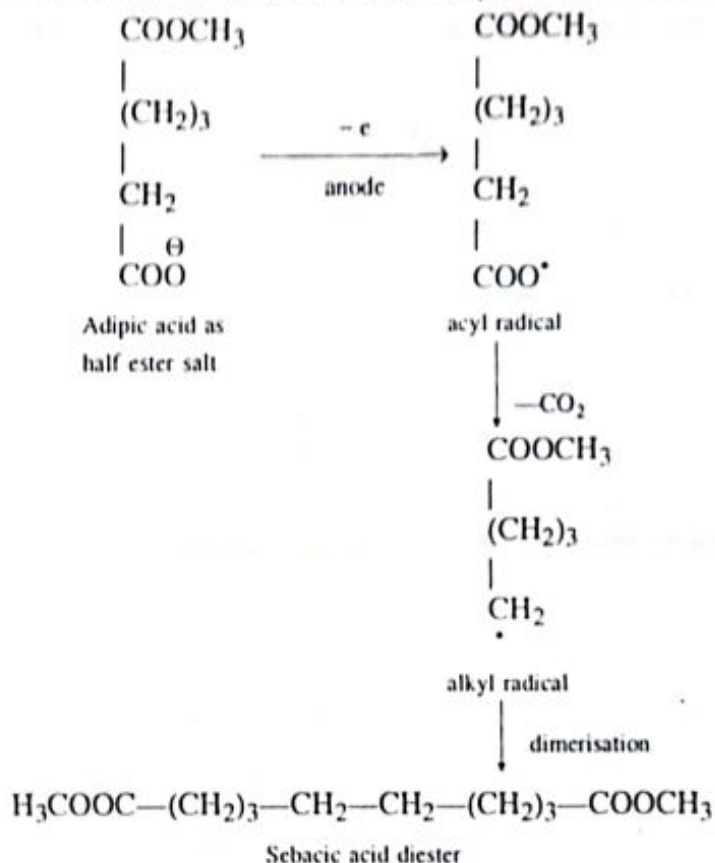


There is also an electrochemical route from adipic acid to sebacic acid (Scheme - 6).

