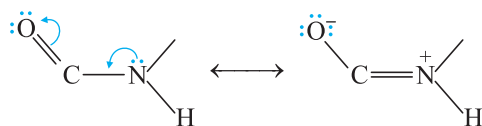


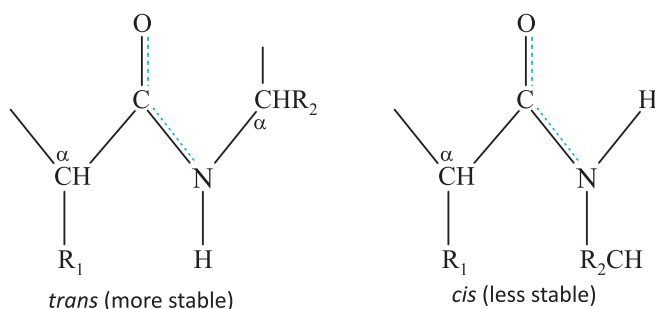
Configuration and conformation of the peptide bond in polypeptides :

The lone pair of electrons on the N-atom in the peptide bond is delocalised over the $>\text{C}=\text{O}$ group. As a result, carbon-nitrogen bond acquires some double bond character. In other words, the rotation about the $\text{C}-\text{N}$ bond is hindered and as a result of this hindered rotation, the peptide bond can show **geometrical isomerism**. Further because of much larger steric repulsions between R_1 and R_2 groups, in the cis-isomer, the trans-isomer is more stable.



Resonance Structure of Peptide Bond

Thus, the atoms forming the peptide bond, i.e., CONH group lie in a plane with the O and H atoms in trans-orientation.



POLYMERS

Section - 3

Introduction :

Polymers form the backbone of the modern civilization and are the chief products of the modern chemical industries. Polymers, (Greek poly means many and mer means unit or part), are very high molecular mass compounds, each molecule of which consists a very large number of simple structural units joined together through covalent bonds in regular fashion. The simple molecules from which the repeating structural units are derived are called **monomers** and the process by which these simple molecules, i.e., monomers are converted into polymers is called polymerisation.

Classification of Polymers :

1. Classification of Polymers on the basis of Origin :

(A) Natural Polymers :

They are available in nature (animals or plants). Examples of such polymers are: natural rubber (1,4-cis-polyisoprene), natural silk, cellulose, starch, proteins, etc. Polymers such as polysaccharides (starch, cellulose), proteins and nucleic acids etc., which control various life processes in plants and animals are called **biopolymers**.

(B) Semisynthetic Polymers :

They are chemically modified natural polymers such as hydrogenated, halogenated or hydro-halogenated natural rubber, cellulotics, i.e., esters and ethers of cellulose such as cellulose nitrate, methyl cellulose, etc.

(C) Synthetic Polymers :

They are man made polymers prepared synthetically such as polyethylene, polystyrene, polyvinyl chloride, polyesters, Bakelite, Buna-S, Nylon, Dacron etc.

2. Classification on the Basis of Thermal Response :

(A) Thermoplastic Polymers : Polymers which can be easily softened when heated and hardened with little change in their properties. They can be softened or plasticized repeatedly on application of thermal energy, without much change in properties if treated with certain precautions, e.g. polyolefins, polystyrene, nylons, linear polyesters and polyethers, polyvinyl chloride, Teflon etc. They normally remain soluble and fusible after many cycles of heating and cooling.

(B) Thermosetting Polymers : Polymers which undergo permanent change on heating. They can be obtained in soluble and fusible forms in early or intermediate stages of their synthesis, but they get packed or cured and become insoluble and infusible when further heated or thermally treated. The curing or packing process involves chemical reactions leading to further growth and cross linking of the polymer chain molecule and producing giant molecules, e.g. Bakelite, melamine formaldehyde, diene rubbers, unsaturated polyesters etc.

Certain plastics do not soften very much on heating. These can be easily softened by the addition of some organic compound which are called *plasticizers*. For example, Polyvinyl chloride (PVC) is very stiff and hard but it is made soft by adding plasticizer e.g. Dioctyl phthalate (DOP).

