## **Polymers**

- **Polymers:** Polymers are high molecular mass substance consisting of large number of repeating structural units. As polymers are single, giant molecules i.e. big size molecules, they are also called macromolecules
- **Monomers:** The simple molecules which combine to form polymers by forming single or multiple bonds are called monomers.
- **Polymerization:** The process of formation of polymers from respective monomers is called polymerization

## • Classification of Polymers:

- 1. Based on source of availability, it is classified into
  - 1. Natural polymers: Polymers obtained from nature, mostly plants and animals. Examples Cellulose, starch, etc.
  - 2. Synthetic polymers: Polymers prepared in laboratory. Examples Teflon, Nylon 6,6, Synthetic rubber (Buna S) etc.
  - 3. Semi synthetic polymers: Polymers derived from naturally occurring polymers by carrying out chemical modifications. Examples Rayon (cellulose acetate), cellulose nitrate, etc.
- 2. Based on the structure of polymer, it is classified into
  - 1. Linear polymers: Polymer consists of long and straight chains. Examples High density polythene, polyvinyl chloride, etc.
  - 2. Branched chain polymers: Polymers contains linear chains having some branches. Examples Low density polythene
  - 3. Cross linked or network polymers: Polymers in which monomer units are cross linked together to form a 3 dimensional network polymers. Examples Bakelite, melamine, etc.

- 3. Based on the mode of polymerisation, it is classified into
  - I. Addition polymers: Polymers are formed by the repeated addition of monomers with double and triple bonds. It is further classified into,

Homopolymers:Polymers formed by the polymerisation of a single monomeric species. Examples - Polythene, Polystyrene.

Copolymers:Polymers formed by addition polymerisation of two different monomers. Examples - Buna-S, Buna -N.

II. Condensation polymers: Polymers formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units with elimination of simple molecules. Examples - Nylon 6, 6, Nylon 6.

Based on Molecular forces, it is classified into

Step 1: Chain initiating step: Organic peroxides undergo homolytic fission to form free radicals which acts as initiator. Initiator adds to C-C double bond of an alkene molecule to form a new free radical

$$C_sH_s-C-O-O-C-C_sH_s$$
  $\longrightarrow$   $2C_sH_s-C-O$   $\longrightarrow$   $2\dot{C}_sH_s$   $+$   $2CO_s$ 

Benzoyl peroxide  $C_sH_s+CH_s-CH_s$   $\longrightarrow$   $C_sH_s-CH_s$   $\longrightarrow$   $C_sH_s$ 

Step 2: Chain propagating step: Free radicals formed by homolytic cleavage adds to a double bond of monomer to form a larger free radical. Radical formed adds to another alkene molecule to form a larger free radical. This process continues until the radical is destroyed. These steps are called propagation steps.

$$C_{6}H_{5}-CH_{2}-CH_{2}+CH_{2}=CH_{2}$$

$$\downarrow$$

$$C_{6}H_{5}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}$$

$$\downarrow$$

$$C_{6}H_{5}-(CH_{2}-CH_{2})_{n}-CH_{2}-CH_{2}$$

Step 3: Chain terminating step: For termination of the long chain, free radicals combine in different ways to form polythene. One mode of termination of chain is shown as under:

$$C_{6}H_{5} - (CH_{3} - CH_{2})_{\pi} - CH_{2} - CH_{2}$$

$$C_{6}H_{5} - (CH_{3} - CH_{2})_{\pi} - CH_{2} - CH_{2}$$

$$\downarrow$$

$$C_{6}H_{5} - (CH_{2} - CH_{2})_{\pi} - CH_{2}$$

$$- CH_{2} - CH_{2}$$

$$- CH_{2} - CH_{2}$$

$$- CH_{2} - CH_{2} - CH_{2}$$

$$- CH_{2} - CH_{2} - CH_{2}$$

$$- CH_{2} - CH_{2} - CH_{2}$$

a). Low density polythene (LDP) is a polymer of ethene.

$$nCH_2 = CH$$
Ethens

350-570k 1000 to 2000 and reacces of  $O$ 
 $(CH_2 - CH_2)_n$ 
Positive re

It is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes

b). High density polythene(HDP) is a polymer of ethene.



It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

c). Polytetrafluoroethene (is a polymer of Teflon)

$$nCF_2 = CF_2$$
Tetrafluoroe the ne

Catta VIII High pressure

 $(CF_2 - CF_2)_n$ 
Teflon

It is used in making oil seals and gaskets and also used for non – stick surface coated utensils

d). Polyacrylonitrile is a polymer of acrylonitrile.



It is used as a substitute for wool in making commercial fibres such as orlon or acrilan.

- 1. Polyamides: Polymers possess amide linkage (-CONH-) in chain. Thesepolymers are popularly known as nylons. Examples:
- (a) Nylon 6, 6: It is prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.

$$nHOOC(CH_2)_4COOH + nH_2N(CH_2)_6NH_2$$

$$\begin{bmatrix} H & H & O & O \\ \parallel & \parallel & \parallel & \parallel \\ [N-(CH_2)_6 - N-C(CH_2)_4 - C]_n \end{bmatrix}$$

It is used in making sheets, bristles for brushes and in textile industry.

(b) Nylon 6: It is obtained by heating caprolactum with water at a high temperature

$$H_{2}C$$
 $C=O$ 
 $H_{2}C$ 
 $CH_{2}$ 
 $H_{3}O$ 
 $CH_{2}$ 
 $H_{3}O$ 
 $CH_{3}$ 
 $H_{3}O$ 
 $CH_{3}$ 
 $H_{3}O$ 
 $CH_{3}$ 
 $H_{3}O$ 
 $CH_{4}$ 
 $C$ 
 $CH_{5}$ 
 $CH_{5}$ 

It is used for the manufacture of tyre cords, fabrics and ropes.

