

4.12. FIBRE SPINNING

'Spinning' is the process by which fibres are made from the polymers. There are three methods of spinning :

- (1) melt spinning
- (2) dry spinning
- (3) wet spinning

In the first process, the polymer is used in the molten state, while in the second and third process, it is used as a solution in a suitable solvent. In all the three cases, a spinneret is used for spinning which is a special kind of plate with extremely fine holes for the fibres to emerge.

(1) **Melt-spinning** : A diagram of melt-spinning process is given below :

Polymer chips are electrically heated and melted in a heating grid. Thus the solid polymer is converted into a viscous mobile liquid. The molten polymer then enters in a metering pump which pumps

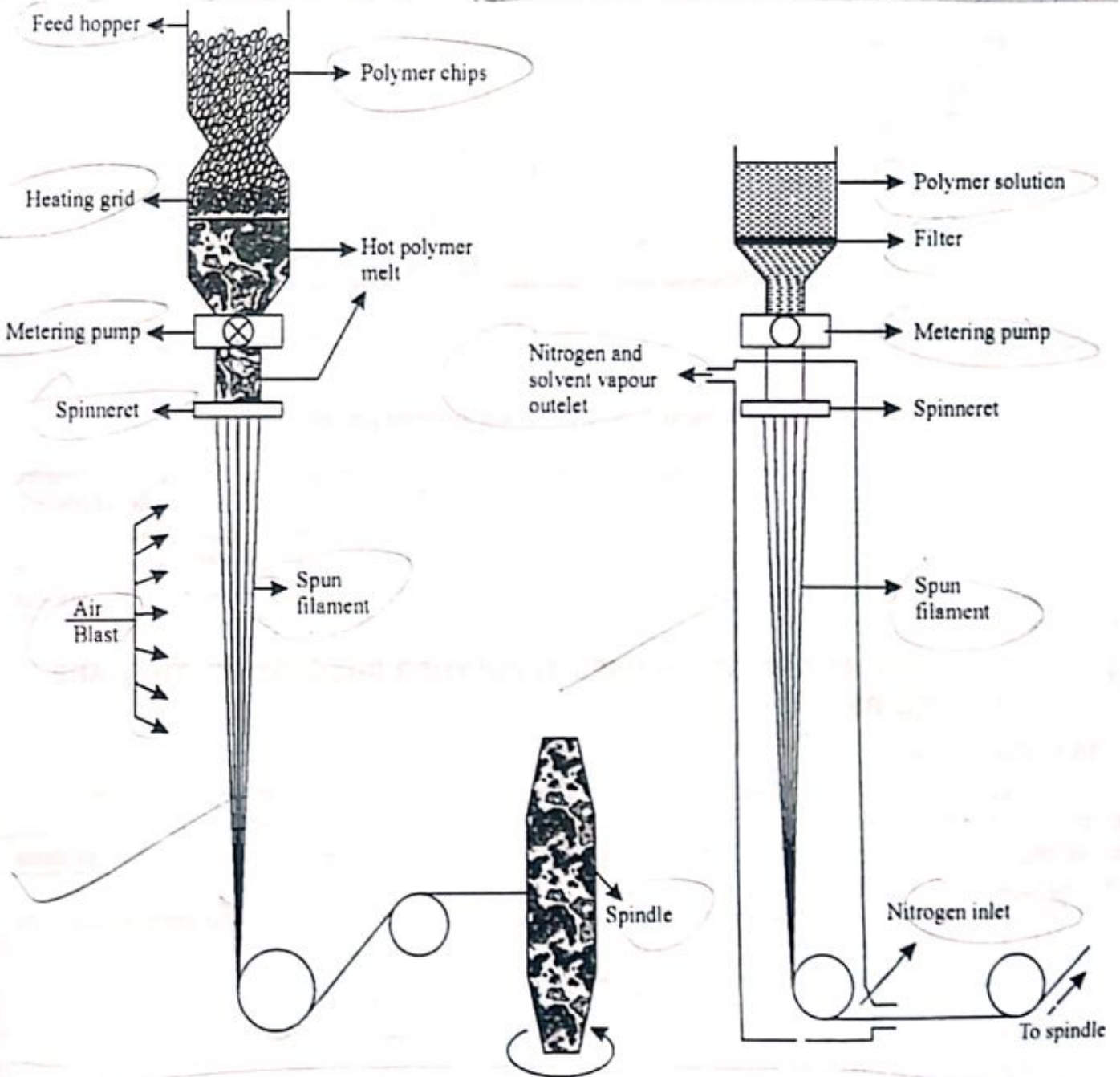


Fig. 11. Schematic diagrams of melt-spinning and dry spinning processes, respectively