(C) Fibres : Polymers which have strong forces between chains. These forces are either H-bonds or dipole-dipole interaction. These are closely packed with a high tensile strength and less elasticity. Therefore, they have sharp melting points. These polymers are long, thin and thread like and can be woven in fabrics. Some of the example of these polymers are Nylon-66, Dacron, etc.

(D) Elastomers : Polymer with elastic character like rubber. In elastomers the polymer chains are bound together by weakest intermolecular forces. These are easily stretched by applying small stress and regains its original shape when stress is removed. For example, natural rubber.

The natural rubber is a gummy material which has poor elasticity. However, when natural rubber is heated with 3-5% sulphur, it becomes non-sticky and more elastic. This process is called *vulcanization*.

(B) Condensation Polymers : A polymer formed by the condensation of two or more than two different monomers with the elimination of the species like water, ammonia, hydrogen chloride or alcohol etc., is called *condensation polymer*. In this type of polymerization generally each monomer contains two functional groups.

Besides —C—C— linkages, they contain atoms such as O, N, S, etc., at regular intervals in the main chain. The process of their formation is called *condensation polymerization* or *step-growth polymerization*. Polyamides, polyesters, polyethers, polyurethanes, terylene, bakelite, epoxy resins and alkyd resins, etc., are examples of condensation polymers.

4. Classification on the Basis of Structure :

(A) Linear Polymers : These can schematically be represented by lines of finite lengths with well packed structure, having high densities, high tensile (pulling) strength and high melting points. They are formed from olefinic, vinylic or related polymerization under suitable conditions or by condensation polymerization of bifunctional monomers. Linear polymers such as high density polyethylene, polyvinyl chloride, polystyrene, Nylon-6, etc. are soluble and fusible.

(B) Branched Polymers : They can be schematically represented by lines of finite lengths with the short or long branch structures of repeated units. The branches appear as a consequence of uncontrolled side reactions during polymerization or by design of polymerization. Branched polymers are usually more readily soluble and fusible than linear polymers of comparable chain length or molecular weight. For example, low density polythene, glycogen, starch etc.

(C) Cross-linked or Network Polymers : They can be represented by a network structure, planar-network as in graphite or space-network as in diamond. Cross-linked polymers are insoluble and infusible as the molecules in them are giant molecules, often of unusually high or infinite molecular weight. Depending on the nature and frequency of cross-links, such polymers may show different orders of swelling in solvents. These polymers are hard, rigid, brittle because of network structure. Examples are: Phenol-formaldehyde resins, epoxy resins, vulcanized rubber etc.

Molecular masses of Polymers :

The molecular mass of a polymer can be expressed in two ways.

(A) Number average molecular mass : If $N_1, N_2, N_3 \dots$ are the number of molecules with molecular masses $M_1, M_2, M_3 \dots$ respectively.

$$\bar{M}_N = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \dots}{N_1 + N_2 + N_3}$$

This may be expressed as
$$\bar{M}_N = \frac{\sum(N_iM_i)}{\sum N_i}$$

where N_i is the number of molecules of the i^{th} type with molecular mass M_i .

(B) Weight average molecular mass : If $m_1, m_2, m_3, \dots$ are the masses of species with molecular masses $M_1, M_2, M_3, \dots$ respectively, then the weight average molecular mass is

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2 + m_3 M_3}{m_1 + m_2 + m_3} \quad \text{or} \quad \bar{M}_w = \frac{\sum(m_i M_i)}{\sum N_i}$$

But $m_i = N_i M_i$, so that $\bar{M}_w = \frac{\sum(N_i M_i^2)}{\sum(N_i M_i)}$

where N_i is the number of molecules of mass M_i .

Poly dispersity index : The ratio of weight average molecular mass to the number average molecular mass is called *poly dispersity index*, PDI.

$$\text{PDI} = \frac{\bar{M}_w}{\bar{M}_n}$$

This gives an idea about the homogeneity of a polymer.

For natural polymers, PDI is usually unity and therefore, natural polymers are monodisperse. For synthetic polymers, the PDI is greater than one and therefore $\bar{M}_w$ is greater than $\bar{M}_n$.