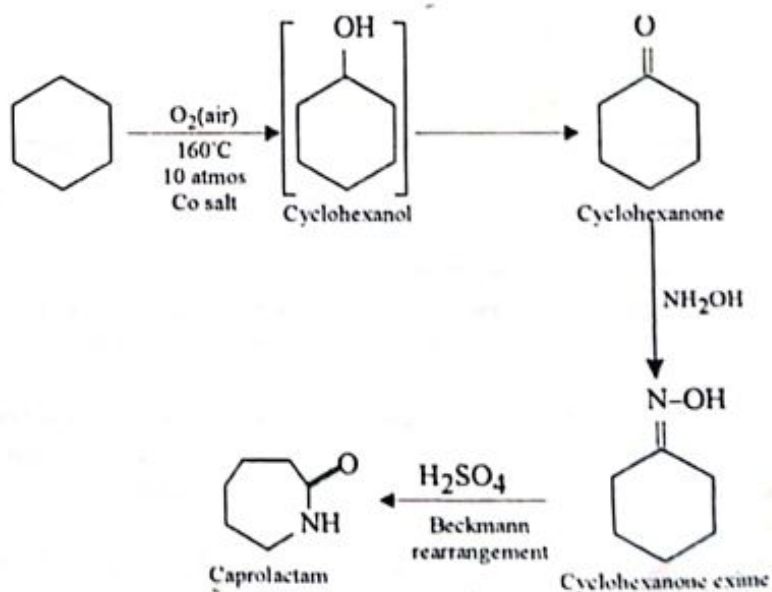


Scheme 6 : Electrooxidative route from adipic acid

Nylon - 6

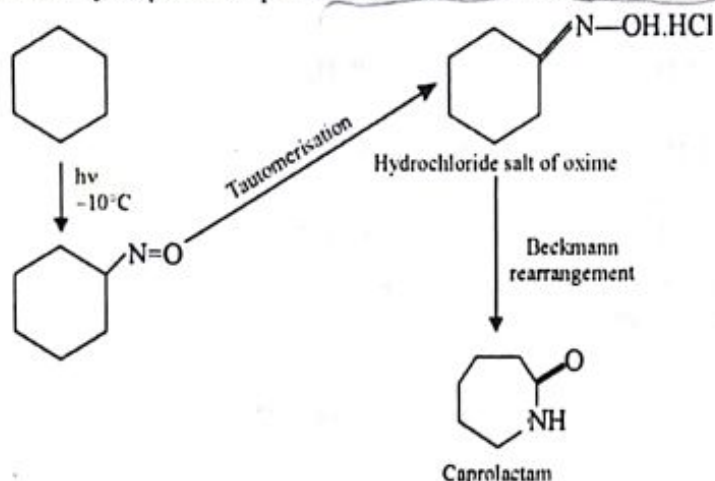
Nylon-6 is used on a large scale. The monomer caprolactam is the cyclic amide of ω -aminohexanoic acid (aminocaproic acid).

The polymer is made from lactam rather than the amino acid since water does not need to be removed during the chain build-up. Furthermore, the lactam does not need to be prepared from the amino acid. Instead, it is prepared from cyclohexane (Scheme - 7).



Scheme 7 : Commercial route of preparation of caprolactam

Another interesting route uses photochemistry. Cyclohexane and nitrosyl chloride in hydrochloric acid are irradiated by a mercury vapour lamp. The reaction is cooled to -10°C (Scheme 8).



Scheme 8 : Photochemical route to caprolactam.

5.3.4. Properties of Nylons

Simple polyamides of these types are tough, flexible, have high-impact strength and are resistant to abrasion. The length of aliphatic unit alters hydrogen bonding and affects glass transition and crystallisation and hence mechanical and physical properties and processing characteristics (Table - 1).

Table 5.1. Physical properties of commercial grade nylon

Nylons	6.6	6	6.10	6.11
Crystalline mp ($^{\circ}\text{C}$)	265	215	215	185
Tensile strength (MPa)	80	75	60	40
Elongation at break (%)	90	150	130	280
Impact strength, (J/m)	40	45	95	95
Water absorption at saturation (%)	8.0	9.0	2.5	2.0

The principal structural difference between various types of nylon is in the length of aliphatic chain segments separating adjacent amide groups. The amide groups lead to *intermolecular* hydrogen bonding so that crystallisation readily occurs to give material of high melting point and tensile strength.

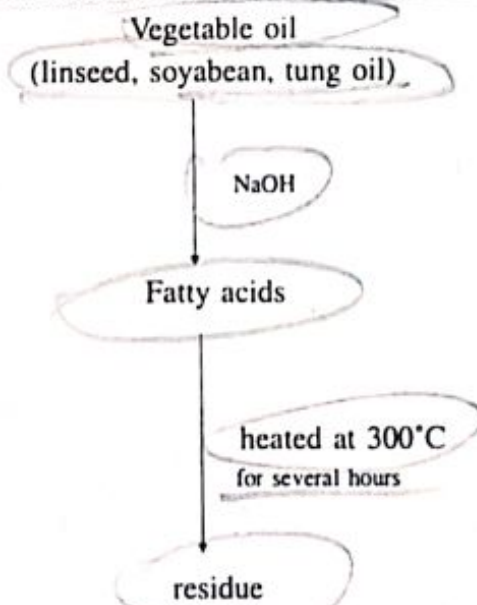
As the length of aliphatic segment increases distance between adjacent amide groups also increases. This increase in distance decreases hydrogen bond strength. Due to decrease in hydrogen bond strength there is reduction in melting point, tensile strength, heat distortion temperature and water absorption and an increase in elongation and impact strength. The selection of a particular nylon for a given application strength generally involves consideration of the relative importance of mechanical properties, water resistance and ease of processing. For example, textile fibres are usually prepared from nylon 6.6 and nylon 6 since these polymers have the highest tensile strengths. Monofilaments for use in such applications as brushes, sports equipments and surgical sutures are normally of Nylon 6.10 and 6.11 since these polymers have greater flexibility and water resistance.

