

Polyesters and polyamides

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Polyesters and polyamides

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2.1 Introduction

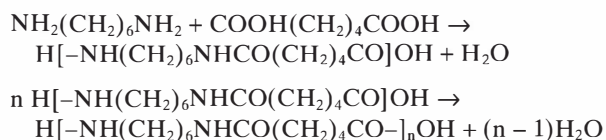
Nylon is a generic word representing a class of polymers as polyamides. Nylon was a product of a basic research started by Wallace Corothers at DuPont in 1928. The polymer age really started when the new synthetic nylon fiber was introduced in the market in 1938. Nylon captured public imagination, as four million pairs of nylon stockings were sold in the first few hours of sale on May 15, 1940. During World War II, nylon fabrics were used as waterproof tents, lightweight parachutes among other things. In the process an important principle was established that it is possible to chemically link hundreds of simple molecules of a kind or more, to make polymers with unique set of properties. One interesting example is the ability of molten polymer undergoing large deformations, which allows continuous production of fine filaments from thicker extrudates and this property of deformation is in turn connected to cumulative interactions of long chain polymeric molecules.

The word nylon was introduced to signify the fineness of the filament i.e. a pound of nylon could be converted to the length equal to the distance between New York (NY) and London (LON). A variety of polyamides are presently manufactured and marketed under several different trade names. Among them nylon 6 and nylon 66 are the two most manufactured polyamides. There are several other nylons such as nylon 46, nylon 610, nylon 612, nylon 10, and nylon 12 which are used for specialized applications.

In general, there are two types of nylons, i.e. nylon XY, and nylon Z. Nylon 66 and nylon 6 are the examples of these two types respectively. In nylon XY type, the X refers to the number of carbon atoms in the diamine monomer, whereas, Y represents the number of carbon atoms in diacid monomer. In nylon Z type, Z refers to the number of carbon atoms in the monomer.

2.2 Nylon 66

Nylon 66 type nylons are synthesized from a diacid and diamine. For nylon 66, hexamethylene diamine (H) and adipic acid (A) are reacted to form H-A salt. The salt is polymerized to produce nylon 66 in the following manner.



The purity of raw material is important in the polymer production and the specifications of these raw materials have been reported [1]. Hexamethylene diamine should be in the crystalline form with melting point of 40°C and boiling point of 204–205°C. Adipic acid is in the white crystalline form with acid number of 368, with melting and boiling point of 152° and 216°C. The color, iron and water content are also controlled.

In the production process, the two monomers of nylon 66 are taken in the molar ratio of 1 : 1. These two components are reacted in methanol at elevated temperature, to obtain the salt which precipitates from methanol solution. The H-A salt is dissolved in water at concentration of 60%. The solution is heated to around 250°C for polycondensation for production of nylon 66. Loss of water in the process of polymerization should be taken into account for the net recovery of polymer [2]. Nylon 66 was earlier produced via a batch process with intermediate H-A salt. However, now the continuous process of production is favored for conversion of monomer to polymer.

To achieve desired molecular weights of the polymers, stabilization processes are used. This is achieved by taking slightly different than equivalent quantities of diacids and diamines. Say an excess of 1 percent of diacids is taken during the polymerization process, at a point of time, all long chain molecules will have carboxylic acid groups at both ends and polymerization does not proceed further. Thus an excess of one of the monomers decides the range of molecular weights achieved in the polymer. An equimolar ratio of 1 diamine to 1.015 diacid gives a polymer with a number average molecular weight of ~18000. This can also be achieved by adding say 1% of mono-functional reagent, such as acetic acid to equimolar quantities of diacids and diamines. Another method to make polyamides could be by using amino acids with one end as an amino group and another end as carboxylic acid. Typically, diamine and diacids are preferred for production of nylons as it is easier and cheaper to make these monomers compared to amino acids. There is no difficulty in making the monomers for making

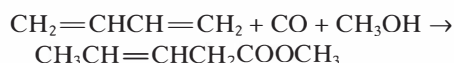
the typical polyamides and usually there are several different routes to select one, depending on the price and availability of raw materials.