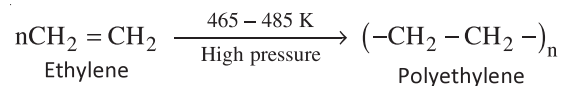
The number average molecular mass, $\bar{M}_n$ is measured on the basis of colligative properties like osmotic pressure. On the other hand, the weight average molecular mass, $\bar{M}_w$ is determined with the help of methods like ultra centrifugation, sedimentation etc.

Some Important Polymers :

- | | | |
|------------------------------|--------------|------------------------|
| 1. Polyolefins | 2. Rubber | 3. Teflon |
| 4. Poly Vinyl Chloride (PVC) | 5. Nylon | 6. Formaldehyde Resins |
| 7. Terylene | 8. Cellulose | |

1. **Polyolefins :** These are generally obtained from ethylene or its derivatives. The polymerization normally takes place at a temperature between 473–673 K under high pressure and in the presence of traces of oxygen.

(i) **Polyethylene or Polyethene :** It is a polymer of ethylene. It is manufactured by heating pure ethylene to 465–485 K under high pressure (1500 – 2000 atm) in the presence of traces of oxygen (0.03 to 0.1%).



It is a whitish, translucent polymer of moderate strength and high toughness.

Uses : Its major uses are as packing films, pipes, containers, laboratory apparatus, bottles, buckets, toys, mould articles and electrical insulators.

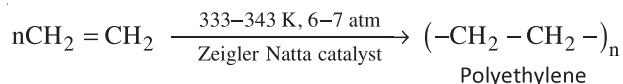
It may be noted that these days two types of polythene are used which have widely different properties. These are, *low density polythene* (LDPE) and *high density polythene* (HDPE).

The low density polythene is prepared as discussed above. It consists of highly branched chain molecules.

Due to branching, the polythene molecules do not pack well and therefore, it has low density (0.92 g/cm³) and low melting point (384 K). Low density polythene is transparent of moderate tensile strength and high toughness. It is mainly used for.

- As a packing material in the form of thin plastic film bags.
- For insulating wires and cables.
- In the manufactures of pipes, toys, bottles, etc.

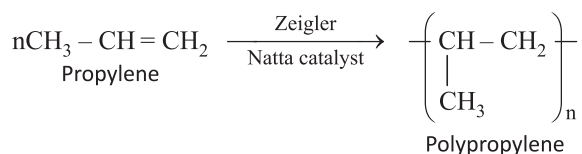
On the other hand, high density polythene is prepared by heating ethylene at about 333–343 K under a pressure of 6–7 atm in the presence of a catalyst such as *triethylaluminium* and *titanium tetrachloride* (known as **Zeigler Natta catalyst**).



This polymer consists of linear chains and therefore, the molecules can get closely packed in space. It has, therefore, high density (0.97 g/cm³), and higher melting point (403 K). It is quite harder, tougher and has greater tensile strength than low density polythene.

It is used in the manufacture of containers, buckets, tubes, pipes, house wears etc.

- (ii) **Polypropylene or Polypropene** : The monomer unit is propylene. It is manufactured by passing propylene through hexane (an inert solvent) containing **Zeigler Natta catalyst** (a mixture of triethylaluminium and titanium tetrachloride).



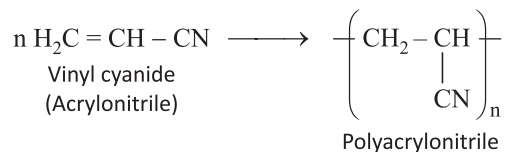
It is harder and stronger than polyethylene.

Uses :

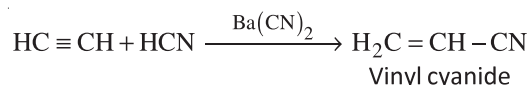
- For packing of textiles and foods,
- For manufacturing liners of bags, lining material for TV cabinets and refrigerators,
- For making ropes, fibres, heat shrinkable wraps for records and other articles.
- For making automobile mouldings, seat covers, carpet fibres etc.

