

# CHEMISTRY PATHSHALA

## POLYMERS

### Polymers

#### Introduction:

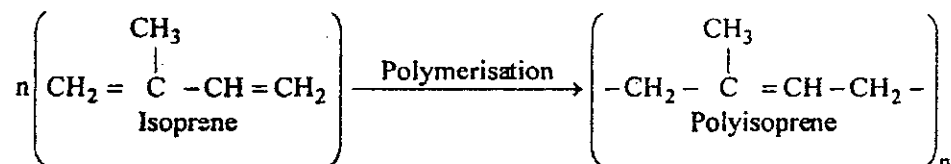
Polymers form the backbone of the modern civilization and are the chief products of the modern chemical industries. Polymers, (Greek meaning: many parts), are very high molecular mass compounds, each molecule of which consists a very large number of simple structural units joined together through covalent 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.

#### Some Important Polymers:

1. Rubber
2. Nylon.
3. Teflon
4. Poly Vinyl Chloride (PVC)
5. Cellulose

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

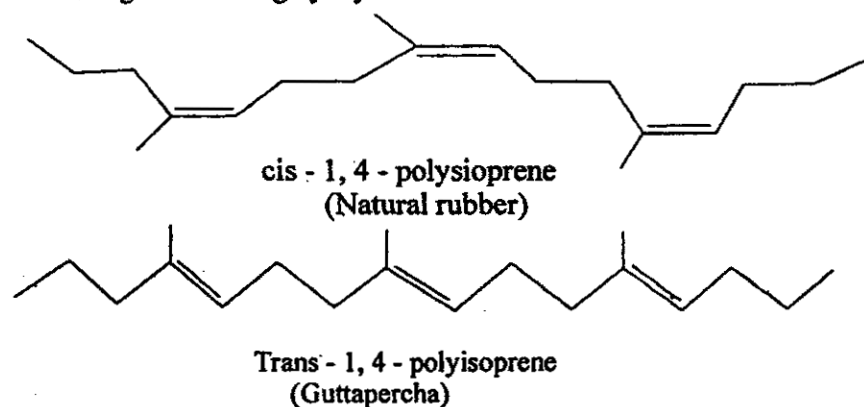
**Natural Rubber:** It is an additional polymer of isoprene (i.e. 2-Methyl-1, 3-butadiene). It is manufacture from latex, a colloidal solution of rubber particles in water, obtained by making incisions in the bark of rubber trees found in tropical and sub-tropical countries.



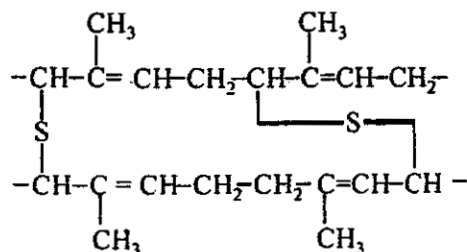
Rubber has an average chain length of 5000 monomer units of isoprene. Since each repeating units in polyisoprene contains a double bond, it may have either cis-or a trans-orientation. Natural rubber has cis-stereochemistry while gutta percha, obtained by free radical polymerisation of isoprene, has trans-configuration.

**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 and becomes even more so at high temperature and brittle at low temperature. 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.

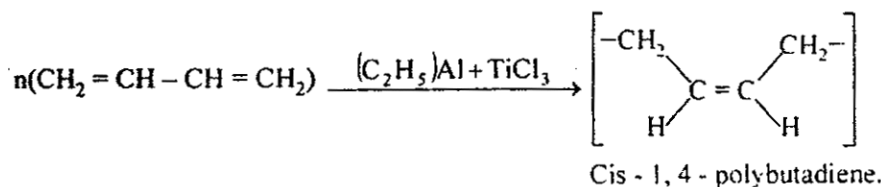


These crosslinks make rubber hard and stronger and remove the tackiness of natural rubber since the individual chains cannot slip past each other due to sulphur bridges. Thus rubber can be stretched only to a certain extent and hydrocarbon chains have the tendency to regain their shape when tension is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

**Synthetic Rubber:**

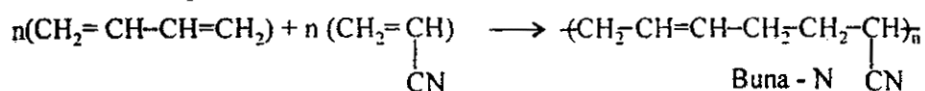
To improve the qualities of natural rubber and to meet the ever increasing demands of mankind, a number of forms of synthetic rubber have been prepared.

- (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 Ziegler-Natta catalyst [i.e., a mixture of  $(C_2H_5)_3Al$  and  $TiCl_3$ ].



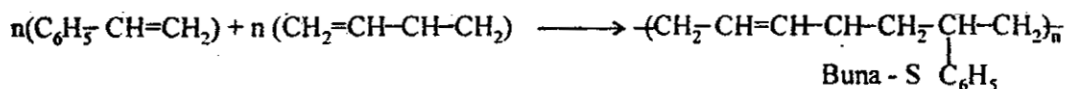
- (ii) **Buna rubbers:** Butadiene polymerises in the presence of sodium to give a rubber substitute viz. BuNa. It is of two types:

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



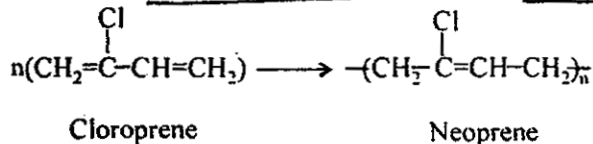
It is more rigid responds less to heat and very resistant to swelling action of petrol, oils and other organic solvents.