the polymer melt through the spinneret at a specified rate, from where continuous and very fine filaments emerge which solidifies in contact with cold air. The solid filaments emerging from the spinneret are then mould upon the spindles.

(2) **Dry-spinning** : A diagram of the process is shown (Fig. 11).

The polymer is dissolved in a suitable solvent to get a solution of high concentration. It is then pumped through the spinneret when fine continuous jets of the solution emerge. The filament is formed from these jets by the evaporation of the solvent. A current of dry nitrogen is passed, as shown in the figure.

It enhances the solvent evaporation. Filaments formed from the polymer solution ultimately reach the spindle where they are wound. Dry spinning process is employed to make fibres from polyvinyl chloride or poly acrylonitrile.

(3) **Wet-spinning** : An outline of the process is given in the diagram.

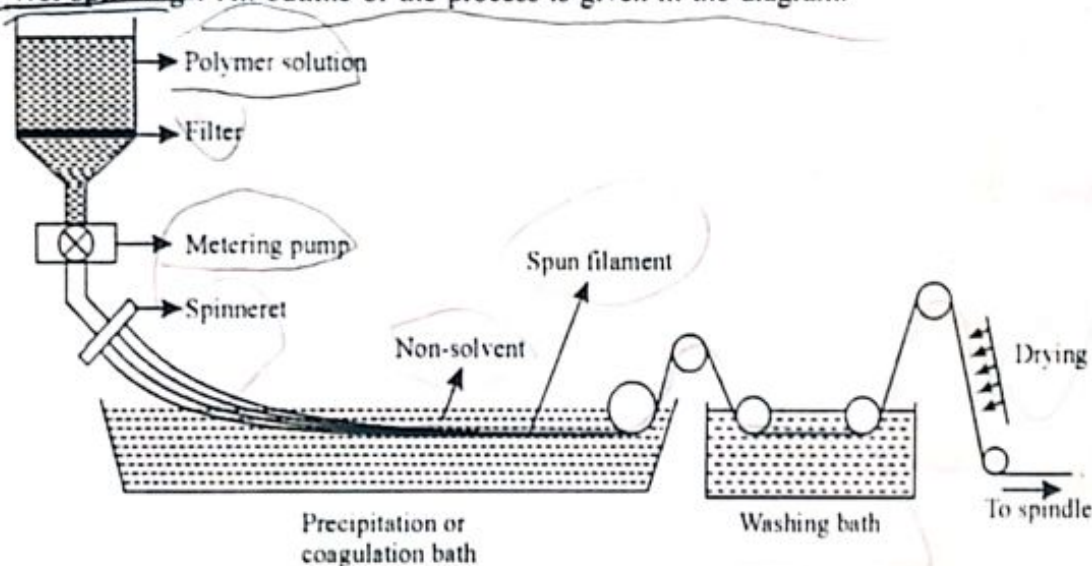


Fig. 12. Schematic diagram of wet spinning process

Here also, concentrated polymer solution is converted into fine jets by passing through the spinneret. These jets are passed into a precipitation bath containing a large volume of a non-solvent which can precipitate the polymer from its solution. When continuous jets of the polymer solution come in contact with a non-solvent, they precipitate in the form of fine filaments. The filaments are collected on a spindle after undergoing washing and drying. Wet-spinning process is used to make fibres from cellulose, viscous rayon, polyacrylonitrile etc.