- (iii) **Polyacrylonitrile (PAN) or Orlon** :

It is a polymerized product of vinyl cyanide (acrylonitrile).



Vinyl cyanide can be prepared by treating acetylene with HCN in the presence of Ba(CN)₂



It is a hard, horny and high melting substance. It is also known as acrilon or orlon.

Uses :

- For making blankets, sweaters, bathing suits, etc.
- For making synthetic carpets.

2. **Rubber** : It is of two types, viz. Natural rubber and Synthetic rubber.

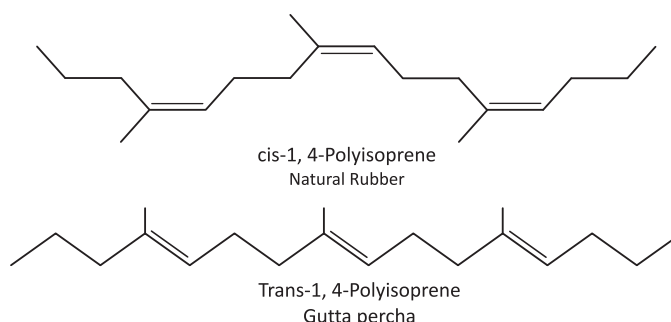
- **Natural Rubber** : It is an addition polymer of isoprene (i.e. 2-Methyl-1, 3-butadiene). It is manufactured from latex, a colloidal solution of rubber particles in water, obtained by making incisions in the bark of rubber trees found in tropical and sub-tropical countries.



Rubber has an average chain length of 5000 monomer units of isoprene. Since each repeating units in polyisoprene contains a double bond, it may have either cis-or a trans-orientation. Natural rubber has **cis-stereochemistry** while gutta percha, obtained by free radical polymerisation of isoprene, has trans-configuration.

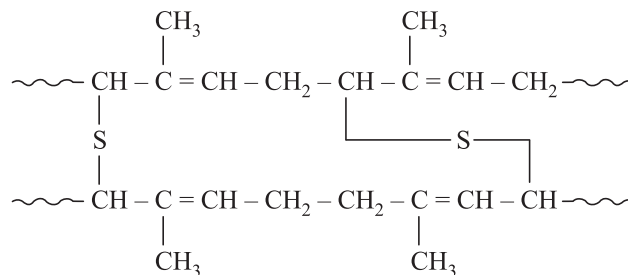
Properties :

1. It has remarkable elasticity but is sticky in nature.
2. It undergoes long range reversible extension even under relatively small applied force.
3. It has weak intermolecular forces and occasional cross-linking. With no highly polar substituents, intermolecular attraction is largely limited to van der Waal's forces. But these are weak because of all cis-configuration about the double bond.
4. The trans-configuration permits highly regular zig-zags that fit together well while the cis-configuration does not.
5. The trans-configuration is highly crystalline and non-elastic.



➤ Vulcanized Rubber :

Natural rubber is soft and tacky (sticky) and becomes even more so at high temperature and brittle at low temperatures. It has a large water absorption capacity, low tensile strength and resistance to abrasion. It is also not resistant to the action of organic solvents and is also easily attacked by oxidising agents. These disadvantages are removed by '**VULCANISATION**' which involves addition of sulphur to rubber and heating the mixture at 373–415 K. The vulcanized rubber thus obtained has excellent elasticity, low water absorption tendency and resistant to the action of organic solvents and oxidising agents. During vulcanization, sulphur bridges or cross-links between polymeric chains are introduced through their relative allylic positions.

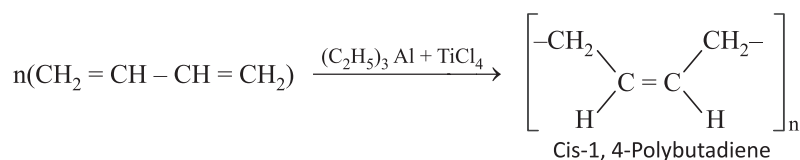


These crosslinks make rubber hard and stronger and remove the tackiness of natural rubber since the individual chains cannot slip past each other due to sulphur bridges. Thus rubber can be stretched only to a certain extent and hydrocarbon chains have the tendency to regain their shape when tension is removed.