2.2.1 Monomer synthesis for nylon 66

Adipic acid

The principal commercial processes are based on the oxidation of cyclohexane, which usually proceeds in two stages. The first step entails oxidation with air, yielding either a mixture of cyclohexanone and cyclohexanol or predominantly cyclohexanol. These reaction products are oxidized in second stage with nitric acid to adipic acid. This process employs a soluble cobalt oxidation catalyst, reaction temperatures in the range of 150°–160°C, pressures between 800 to 1000 kPa, and catalyst concentrations of 0.3–3 ppm.

An interesting approach involves a two-step carbonylation of butadiene. In the first step butadiene is reacted with carbon monoxide and methanol in the presence of dicobaltoctacarbonyl and heterocyclic structure containing a tertiary nitrogen moiety (pyridines, picolines, quinolines, isoquinoline):



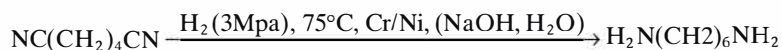
This reaction is carried out at 120°C and at pressure of 60 MPa. After removal of unreacted butadiene, the second step carbonylation is carried out at about 185°C and 3 MPa:



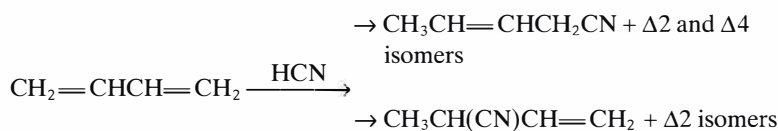
The dimethyl adipate is isolated by distillation and converted to adipic acid by hydrolysis.

Hexamethylene diamine

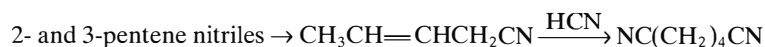
The commercial processes for manufacture of hexamethylene diamine entail hydrogenation of adiponitrile. It is a continuous liquid phase process that is usually conducted at 75°C and 3 MPa pressure in the presence of chromium containing Raney nickel catalyst and aqueous sodium hydroxide:



A newer DuPont process is characterized by the direct addition of HCN to butadiene. It is essentially a two stage process. The first step is a vapor phase operation. A gaseous mixture of butadiene, hydrogen cyanide, nitrogen, and hydrochloride in a ratio of 1:1:1:0.1 is contacted at about 215°C and atmospheric pressure with a copper magnesium chromite fixed bed catalyst for about 50 min:



The second step entails catalytic isomerization of the 2- and 3-pentene nitriles to 4-pentene nitrile, and the addition of a second mole of HCN:



2.3 Nylon 6

Nylon 6 is a nylon Z type of polymer, where the Z represents the number of carbon atoms in the monomer. Nylon 6 is typically produced from caprolactam in the following manner.



The purity of the caprolactam is critically assessed for the production of nylon 6 polymer. The specificities of the monomer are freezing point 69°C; permanganate number 71; molar ratio %; iron content as 0.5 ppm. Detailed analytical methods for purity analysis are reported in literature [3–5].

Caprolactam requires a catalyst, which converts small amounts of caprolactam to ε-aminocaproic acid which helps in polymerization process. The catalyst could be water, where the control of reaction is easy. Acid or base catalyst system may also be used, where the base catalyst system has the advantage of high production rate, high molecular weight, although the control of reaction in the system is rather critical. Some characteristics of catalyst system [6] are given in [Table 2.1](#).

2.3.1 Molecular weight in water catalyst system

In a water catalyst system the critical parameters during reaction are temperature of 225–285°C, amount of water 5–10% and stabilizer content of 1% and time of polymerization.