4.13. CERTAIN TERMS ARE OFTEN USED IN POLYMER PROCESSING, THEY ARE EXPLAINED BELOW IN BRIEF :

4.13.1. Plasticisers :

Plasticisers are added to plastics to improve flow and, therefore, processability and to reduce the brittleness of the product. This is achieved by lowering the glass transition temperature below room temperature, thus achieving a change in properties from those of a hard, brittle, glass like solid to those of a soft, flexible, tough material.

The basic requirements that must be met by a plasticiser are compatibility and permanence. The plasticiser must be miscible with the polymer.

Few example of plasticisers are given below :

- (1) Phthalate esters : It is a dominant plasticiser for polyvinyl chloride.
- (2) Adipates, oleates and sebacates are used in vinyl resins for improving low-temperature flexibility.
- (3) Epoxy plasticisers.

4.13.2. Antioxidants

The role of antioxidants is to prevent the oxidation of polymers. They are substances which, itself are readily oxidised. Common antioxidants are phenols, aromatic amines, and salts and condensation products of amines with aldehydes, ketones and thio compounds.

4.13.3. Colourants

Colourants for plastics include a wide variety of inorganic and organic materials. They may be oil-soluble dyes, organic pigments such as phthalocyanines. Inorganic pigments may also be used as colourants. Common example of colourants are titanium dioxide and barium sulphate (white), phthalocyanine blues and greens, ultramarine blues, chrome greens, cadmium reds and yellows, ironoxide and chrome yellows, carbon black etc.

4.13.4. Stabilisers

Stabilisers are almost invariably added to improve the heat and light stability of the polymer. Metallic salts of lead, barium, tin or cadmium are used as stabilisers.

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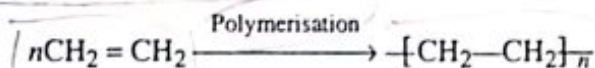
PROPERTIES OF COMMERCIAL POLYMERS

5.1. POLYETHYLENE

The bulk polymer polyethylene is used on such a large scale and in so many applications that it is difficult to sum up specific properties within the constraints of this Primer, particularly since continued development and improvement has resulted in widespread usage as copolymers, blends, composites or after post-polymerisation modification.

Polyethylene has complexities in various forms : low-density (LDPE), high-density (HDPE), ultra high molecular weight (UHMWDE) as well as copolymers such as linear-high-density (LHDPE) (a copolymer with a substituted alkene to limit branching), EVA (a copolymer with vinylacetate), ionomers (copolymer with low amounts of methacrylic acid in which divalent metals such as Mg^{2+} form ionic cross-links between chains to give strength).

Polyethylene is obtained by the polymerisation of ethylene.



There are two varieties of polyethylene viz. low density and high density. Low density consists of molecules with branches whereas the high density variety is linear.

LDPE : When ethylene is polymerised at a high pressure (approximately 1500 atmospheres) and in the temperature range of 180-250°C in the presence of free radical initiators like oxygen or peroxides, low density polyethylene (LDPE) is produced. The presence of branches in the polyethylene molecule does not allow it to pack close together, and hence its density is low.

Low density polyethylene films are mainly used for packing and wrapping frozen food, textile products etc. Its inertness to chemicals and resistance to breakage is made use of in "Squeeze bottles" and in many attractive containers. Pipes made of LDPE are used for both agricultural irrigation and domestic water line connections. Due to its non-polar nature it is used for providing insulations to electric cables.

HDPE : It is produced by following two methods :

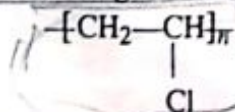
(i) Ethylene is polymerised under 6-7 atmospheric pressure at 60-70° in the presence of a Ziegler catalyst e.g. triethyl aluminium ($AlEt_3$) and titanium tetrachloride ($TiCl_4$) dispersed in an inert solvent such as heptane.

(ii) Ethylene is polymerised under 35 atmospheric pressure at a temperature of 60-200° in the presence of metal oxide catalysts such as chromium or molybdenum oxides supported over alumina-silica bases.

The polyethylene molecules produced by these methods are linear and since the linear molecules can pack themselves, the density of these polyethylene molecules is high. HDPE are more stiffer and harder and possess a greater tensile strength. It is used in the manufacture of toys and other household articles.

