Unit
15

Polymers

- **Polymers** are macro-sized, high molecular mass compounds, formed by the combination of a large number of simple molecules or repeating units.

  These simple molecules or repeating units which combine to give polymers are called **monomers**.

  The process of joining together of a large number of the monomers is termed as **polymerization**.

  A polymer formed from one type of monomers is called **homopolymer**, *e.g.*, polyethene, PVC, polyacrylonitrile, etc.

  A polymer formed from two or more different monomers is called **copolymer**, *e.g.*, Nylon-6,6, polyester, bakelite, etc.

  The number of times a monomer unit is repeated in a polymer, is called its degree of polymerization.

CLASSIFICATION OF POLYMERS

Classification based on

Source/Origin	Structure	Molecular forces	Synthesis
1. Natural polymers	1. Linear polymers	1. Elastomers	1. Addition polymers
2. Synthetic polymers	2. Branched chain polymers.	2. Fibres	2. Condensation polymers
3. Semi-synthetic polymers	3. Cross-linked polymers	3. Thermo-plastics	
		4. Thermosetting	

- **Natural polymers** are substances of natural origin and are mainly found in plants and animals, *e.g.*, starch, cellulose, proteins, etc.
- **Synthetic polymers** are those polymers which are prepared in the laboratories, they are also called man-made polymers, *e.g.*, teflon, terylene, synthetic rubber, etc.
- **Semi-synthetic polymers** are mostly derived from naturally occurring polymers by chemical modifications, *e.g.*, vulcanised rubber, cellulose nitrate, etc.
- **Linear polymers** are those polymers in which monomers are linked together to form linear chains, *e.g.*, polyethene, polyester, nylon, etc.
- **Branched chain polymers** are those in which the monomers are joined to form long chains or branches of different lengths, *e.g.*, glycogen, starch, etc.
- **Cross-linked polymers** are those in which the monomer units are cross-linked together to form a three-dimensional network. They are also called three-dimensional network polymers, *e.g.*, bakelite, melamine, etc.
- **Elastomers** are polymers having very weak intermolecular forces between the polymer chains. The weak forces permit the polymer to be stretched. Elastomers, thus, possess elastic character, *e.g.*, vulcanised rubber.
- **Fibres** are polymers which have strong inter- molecular forces between the chains. These are either hydrogen bonds or dipole-dipole interactions, *e.g.*, Nylon-6,6.
- Thermoplastics are those polymers in which the intermolecular forces of attraction are intermediate between those of elastomers and fibres. These polymers do not have any cross-links between the chains, they can be easily moulded on heating, *i.e.*, thermoplastics soften on heating and become hard on cooling, *e.g.*, polyethene, polystyrene, PVC, etc.
- **Thermosetting polymers** have extensive cross links formed between polymer chains on heating. They undergo the permanent change on heating, *e.g.*, bakelite, melamine, etc.

METHODS OF POLYMERISATION

- **Addition or Chain growth polymerisation :** A polymer formed by direct addition of repeated monomers without the elimination of by product molecules is called **addition polymer** and the phenomenon is known as **addition polymerization.**

$$\underset{\text{Ethene}}{n CH_2 = CH_2} \longrightarrow \underset{\text{Polyethene}}{+CH_2 - CH_2+_n}$$

Mechanism of chain growth polymerization involves a series of reactions, each of which consumes a reaction particle and produces a similar one. These reactive particles may be free radicals or cations or anions to which monomers get added by a chain reaction. It is an important reaction of all kinds of compounds having C=C bond.

Chain growth polymerization follows two basic mechanisms :

➢ **Free-radical mechanism :** This type of polymerization is initiated by organic peroxide or other reagents which decompose to give free radicals. Following steps are involved.

– **Chain initiation :** $R - CO - O \overset{\Delta}{\vdots} O - CO - R \longrightarrow$

$$\underset{\text{unstable}}{[RCOO^{\bullet}]} \longrightarrow R^{\bullet} + CO_2$$

– **Chain propagation :**

$$R^{\bullet} + CH_2 :: CH_2 \longrightarrow R - CH_2 - \dot{C}H_2$$

$$RCH_2\dot{C}H_2 + CH_2 :: CH_2 \longrightarrow RCH_2CH_2CH_2\dot{C}H_2$$