Because of their crystallinity, the nylons are soluble at room temperature in polar protic solvents, such as acetic acid, formic acid and phenols. Nylons are also soluble in alcohols, nitrobenzene, benzyl alcohol and glycols at elevated temperatures.

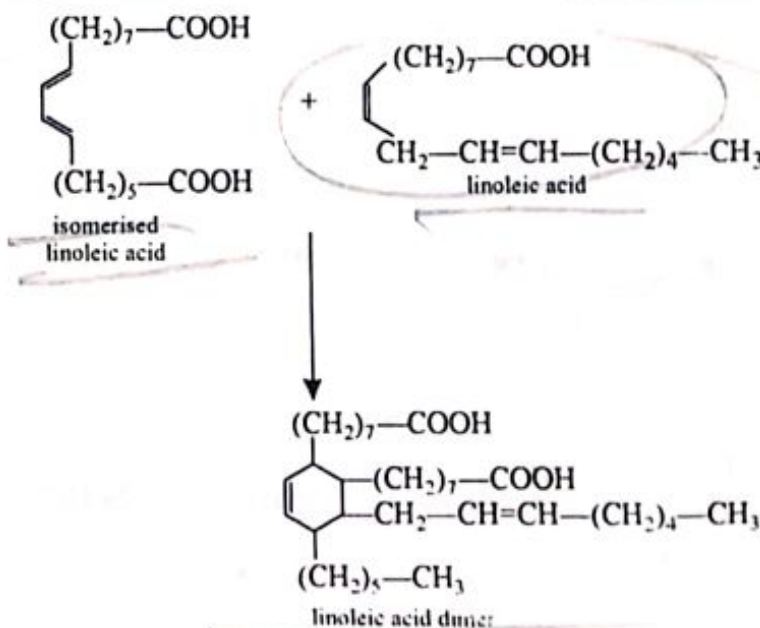
Concentrated mineral acids attack nylons rapidly at room temperature but dilute acids have a less marked effect. Resistance to alkali is very good at room temperature but is generally reduced at elevated temperatures. Oxidising agents such as chlorine and H_2O_2 attack nylons. Oxidation of nylons also occurs in air on exposure to ultraviolet light and/or temperature above $70^\circ C$, discolouration and reduction in mechanical properties occur.

5.4. FATTY POLYAMIDES

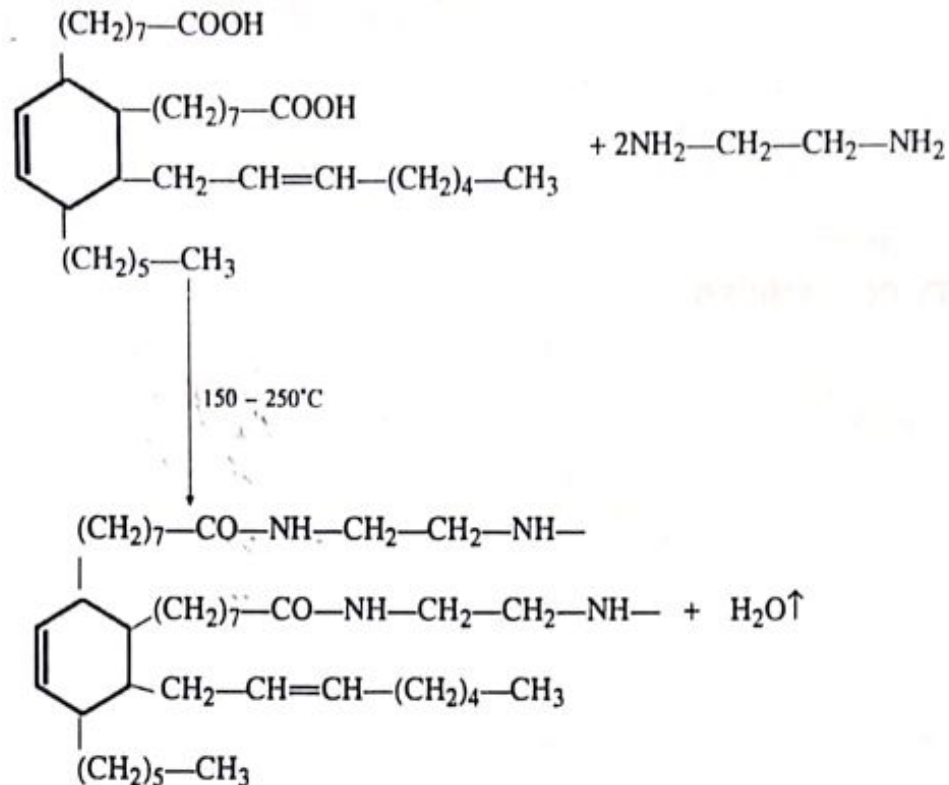
Fatty polyamides are products obtained by the reaction of di and polyfunctional amines with polybasic acids prepared from unsaturated vegetable oil acids. Suitable amines are ethylenediamine and diethylenetriamine. The acids from the oil are obtained as follows.:



The residue is known as dimer acid. This dimer acid is used for the production of polyamides. The main constituents of residue are substituted cyclohexenes which arise through Diels-Alder additions.



Linoleic acid dimer reacts with diamine to give polyamide.



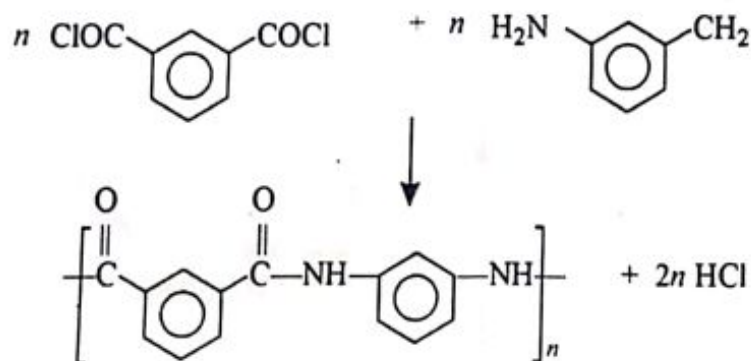
The fatty polyamides prepared from dimer acids are of two main types, namely solid polyamides and liquid polyamides. Solid polyamides are largely linear polymers obtained by the reaction of dimer acids and diamines. These polyamides have molecular weights in the range of 2000 - 15000. Solid polyamides find use in such applications as coatings for flexible substrates like papers, plastic films and aluminium foil. The coatings are heat-sealable and relatively impermeable to water vapour.

The liquid polyamides are highly branched products of lower molecular weight which result from dimer acids and polyamines containing three or more amino groups. The principal use of liquid fatty polyamides is in conjugation with epoxy resins.

5.5. AROMATIC POLYAMIDES

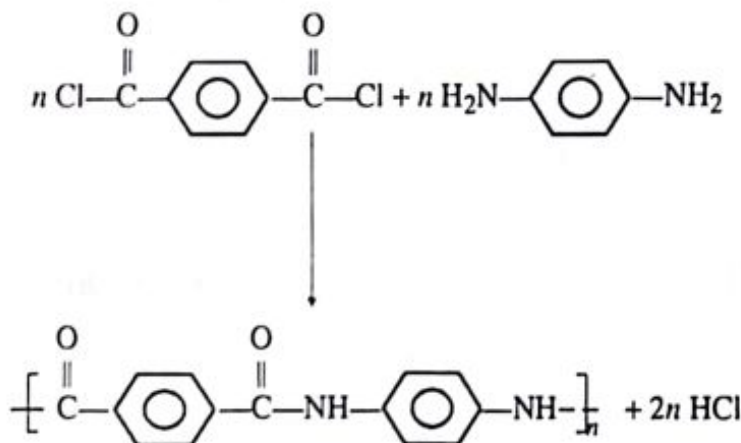
Aromatic polyamides are obtained from aromatic dibasic acids and aromatic amines. Aromatic polyamides are characterised by greater thermal stability and strength. Most important aromatic polyamides are fibre-forming aromatic polyamides. The main examples are: poly(*m*-phenylene isophthalamide and poly(*p*-phenylene terephthalamide).