➤ **Synthetic Rubber :**

To improve the qualities of natural rubber and to meet the ever increasing demands of mankind, a number of forms of synthetic rubber have been prepared.

- (i) **Cis-Polybutadiene :** This polymer has properties similar to those of natural rubber and can also be vulcanised in the same way. It is prepared by the polymerisation of 1, 3-butadiene in the presence of Zeigler-Natta catalyst [i.e., a mixture of $(C_2H_5)_3Al$ and $TiCl_4$].



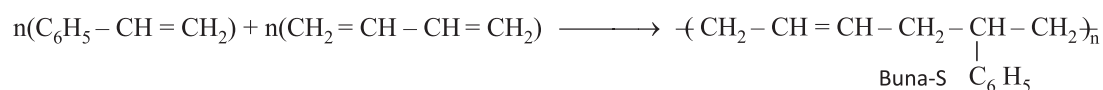
- (ii) **Buna Rubbers :** Butadiene polymerises in the presence of sodium to give a rubber substitute viz. BuNa. It is of two types :

- (a) **Buna-N or GRA :** It is synthetic rubber obtained by co-polymerisation of one part of acryl nitrile and two parts of butadiene.



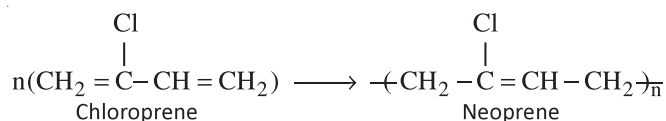
It is more rigid responds less to heat and very resistant to swelling action of petrol, oils and other organic solvents.

- (b) **Buna-S or GRS :** It is a copolymer of three moles of butadiene and one mole of styrene and is an elastomer. It is obtained as a result of free radical co-polymerisation of its monomers.



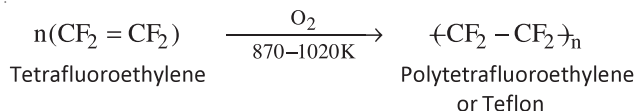
It is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and find use in the manufacture of tyres and other mechanical rubber goods.

- (iii) **Neoprene :** It is a polymer of chloroprene and is obtained by free radical polymerisation of chloroprene.



It is an excellent rubber like material. It is a thermoplastic and need not to be vulcanised. It is superior to natural rubber as it is resistant to the reaction of air, heat, light, chemicals, alkalies and acids below 50% strength. It is used for making transmission belts, printing rolls and flexible tubing employed for conveyance of oil and petrol.

3. **Teflon** : It is also called *polytetrafluoroethylene* (**PTFE**). It is a polymer of tetrafluoro ethylene ($F_2C = CF_2$) which on polymerisation gives Teflon.

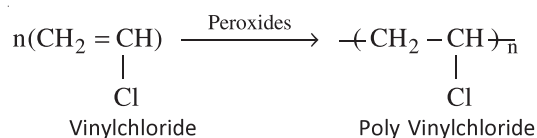


It is thermoplastic polymer with a high softening point (600 K). It is very tough and difficult to work. It is inert to most chemicals except fluorine and molten alkali metals. It withstands high temperatures. Its electrical properties make it an ideal insulating material for high frequency installation.

Due to its chemical inertness and high thermal stability, it is used in making non stick utensils. For this purpose, a thin layer of Teflon is coated on the inner side of the vessel. It is also used for making gaskets, pump packings, valves, seals, non-lubricated bearings, filter cloth, etc.

4. Poly Vinyl Chloride :

It is commonly named as PVC. It's starting material is vinyl chloride ($CH_2 = CH - Cl$). It is prepared by the polymerisation of vinyl chloride in presence of peroxides.