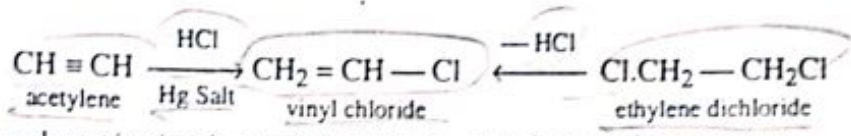
5.2. POLYVINYL CHORIDE

The polymer has the following structure :



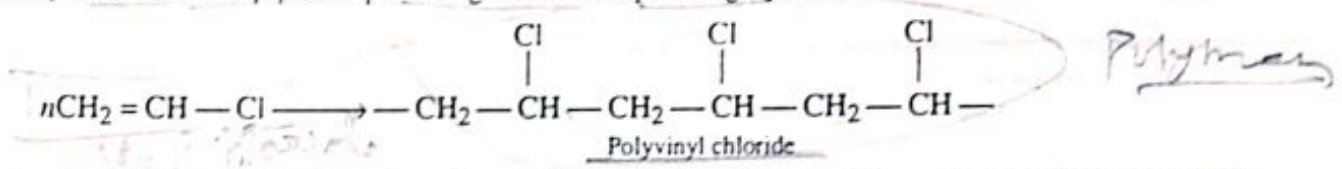
The monomer, vinyl chloride may be prepared by the following two methods :

PVC is also known as Koroseal 119

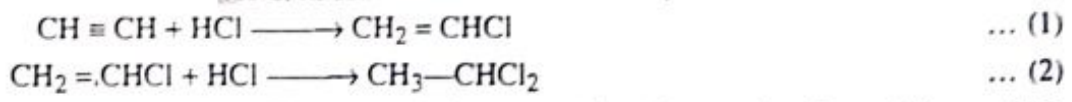
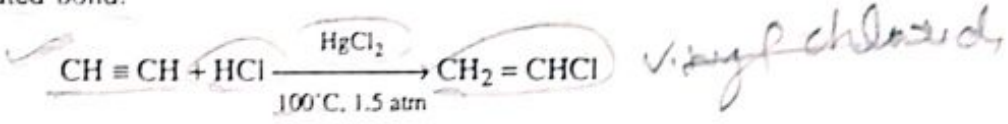


The polymerisation is carried out in an autoclave under pressure.

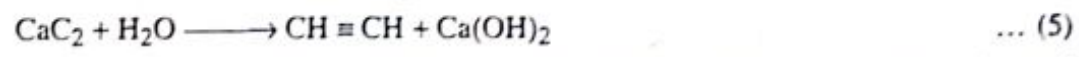
PVC is one of the cheapest and most widely used plastics. It is used for the large scale production of cable insulations, equipment parts and laminated materials. PVC polymer is also known as Koroseal and is widely used as PVC pipes in plumbing and lawn sprinkling systems.



Production of vinyl chloride requires the addition of hydrochloric acid to acetylene. Optimisation of the process is necessary (appropriate catalysts and temperature control) to avoid second addition to the remaining unsaturated bond.



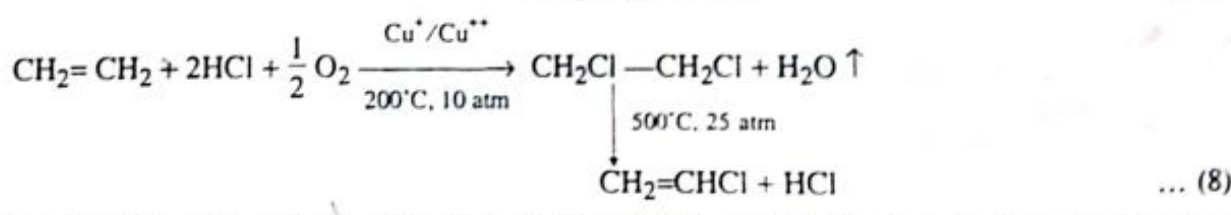
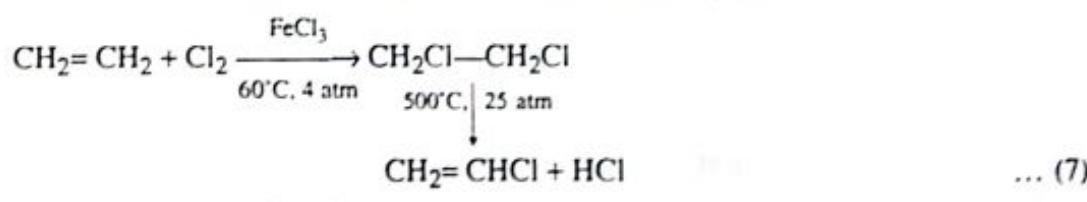
Acetylene was obtained from chalk and limestone by heating with carbon to give first calcium carbide and then reacting with water to produce ethylene gas.