Poly (*m*-phenylene isophthalamide) is produced by reaction of isophthaloyl chloride and *m*-phenylenediamine :



This type of polyamide has very high melting point (380 – 390°C). At ordinary temperature this has mechanical properties comparable to those of the aliphatic nylons, but at elevated temperatures the aromatic polyamide is greatly superior. The fibre of this polymer is used in electrical insulating applications where resistance to elevated temperatures is required.

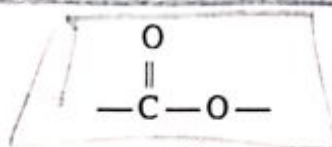
Poly (*p*-phenylene terephthalamide) is other important aromatic polyamide. It is produced by reaction of terephthaloyl chloride and *p*-phenylenediamine.



This polyamide is supplied in fibre form. It is an extraordinarily strong material. The specific tensile strength (tensile strength/density) of the fibre is higher than that of any other fibre commercially available. The polymer does not melt but carbonize at about 425°C. It retains its mechanical properties over a wide range of prolonged periods. There is little change up to about 180°C and even at 250°C. The material is attacked by mineral acids and alkalis and is also sensitive to UV light. The fibre of this polymer have three major applications. It is used as reinforcement in radial tyres and mechanical rubber goods, in ballistic protective fabrics and ropes, and as reinforcement in polymer composites for aircraft and aerospace components.

5.6. POLYESTERS

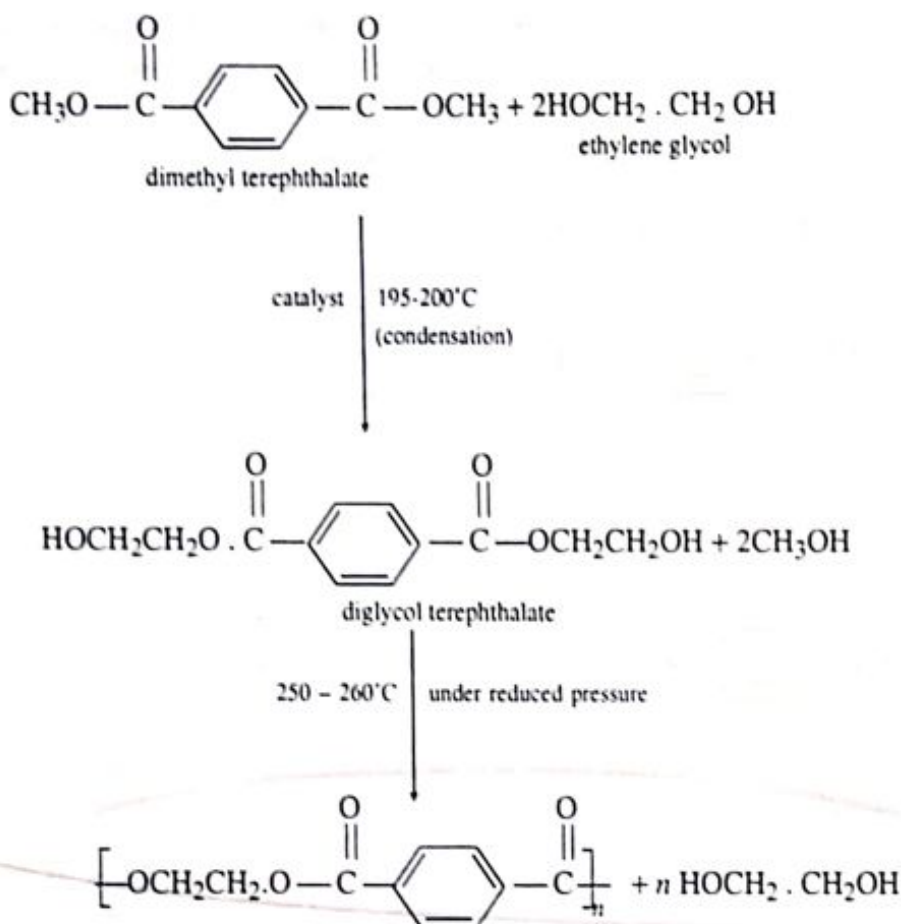
Polyesters are defined as polymers containing recurring



gp in the main chain

groups in the main chain. They are prepared by a polycondensation reaction between a dicarboxylic acid and a diol. Poly ethylene terephthalate (PETP) is a very important polymer from which terylene (dacron) textile fibres are made. The starting materials *i.e.* terephthalic acid and ethylene glycol are obtained from *p*-xylene and ethylene glycol respectively. The synthesis of terylene may be summarised in the following two steps :

- (i) The acid is first converted into its dimethyl ester which is then reacted with excess of glycol in an inert atmosphere at 195-200°C temperature with the continuous removal of alcohol.