Table 2.1 Influence of catalyst system on nylon 6 production

Parameter	Catalyst systems		
	Acid	Base	Water
Type	Strong, e.g. hydrochloric acid or their salts	Carbonate, hydride, alcoholate and hydroxide of alkali and alkaline earth metals	–
Rate	Fast	Very fast	Slow
Special condition	Anhydrous	Anhydrous	–
Yield	Low	High	High
Use	Not used commercially	Shows promise	Commercially used

The DP of Nylon 6 is governed by the following relationship

$$DP = (p + r + q)/(1 + r) (1 - p)$$

where

$$p = 1 - \{(X + Y)/(X_0 + Y_0)\}$$

$$q = X_{00}/X_0$$

and $r = Y_0/X_0$

Here X_0 and X represents the carboxyl group concentration at the start of polymerization and after some time, t , respectively. Y_0 and Y represent the amino group concentrations at the initial and final stage, respectively. X_{00} represents the initial concentration of carboxyl group of a monofunctional acid acting as a stabilizer. Acetic acid is typically used as a stabilizer.

2.3.2 Monomer synthesis for nylon 6

Caprolactam

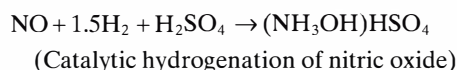
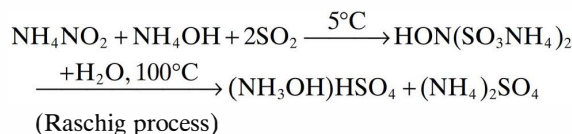
There are three important commercial processes for the caprolactam synthesis and all processes start from materials that belong to the group consisting of phenol, benzene, toluene, and cyclohexane. The principal intermediates are cyclohexanone and cyclohexanone oxime for process 1, cyclohexanone oxime for process 2, and cyclohexane carboxylic acid for process 3. The cyclohexanone may be produced by any of the following methods:

1. Catalytic hydrogenation of phenol and subsequent dehydrogenation of the resulting cyclohexanol.
2. One step catalytic hydrogenation of phenol using a palladium on carbon catalyst.
3. Catalytic oxidation (air) of cyclohexane to a cyclohexanol/cyclohexanone mixture.
4. Reductive catalytic hydrolysis of cyclohexylamine in one stage operation.

Though process 1 is still practiced, 2 and 3 are the most significant commercial processes. Cyclohexanone oxime may be produced by any of the following methods.

1. Reaction of cyclohexanone with hydroxylamine (process 1).
2. Photonitrosation of cyclohexane with nitrosyl chloride (PNC process) (process 2).

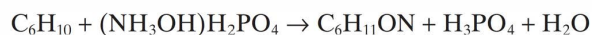
The hydroxylamine used for the reaction with cyclohexanone is obtained by the Raschig process or by catalytic hydrogenation of either nitric oxide or nitric acid.



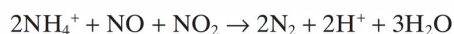
The catalytic hydrogenation of nitrate ions involves Pd/C as catalyst in a phosphoric acid ammonium hydrogen phosphate buffering system:



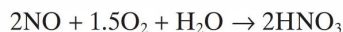
Since the hydroxyl ammonium ion is unstable, the reaction product is directly contacted with cyclohexanone in a toluene solution to effect formation of cyclohexanone oxime:



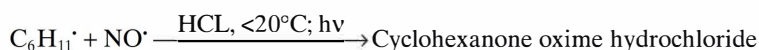
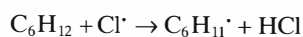
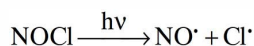
The aqueous H_3PO_4 – $\text{NH}_4\text{H}_2\text{PO}_4$ solution is reacted with a mixture of NO and NO_2 which results in the conversion of any ammonium ions to nitrogen:



Simultaneous introduction of air results in the formation of nitric acid which is recycled in the process.



