While the Carothers group had made both polyesters and polyamides, they initially emphasized work on the polyesters since they were more soluble and easier to work with. One of Carothers' co-workers, Julian Hill, noticed that he could form fibers if he took a soft polyester material on a glass stirring rod and pulled some of it away from the clump. Because the polyesters had too low softening points for use as textiles, the group returned to work with the polyamides. They found that fibers could also be formed by the polyamides similar to those formed by the polyesters. These fibers allowed the formation of fibers that approached, and in some cases surpassed, the strength of natural fibers. This new miracle fiber was introduced at the 1939 New York World's Fair in an exhibit that announced the synthesis of this wonder fiber from "coal, air, and water"—an exaggeration—but nevertheless eye catching. When the polyamides—nylons—were first offered for sale in New York City, on May 15, 1940, over 4 million pairs were sold in the first few hours. Nylon sales took a large drop when it was noted that nylon was needed to produce the parachute material so critical to World War II.

The first polyesters, produced by Carothers, had relatively low molecular weights because of low fractional conversions. Carothers was successful in producing higher molecular weight polymers by shifting the equilibrium by removing the water produced. However, these aliphatic polyesters, which he called “superpolymers,” lacked stiffening groups in the chain and thus had melting points that were too low for laundering and ironing.

Carothers’ next step was to increase the fractional conversion (p) by making salts by the reaction of hexamethylenediamine and adipic acid. These were recrystallizable from ethanol. Thus, a high molecular weight polyamide known generally as nylon, which had a melting point of 265°C, could be produced by the thermal decomposition of this pure, equimolar nylon-66 salt, as shown by

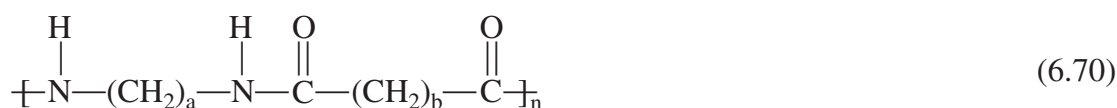


Since the molecular weight of the original nylon-66 produced by Carothers in 1938 was higher than he desired, he added 1% of acetic acid to the reactants in order to reduce the $\overline{\text{DP}}$ value. Because of the stiffening effect of the amide groups, the melting point of nylon-66 is 200°C greater than that of the corresponding polyester. The melting point of nylons (PA) increases as the number of methylene groups between amide groups in the chain are reduced.

In the early 1950s George deMestral was walking in the Swiss countryside. When he got home he noticed that his jacket had a lot of cockleburs on them. For some reason he examined the cockleburs and noticed that they had a lot of tiny “hooks.” His cotton jacket had loops that “held” the cockleburs. He began putting into practice his observations, making combinations of materials with rigid hooks and flexible loops or eyes. The initial hook-and-eye for commercial use was made in France. Today, Velcro, the name given to the hook-and-eye combination, is based on nylon as both the hook and eye material. Remember that nylon can be made to behave as both a fiber and a plastic. Polyester is blended with the nylon to make it stronger. Polyesters have also been employed to make hook-and-eye material. The hook-and-eye material is used to fasten shoes, close space suits, and in many other applications.

Molded nylon-66 is used for lawnmower blades, bicycle wheels, tractor hood extensions, skis for snowmobiles, skate wheels, motorcycle crank cases, bearings, and electrical connections. The radiator in the 1982 model Ford Escort was molded from nylon-66. Mono- and biaxially oriented nylon film is available.

The structure of nylons (e.g., nylon-ab) is



where a and b are equal to the number of carbon atoms in the repeating units of the diamine and dicarboxylic acid.

Nylon-610 and nylon-612 produced by the condensation of hexamethylenediamine and sebacic or dodecanoic acid, respectively, are more resistant to moisture and more ductile than nylon-66. The properties of these polyamides may be improved by the formation of polyether blocks (NBC) and by blending with thermoplastics, such as EPDM, PET, PBT, and TPE.

NBC (Nyrin) is more expensive than RIM polyurethane, but it may be heated to 200°C without softening. NBC moldings are produced by the reaction injection molding (RIM) of poly(propylene glycol) and caprolactam in the presence of a catalyst. The tendency for this copolymer to swell in the presence of water is reduced by reinforcing with glass fibers.

Since the chains of nylons having an even number of carbon atoms between the amide groups pack better, their melting points are higher than comparable nylons with odd numbers of carbon atoms. The melting points decrease and the water resistance increases as the number of methylene groups between amide groups is increased.