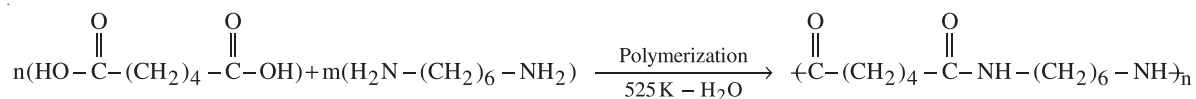


PVC is by and large a linear polymer, colourless and thermoplastic in nature and having a chloride content of about 56.8%. The polymer is thermally unstable and extensive heating transforms it into a dark coloured residue resembling polyacetylene and liberating HCl as the volatile. It is insoluble in all hydrocarbons as events. It possesses flame retardation and self extinguishing characteristics.

PVC is a pliable (easily moulded) polymer and thus has a wide range of applications.

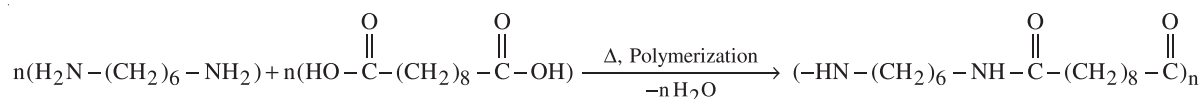
- (i) When plasticised with high boiling esters such as di-n-butylphthalate, it is used for making raincoats, hand bags, plastic dolls, etc.
 - (ii) It is a good electrical insulator and hence is used for coating wires, cables and other electrical goods.
 - (iii) It is also used in making ; gramophone records and hose pipes.
5. **Nylon** : These are polymers having amide linkage and are known as polyamides. These are prepared by the condensation polymerization of dibasic acid with diamines or their equivalents.

- (i) **Nylon-6, 6** : It is a polymer resin. It is condensation polymer formed by reaction between adipic acid and hexamethylene diamine at 525 K under pressure. As both monomer units consist of 6 carbon atoms, so it is known as nylon-66.



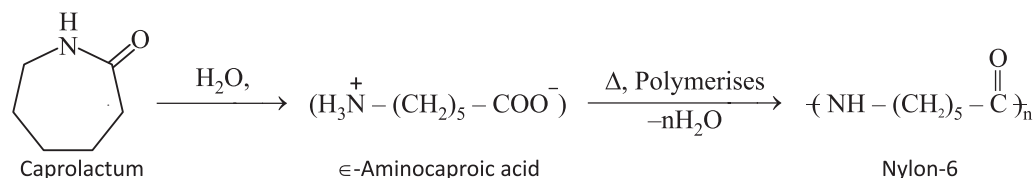
It is a thermoplastic polymer when extruded above its melting point (536 K) through spinneret, it gives nylon fibre which is extremely tough and resistant to friction. It possesses greater tensile strength, elasticity and lusture than any natural fibre. It is chemically inert and is fabricated into sheet, bristles and textile fibres.

- (ii) **Nylon-6, 10** : It is another type of nylon, obtained by the condensation of hexamethylenediamine and sebacic acid, a dibasic acid containing ten carbon atoms.



It is tough, elastic and has high tensile strength. It is used in the manufacture of carpets, textile fibres and bristles for brushes.

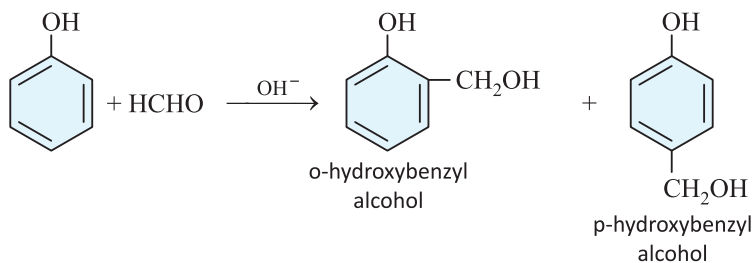
- (iii) **Nylon-6** : It is also called Perlon-L. It is manufactured by prolonged heating of caprolactam, having amino group at one end and a carboxyl group at the other, at 530–540 K.



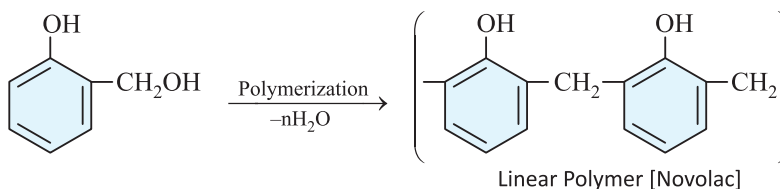
The fibres of nylon-6 are obtained when molten polymer is forced through a spinneret and the fibres formed are cooled by the stream of air. It is used in the manufacture of tyre cords, fabric and mountaineering ropes.