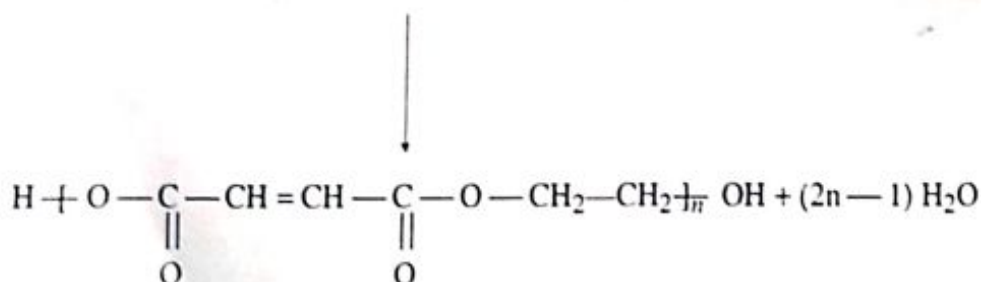
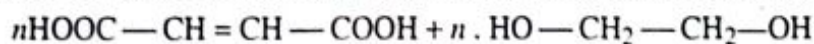


(ii) In second step, diglycol terephthalate is heated at high temperature around 250–260°C under a very high vacuum to remove the excess of glycol and complete the polymerisation reaction.

The polyesters derivative from aliphatic acids and alcohols are not of much industrial importance, mainly because of their low melting points. Introduction of aromatic rings into the polyester chain increases the melting point of the polymer. Thus, the polyester polyethylene terephthalate (PETP) has a high melting point (265°C) and is resistant to heat and moisture. This polyester is virtually unattacked by many chemicals.

It is extensively used to make textile fibres. Garments made from its fibres resist the formation of wrinkles and are easy to wash. Moreover, terylene fibres are blended with other fibres, such as wool and cotton to produce "wash and wear" fabrics. Polyethylene terephthalate is also useful for film making because its film has got some important properties, such as high tensile strength, and resistance to tearing and is used to make magnetic recording tapes. A film of this polyester is sold under the name 'mylar'.

Aliphatic unsaturated polyesters, however find some industrial use. Unsaturation is introduced in the polyester by the reaction of unsaturated dicarboxylic acid such as maleic acid with ethylene glycol.

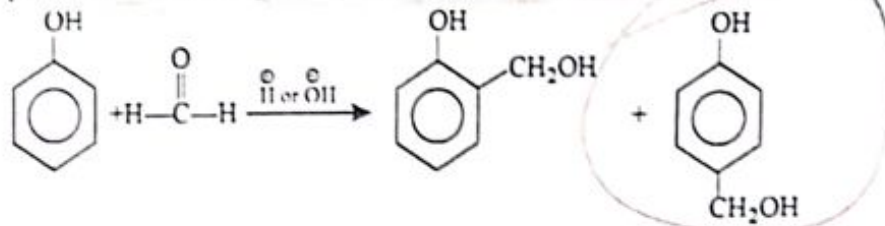


The double bond present in the backbone of the chain is utilised to cross-link the resin with styrene using free-radical catalysts. The unsaturated polyester-styrene combination, is used as the resin matrix, in fibre-reinforced plastics and as decorative coatings.