Nylon-6, which has a heat deflection temperature of 80°C, was produced by the ring-opening polymerization of caprolactam in Germany in the 1940s. Molded articles made of these polymers may be produced in situ in the RIM process. Nylon-11 and nylon-12, produced by the anionic polymerization of 11 and 12 amino acids, are also characterized by good resistance to moisture and superior ductility. The structure of the repeating unit in monadic nylons, such as nylon-6, is:



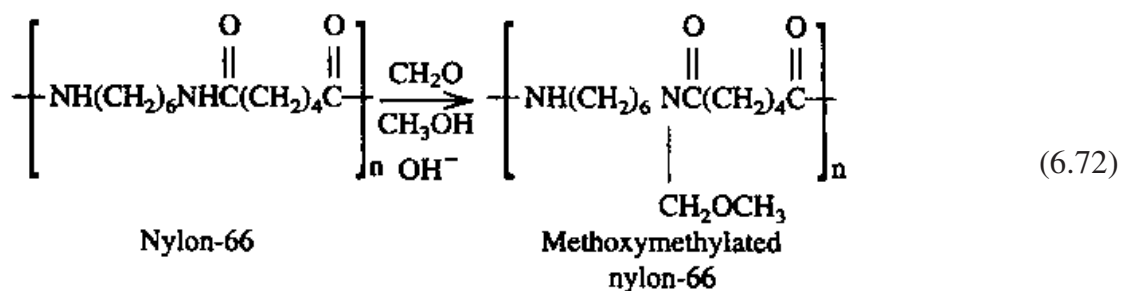
The copolymer of nylon-6 and nylon-66 is tougher and has a smoother surface than either of the homopolymers.

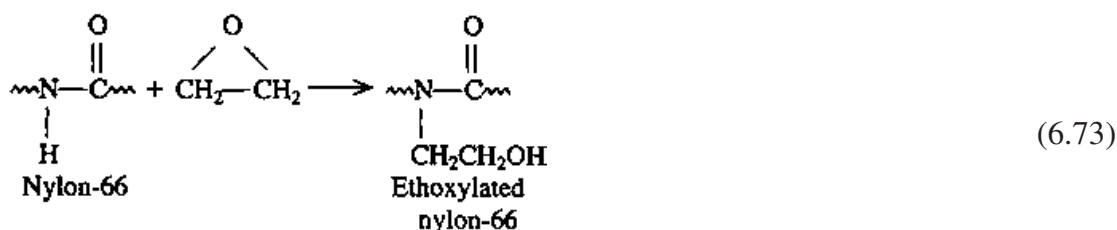
Injection-moldable, yellow, transparent polyamide (PA7030) is also available.

The aromatic polyamides (aramids) have been produced by the interfacial condensation of aromatic diamines, such as 1,3-phenylenediamine and isophthaloyl chloride in chloroform. Amorphous transparent aramids with heat deflection temperatures of 160°C have been produced from 2,2-bis-4-(aminocyclohexyl)propane.

Aromatic nylons prepared from terephthalic acid (Kevlar) have very high melting points and are called aramids. The solubility and ease of fabrication of aramids is improved by the preparation of ordered copolyamides. For example, a copolymer consisting of metabenzamide and isophthalamide units is more readily processed than poly(orthophenylene phthalamide).

Because of the presence of the bulky methoxymethyl pendant group, the hydrogen-bonding forces are reduced, the melting point is reduced, and the flexibility is increased in methoxymethylated nylon-66. Comparable results are observed when nylon-66 is condensed with ethylene oxide. The equations for these reactions are shown below.





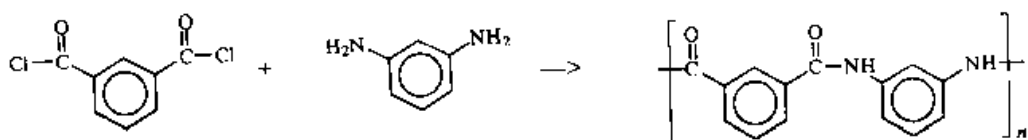
Comparable changes in physical properties are observed when branched dicarboxylic acids and branched diamines are used as the reactants for producing nylons. Thus, nylons produced from α -methyladipic acid and hexamethylenediamine and from adipic acid and 3-methylhexamethylenediamine have melting points that are at least 80°C less than that of nylon-66. These nylons are not suitable for fiber use because of the presence of branches on the chain.

Nylon-6,6 is the dominant (sales-wise) nylon in the United States while nylon-6 is the dominant nylon in Europe.

While aliphatic-containing polyamides are given the name nylons, those in which at least 85% of the amide groups are attached to an aromatic are called aramids. Aramids are stronger and tougher than nylons but they are also more difficult to solubilize and fabricate. Because the presence of the aromatic groups causes the aramids to be stiff, they often form liquid crystals that are present in a nematic liquid crystal state in concentrated solution.

Aramids are generally prepared by the solution or interfacial polycondensation of meta- and para-substituted diacid chlorides and/or diamines. In some systems, synthesis is achieved under rapid stirring conditions where the polymer is quasi-soluble in the system. The polymer mixture is forced through a small opening into a nonsolvent forming a fiber without the need to dissolve the polymer before fiber formation.