- (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.

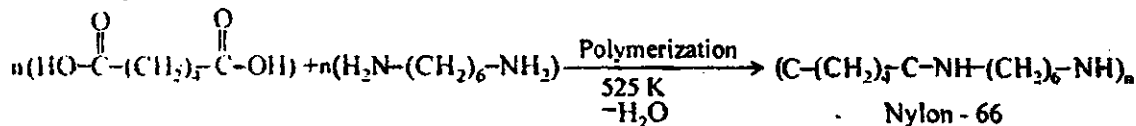
- (iii) **Neoprene:** It is a polymer of chloroprene and is obtained by free radical polymerisation of chloroprene.



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.

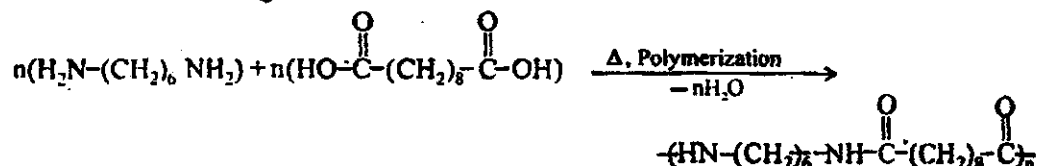
2. **Nylon:** These are polymers having amide linkage and are known as polyamides. These are prepared by the condensation polymerization of dibasic acid with diamines or their equivalents.

(i) **Nylon-66:** 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



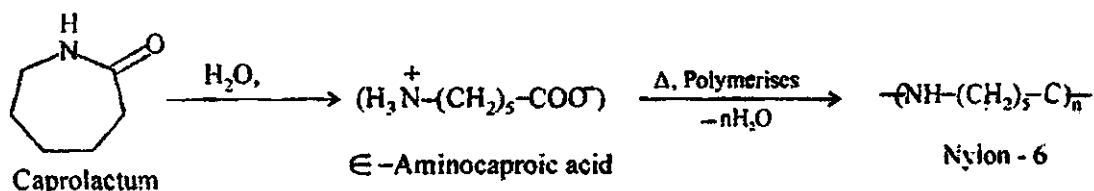
It is a thermoplastic polymer when extruded above its melting point (536 K) through spinneret, it gives nylon fibre which is extremely tough and resistant to friction. It possesses greater tensile strength, elasticity and lustre than any natural fibre. It is chemically inert and is fabricated into sheet,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

(ii) **Nylon-610:** 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.

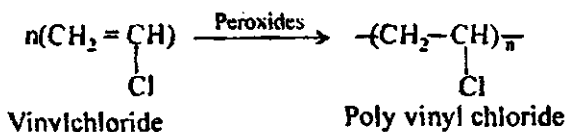
(iii) **Nylon-6:** It is also called Perlon-L. It is manufactured by prolonged heating of caprolactum, having amino group at one end and a carboxyl group at the other, at 530-540 K.



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.

### 3. Poly Vinyl Chloride:

It is commonly named as **PVC**. Its starting material is vinyl chloride ( $\text{CH}_2 = \text{CH} - \text{Cl}$ ). It is prepared by the polymerisation of vinyl chloride in presence of peroxides.



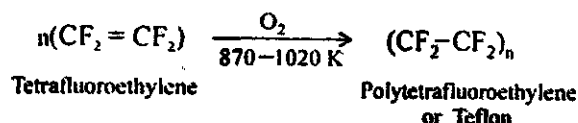
PVC is by and large a linear polymer, colourless and thermoplastic in nature and having a chloride content of about 56.8%. The polymer is thermally unstable and extensive heating transforms it into a dark coloured residue resembling polyacetylene and liberating HCl as the volatile. It is insoluble in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

#### 4. Teflon:

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



It is a 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.

#### 5. Cellulose:

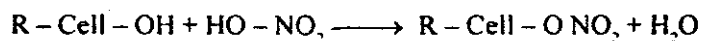
Cellulose is the most abundant constituent of the vegetables or plant kingdom. More than 50% of all the living matter is cellulose. It is the chief structural material of cell walls of all plants. It is also the chief component of wood (45–50% cellulose), cotton (90–95% cellulose), etc. The molecular 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. However, on heating with dil.  $H_2SO_4$  under pressure, it does not undergo hydrolysis to give only D-glucose,

**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 (R – Cell – O H) into the nitrate may be written as:



Cellulose nitrates for plastics and coating (lacquer) applications have N<sub>2</sub> content in the range 11.5 – 12.2%. They are available in a large number of viscosity grades and they are soluble in ester ketones, ether alcohol mixture and glycol ethers. Cellulose nitrates with 10.9 – 11.2% N<sub>2</sub> content find use in lithographic 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 cellulose

- (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<sub>2</sub>SO<sub>4</sub> 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.

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