6. Formaldehyde Resins : These include polymers like Bakelite and Melamine polymers.

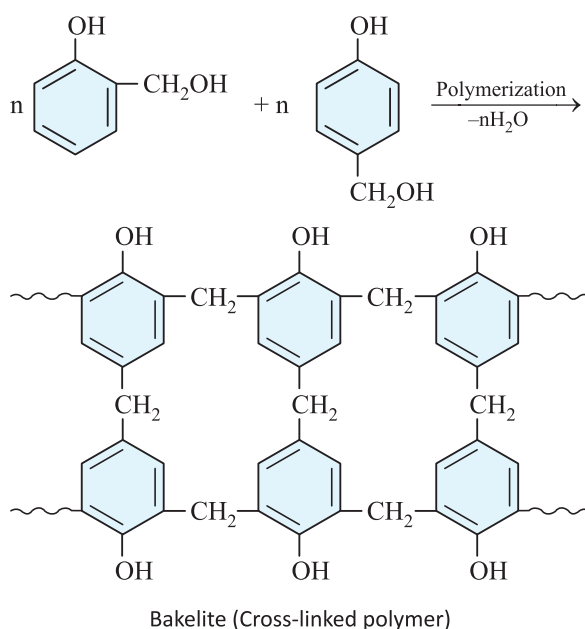
- (i) **Phenol formaldehyde resins (Bakelite)** : It is a condensation polymer and is obtained from phenol and formaldehyde in the presence of basic catalyst.



The condensation of o-hydroxybenzyl alcohol or p-hydroxy benzyl alcohol gives a linear polymer.



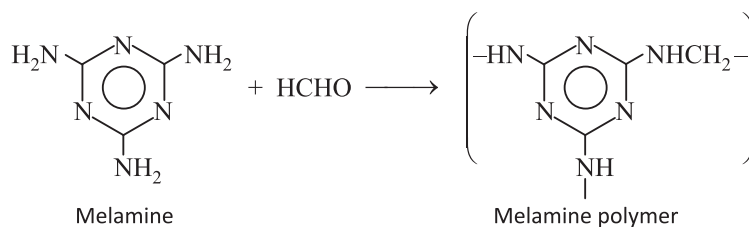
The ortho and para substituted phenols can undergo polymerization to produce a cross-linked polymer known as bakelite.



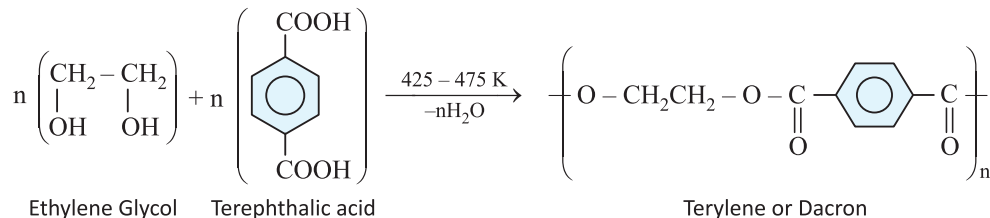
Uses :

Soft bakelites with low degree of polymerization are used for making glue for binding laminated wooden planks and in varnishes. High degree polymerization gives hard bakelites which are used for making combs, fountain pens, barrels, electrical goods, formica table tops and many other products.

- (ii) **Melamine formaldehyde resin:** It is a polymer formed by the condensation of melamine which is a heterocyclic diamine with formaldehyde. The polymerization occurs as

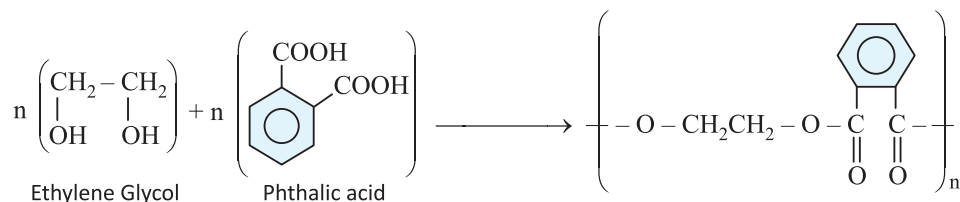


7. **Terylene :** It is a condensation polymer which is known as polyester. Terylene is a polymer of ethylene glycol and terephthalic acid. It is known as terylene or Dacron.