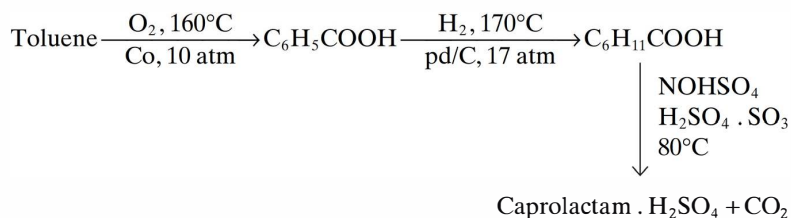
An interesting process developed and operated since 1962 by Toray for manufacturing cyclohexanone oxime is the photo-nitrosyl chlorination (PNC) process. This process may be explained by the following mechanism:



The nitrosyl chloride for synthesis is obtained by a sequence of reactions that includes:

1. Oxidation of ammonia: $2\text{NH}_3 + 3\text{O}_2 \rightarrow \text{NO}.\text{NO}_2 + 3\text{H}_2\text{O}$
2. Formation of nitrosyl sulfuric acid: $2\text{H}_2\text{SO}_4 + \text{NO}.\text{NO}_2 \rightarrow 2\text{NOHSO}_4 + \text{H}_2\text{O}$
3. Sulfuric acid regeneration: $\text{NOHSO}_4 + \text{HCl} \rightarrow \text{NOCl} + \text{H}_2\text{SO}_4$

Toluene is the starting material of a commercial process 3 developed by SNIA Viscosa. It involves the following reactions:



Reaction of cyclohexane carboxylic acid with nitrosylsulfuric acid in oleum results directly in the formation of caprolactam sulphate by a mechanism that entails simultaneous nitrosation, decarboxylation, and rearrangement of the formed oxime.

2.3.3 Molecular weights suitable for filament production

With appropriate molecular weights, it is possible to produce filaments through melt spinning process. Typically the number average molecular weight used for fiber production process is 18000–20000. Technical grade nylons are made from 24000–26000 number average molecular weight polymers. These high molecular weight nylons are produced by solid state

polymerization from low molecular weight chips obtained through melt polycondensation process [7].

2.4 Thermal properties of nylon fibers

2.4.1 Glass transition temperature

Glass transition temperature (T_g) is associated with amorphous regions and has a significant effect on both processing and physical properties of nylon filaments. The segmental mobility during glass transition in nylon is associated with both flexibility of $-(CH_2)_n-$ sections, as well as to inter- and intra-molecular hydrogen bonding in the molecular chains. In nylon fibers, the most critical parameter for T_g is moisture regain, which is associated with flexibility introduced by water molecules acting as plasticizer. Amorphous nylon 6 has T_g varying from around -10°C in wet conditions to around 90°C in dry conditions. T_g also depends on number of (CH_2) units: as (CH_2) unit increases, T_g decreases [8]. In the semi-crystalline state of the filament, glass transition temperature is highly dependent on crystallinity, orientation as well as on moisture regain and the rates of testing. Typical T_g values for nylon filaments are in the range of 40°C to 55°C and increase to around 90°C in dry conditions. Dynamic mechanical methods give higher value of T_g by $20^\circ\text{--}30^\circ\text{C}$, as compared to DSC method.

In the melt spinning process, essentially dry nylon is melted and spun in filament form. Filaments absorb moisture in the various steps of production process, i.e. during quenching, spin finish application and further processing. Thus, T_g dependence on varying moisture conditions during production processes is quite critical. T_g is known to have a non-linear relationship with moisture regain for amorphous nylons [9–12]. There have been several attempts to explain the T_g and moisture regain relationship [10, 13–15]; a reasonable explanation is obtained by three step moisture absorption [12] by nylons. The nature of absorption of molecules [16] is shown in Figure 2.1. In the process of moisture absorption from dry nylon, the initial water molecules form double hydrogen bonds between two carbonyl groups by means of free electron pairs on oxygen atoms and may be assessed as firmly bound. Water molecules are also attached by replacing the hydrogen bond between two carbonyl and amide groups and may be classified as loosely bound molecules. Further absorption can take place by multilayer formation of water molecules. These three different kinds of water molecules affect the T_g in a very different manner and this in turn affects the processing and properties of nylon fibers.

In the case of drawn nylons, some of the observations on T_g vs. regain are still valid. The results on linear expansion coefficients of Nylon 6 both parallel and perpendicular demonstrate this [17]. With increasing moisture