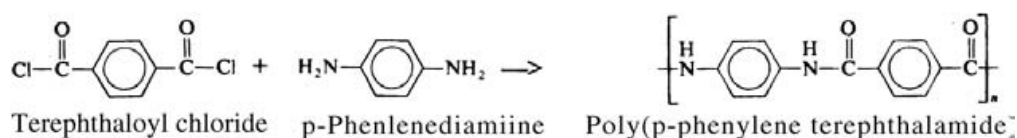
Poly(m-phenylene isophthalamide), sold under the trade name Nomex, exhibits good thermal stability, decomposing above 370°C. It is used in flame-resistant clothing. It is also used in the form of thin pads to protect sintered silica-fiber mats from stress and vibrations during the flight of the space shuttle.



Isophthaloyl chloride m-Phenylenediamine Poly(m-phenylene isophthalamide)

(6.74)

The corresponding aramid produced using the para reactant in place of the meta gives poly(p-phenylene terephthalamide) (PPT), produced under the tradename Kevlar. It also exhibits good thermal stability decomposing above about 500°C. By weight it has a higher strength and modulus than steel and is used in the manufacture of so-called bullet-proof clothing. Because of its outstanding strength, it was used as the skin covering of the Gossamer Albatross which was flown, using only human power, across the English Channel.

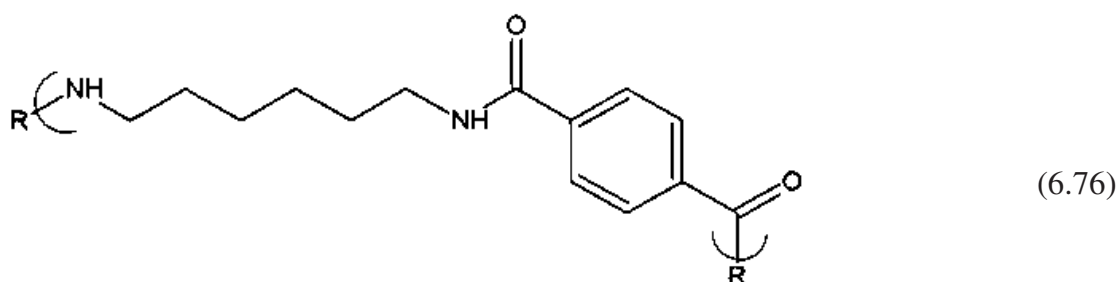


Terephthaloyl chloride p-Phenylenediamine Poly(p-phenylene terephthalamide)

(6.75)

Aramids are also used as fiber reinforcement in composites and as tire cord.

Several so-called semiaromatic nylons have been produced. Nylon 6, T is produced from condensation of terephthalic acid and 1,6-hexanediamine (below). Both reactants are readily available and inexpensive and the resulting materials offer greater strength than simply wholly aliphatic nylons such as nylon 6,6. Nylon 6,T has a very high T_m of 370°C and a T_g of 180°C. The high T_m results in the need for a high temperature to be employed in processing so that a third reactant is often introduced to lower the T_m and the needed processing temperature. “Third reactants” often used are adipic acid, caprolactam, isophthalic acid, and 1,5-hexyl diamine. These materials are sold under the tradenames of Zytel HTN, Ultramid T, and Amodel R.



Nylon 6, T

Nylons offered new challenges to the chemical industry. Because of the presence of polar groups the attractive forces between chains was high in comparison to vinyl polymers. Nylons are generally semicrystalline, meaning they have a good amount of order. Thus, while they have a T_g , the main physical transition is the T_m so that they undergo a sharper transition from solid to melt in comparison to many of the vinyl polymers discussed in the next three chapters. Thus, the processing temperature window is more narrow. If melt flow is required for processing, then the temperature must be high enough to allow for ready flow but low enough so as not to break primary bonds within the processed material. Even so, processing techniques have been developed that allow nylons to be readily processed using most of the standard techniques.

The presence of the polar groups result in materials with relatively high T_g and T_m values so that unlike many vinyl polymers that must be above their T_g to allow needed flexibility, nylons, and many condensation polymers function best where strength, and not flexibility, is the desired behavior.

Because of the presence of these polar groups that also allow for hydrogen bonding, nylons and most condensation polymers are stronger, more rigid and brittle, and tougher in comparison to most vinyl polymers. Nylons are also “lubrication-free” meaning they do not need a lubricant for easy mobility so that they can be used as mechanical bearings and gears without need for periodic lubrication.

In general, more crystalline nylons are fibrous while less crystalline nylon materials are more plastic in behavior. The amount of crystallinity is controlled through a variety of means including introduction of bulky groups and asymmetric units, rapid cooling of nonaligned melts, and introduction of plasticizing materials. The theme of using asymmetric units was used by Grace and Company in developing Trogamid T, an amorphous transparent nylon, from the condensation of terephthalic acid with a mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diamines.