It is a very strong fibre and is used for making cloth by mixing with cotton, magnetic recording tapes, etc.

An important polymer of polyesters class is glyptal. Glyptal is a polymer of ethylene glycol with phthalic acid.



It was commonly used in manufacture of paints, lacquers, building materials such as asbestoss, cement, etc.

Uses :

These films are suitable in electrical applications and packaging and as magnetic recording tapes. The fibre is made by a melt spinning process. Poly ethylene terephthalate is the most important synthetic fiber to have found widespread textile applications either alone or more commonly as different blends with cotton or wool. The fibre is widely known as Terylene or Dacron. The polyester fibres possess good crease resistance and wash and wear properties. A sizable fraction of the polyester fibre is used as the reinforcing cord in the tyre and related industry.

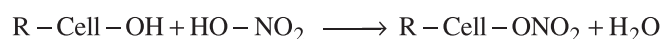
- 8. Cellulose :** Cellulose is the most abundant constituent of the vegetables or plant kingdom. More than 50% of all the living matter is cellulose. It is the chief structural material of cell walls of all plants. It is also the chief component of wood (45 – 50% cellulose), cotton (90 – 95% cellulose), etc. The molecular mass of cellulose varies from 50,000 to 500,000 suggesting thereby that cellulose may contain 300-3000 glucose units.

Cellulose is a non-reducing sugar since it does not reduce Tollen's reagent or Fehling's solution. It also does not form an osazone and is not fermented by yeast. It also does not undergo hydrolysis easily.

Types of Polymers of Cellulose :

- (i) **Cellulose Nitrate :** Cellulose nitrate is the oldest cellulosic or cellulose derivative known and it is the only inorganic ester of cellulose of commercial importance. Nitration of cellulose is carried out by using a mixture of HNO_3 and H_2SO_4 over a specific time period under controlled conditions of temperature and mixed acid composition.

The transformation of cellulose ($\text{R}-\text{Cell}-\text{OH}$) into the nitrate may be written as :



Cellulose nitrates for plastics and coating (lacquer) applications have nitrogen (Nitrogen) content in the range of 11.5 – 12.2%. They are available in a large number of viscosity grades and they are soluble in esters, ketones, ether alcohol mixture and glycol ethers. Cellulose nitrates with 10.9 – 11.2% nitrogen content find use in fiexographic inks, lacquer coatings for paper, foils. For plastics application cellulose nitrate is invariably plasticized with nearly 25% by weight of camphor. The camphor plasticized product is known as celluloid.

- (ii) **Cellulose Acetate :** The most important organic ester of cellulose is cellulose acetate. Cellulose acetate is prepared by acylation of cellulose using a mixture of acetic anhydride and glacial acetic acid as the acetylating agent under a controlled condition. Small proportion of H_2SO_4 is used as catalyst.

A major outlet of cellulose acetate is in the area of sheets, films and membranes. Its exceptional clarity makes it suited for photographic films. Injection moulded items include tooth brush handles, combs, etc. Films are useful in packaging and wrapping. The toughness, low flammability (compared to cellulose nitrate), good clarity are advantageous. On the other hand its high water absorption, poor solvent and chemical resistance and limited heat resistance and dimensional stability are its limitations.

Mixed organic esters of cellulose also have been developed commercially. The most important mixed esters are cellulose acetate butyrate and cellulose acetate propionate. Cellulose acetate butyrate is more suitable than cellulose acetate for movie films. Its excellent appearance and clarity, toughness and ease of mouldability are of special advantage. The mixed ester is used in the making of automobile parts, tool handles, toys, telephone housing and pipes.