More recently, acetylene has been obtained as a product of catalytic cracking and reforming of natural gas, although the procedure is more complex.



There is an interesting economic point in vinylchloride preparation, since chlorine (prepared by electrolysis of NaCl) is a relatively expensive feedstock. The reaction in equation (7) wastes one chlorine atom as an HCl by product while the reaction (8) requires HCl as the main product.



Straight poly (vinyl chloride) is a colourless rigid material. It has a relatively high density and low softening point. Poly (vinylchloride) has a higher dielectric constant and power factor than polyethylene

owing to the polar carbon-chlorine bond. However, at the temperatures below the glass transition temperature (80°C) the power factor is still comparatively low due to the immobility of the dipole. The high chlorine content of the polymer renders it **flame retarding**. Poly (vinylchloride) is soluble at room temperature in oxygen-containing solvents such as ethers, e.g., dioxane, THF; ketones, e.g., cyclohexanone, methyl isobutyl ketone; and nitrocompounds, e.g., nitrobenzene. Poly (vinyl chloride) is also soluble in ethylene dichloride. Plasticisers for this polymer includes alkyl phthalates (di-isooctyl phthalate, aryl phthalates), tritotyl phosphate, dibutyl sebacate.

Poly (vinyl chloride) is unaffected by acids, alkalis and aqueous solutions; even strong oxidising agents such as chromic acid and nitric acids have little action.

Poly (vinylchloride) undergoes thermal and photochemical degradation. The result of degradation is discolouration and change in mechanical properties.

5.3. POLYAMIDES

Polyamides are defined as polymers which contain recurring amide group ($-\text{CO}-\text{NH}-$) in the main polymer chain. Various types of polyamides fall within this definition.

The most important commercial polymers in this group are synthetic linear aliphatic polyamides which are capable of fibre formation; these polymers are very commonly termed as **nylons**. It may be noted that by far the greater part of the total output of nylons is used for fibre production but the materials have also some importance in non-fibrous applications, particularly engineering applications.

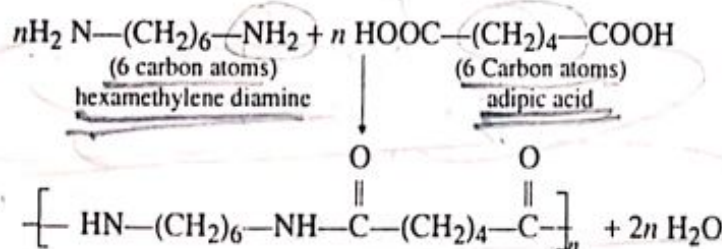
There are also available more complex synthetic aliphatic polyamides which are not fibre-forming but which have found use in such applications as adhesives and coatings. These products are known as **Fatty polyamides** and are not generally regarded as nylons.

More recently, synthetic aromatic polyamides which are capable of fibre formation have been introduced; these polymers are commonly called **aramides** :