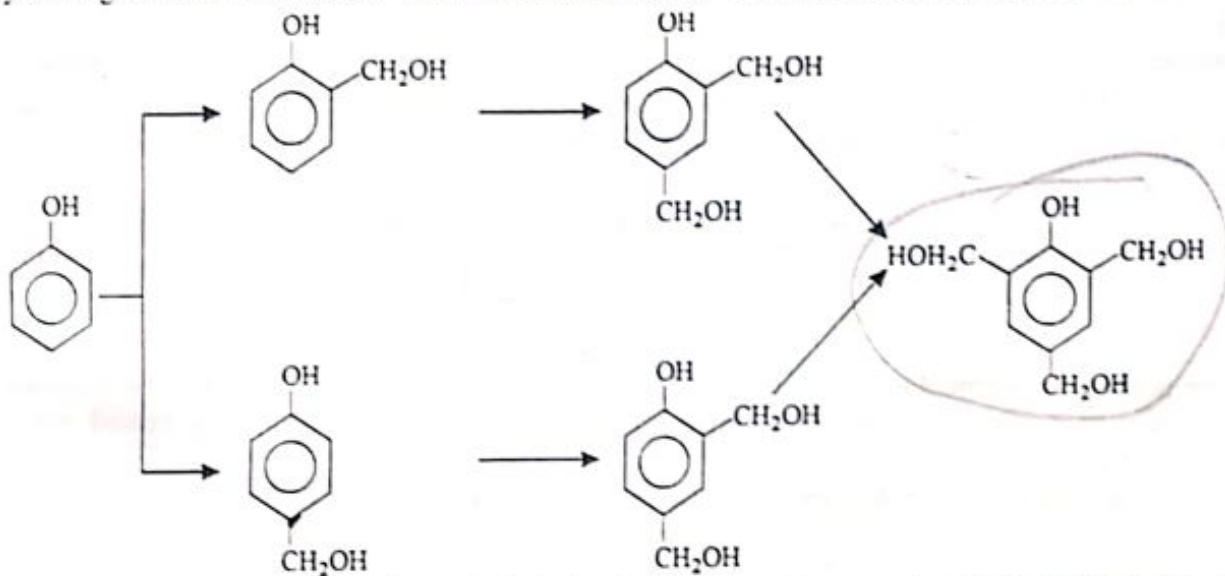
5.7. PHENOLIC RESINS (Phenol-Formaldehyde Resins)

Phenol-formaldehyde (PF) resins are formed by the polycondensation between phenol and formaldehyde. Two important type of reactions are involved between the phenol and formaldehyde during the formation of phenol-formaldehyde resins.

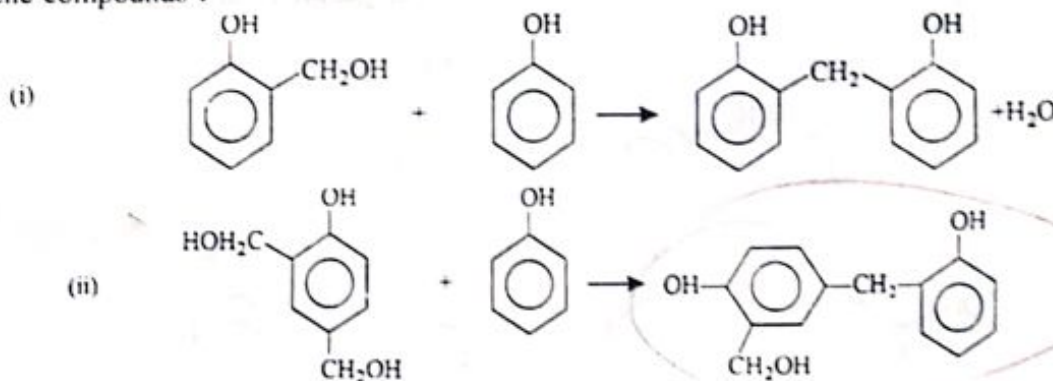
(i) Firstly, the two components react with each other in the presence of acid or better in the presence of base which will accelerate the reaction by forming the phenoxide ion, to introduce the methylol groups in the ortho and para positions to the —OH group of the phenol.



The resulting *o*- and *p*-methylol phenols are more reactive towards formaldehyde than the phenol and rapidly undergo further substitution with the formation of di- and trimethylol phenol derivatives.



(ii) In the second type of reaction methylol phenols further undergo condensation with phenol to give the methylene compounds :



Two types of phenol-formaldehyde resins have been synthesised depending upon the phenol-formaldehyde ratio (P/F), nature of catalyst and the number of steps in the process.