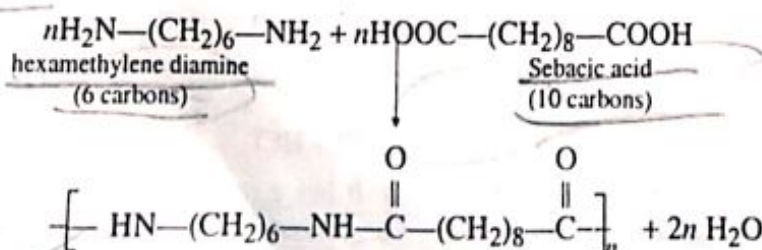
5.3.1. Nylons

The commercial development of nylons was an outcome of the fundamental researches into polymerisation which were begun in 1929 by Carothers of E.I. du Pont de Nemours and Co. Several polyamides were investigated. Nylon 6.6 was selected as the most promising fibre-forming material. The commercial availability of nylon 6.6 in 1940, for nylon stockings led to immediate success because of the high added value application for hosiery in the fashion industry. The search for the nylon analogues not covered by Du Point's Patents led to the development of the isomeric polymer **nylon 6** by I.G. Farben industries in Germany. Structures of the most commercial important nylons are given below in the Scheme-1.

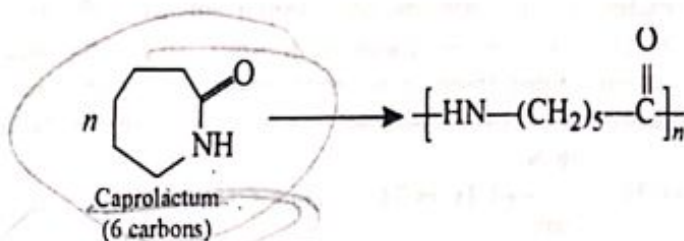
Nylon 6.6.



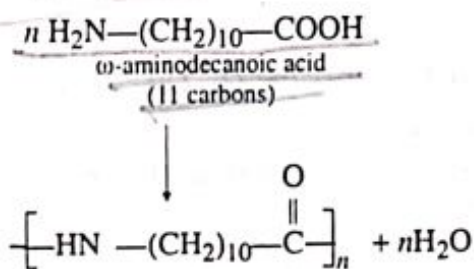
Nylon 6.10.



Nylon - 6



Nylon - 11

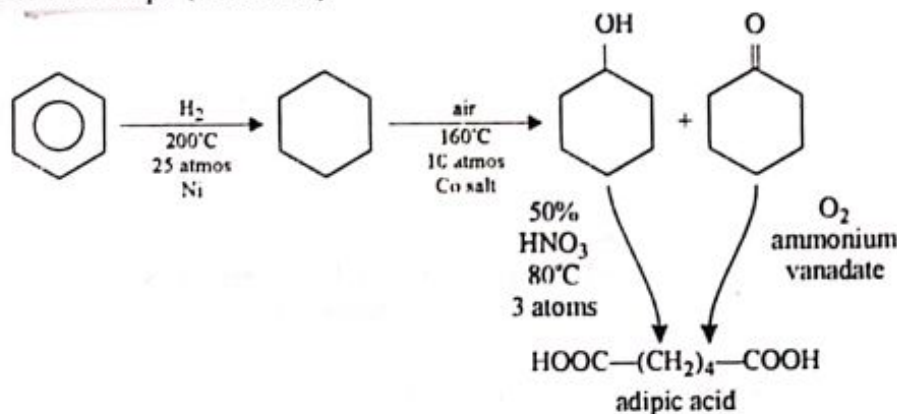


Scheme 1 : Structures of important nylons

5.3.2. Raw materials

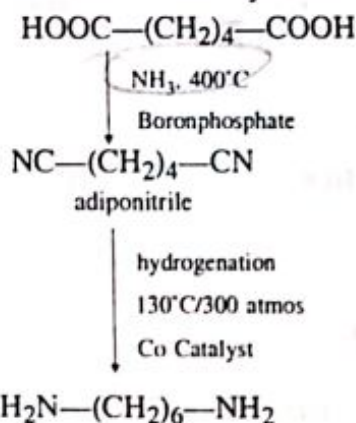
Nylon 6.6.

Both components are six carbon units and it is cost-effective to prepare one through the other. The cheapest six carbon feedstock is benzene which is converted to adipic acid by first hydrogenation and then oxidation in two different steps (scheme-2).



Scheme 2 : Commercial route to adipic acid

Adipic acid may be converted to hexamethylenediamine via the dinitrile as shown in scheme 3.



Scheme 3 : Conversion of adipic acid to hexamethylenediamine