2. Polyesters: These are the polycondensation products of dicarboxylic acids and diols Example: Terylene or Dacron

n HOH<sub>2</sub>C - CH<sub>2</sub>OH + n HOOC 
$$\longrightarrow$$
 COOH  $\longrightarrow$  COCH<sub>2</sub>-CH<sub>2</sub>-C  $\longrightarrow$  C  $\longrightarrow$  C  $\longrightarrow$  Ethylene glycol [Ethane-1, 2 - diol] Terephthalic acid [Benzene-1,4 - di

It is used to create resistance in polymerised product and is used in blending with cotton and wool fibres and also as glass reinforcing materials in safety helmets, etc.

- 3. Phenol formaldehyde polymer (Bakelite and related polymers)
- a). Bakelite: These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst. The initial product could be a linear product Novolac used in paints.

$$\begin{array}{c} \text{OH} \\ & \stackrel{\text{H* or}}{\bigcirc} \\ & \downarrow \\ & \downarrow \\ & \stackrel{\text{OH}}{\bigcirc} \\$$

b). Novolac on heating with formaldehyde forms Bakelite

$$-H_{2}C$$
  $CH_{2}$   $CH_{3}$   $CH_{2}$   $CH_{2}$   $CH_{3}$   $CH_{2}$   $CH_{3}$   $CH_{4}$   $CH_{5}$   $CH_{5}$ 

It is used for making combs, phonograph records, electrical switches and handles of various utensils

4. Melamine – formaldehyde polymer: Melamine formaldehyde polymer isformed by the condensation polymerisation of melamine and formaldehyde

$$H_{2}N \xrightarrow{N} NH_{2}$$
 + HCHO  $\longrightarrow$   $H_{2}N \xrightarrow{N} NHCH_{3}OH$ 
 $NH_{2}$   $NH_{2}$   $NH_{2}$ 

Melamine Formaldehyde Resin intermediate

 $\longrightarrow$   $H_{2}N \xrightarrow{N} NHCH_{3}OH$ 
 $NH_{2}$ 
 $NH_{2}$ 
 $NH_{2}$ 
 $NH_{3}$ 
 $NH_{2}$ 
 $NH_{3}$ 
 $NH_{4}$ 
 $NH_{5}$ 
 $NH_{5}$ 

It is used in the manufacture of unbreakable crockery.

$$CH_3$$
  $CH_3$   $CH_3$   $-CH_2 - CH_3 - CH_4$   $-CH_5$   $-$ 

Sulphur cross links in vulcanised rubber

a). Natural rubber: Natural rubber is a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as *cis* - 1, 4 - polyisoprene.

$$H_3C$$
 $C = C$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_4$ 
 $CH_5$ 
 $CH_5$ 

- b). Synthetic rubber: Synthetic rubbers are either homopolymers of 1, 3 butadiene derivatives or copolymers of 1, 3 butadiene or its derivatives with another unsaturated monomer.
- A) Neoprene or polychloroprene

$$nCH_2 = C - CH = CH_2$$

$$2 - chloro - 1, 3 - butadieve$$

$$CI$$

$$CI$$

$$CH_2 - C = CH - CH_2]_n$$
Neotrens

It is used for manufacturing conveyor belts, gaskets and hoses

## B) Buna - N

It is used in making oil seals, tank lining, etc. because it is resistant to the action of petrol, lubricating oil and organic solvents

$$nCH_2 = CH - CH = CH_2 + nC_6H_5CH = CH_2$$
 Squrene 1,3-butadiene 
$$\begin{bmatrix} C_6H_5 \\ CH_2 - CH = CH - CH_2 - CH_2 - CH \end{bmatrix}_n$$
 Butadiene-squrene copolym er (Bura-S)

a). Poly -  $\beta$ -hydroxybutyrate – co- $\beta$ -hydroxyvalerate (PHBV):

It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3 – hydroxypentanoic acid

It is used in speciality packaging, orthopaedic devices and in controlled release of drugs.

b). Nylon 2-nylon 6: It is an alternating polyamide copolymer of glycine(H2N-CH2-COOH) and amino caproic acid (H2N (CH2)5 COOH)

$$nH_2N-CH_2-COOH+nH_2N-(CH_2)_5-COOH \\ \downarrow \\ \rho \\ (HN-CH_2-C-HN-(CH_2)_5-C)_n$$

Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$CH_3$ $(CH_2-CH)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Glyptal	<ul><li>(a) Ethylene</li><li>glycol</li><li>Manufacture of</li><li>(b) Phthalic acid</li></ul>	<b>(</b> ocH₂-cH₂ooc co <b>)</b> <sub>n</sub>	Manufacture of paints and lacquers
Polystyrene	Styrene	$(CH_2 - CH)_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets
Polyvinyl chloride (PVC)	Vinyl chloride	$(CH_2 - CH)_n$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes

- Elastomers: Polymer chains are held together by weakest intermolecular forces.
   Polymers are rubber like solids with elastic properties. Examples Buna S, Buna N, Neoprene.
- 2. Fibre: Polymers have strong intermolecular force like hydrogen bonding. Fibres are the thread forming solids which possess high tensile strength and high modulus. Examples Nylon 6, 6, Polyesters.
- 3. Thermoplastic polymers: Polymers are held by intermolecular forces which are in between those of elastomers and fibres. These polymers are capable of repeated softening on heating and hardening on cooling. Examples Polythene, Polystyrene.

- 4. Thermosetting polymers: Polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and eventually undergo a permanent change. Examples Bakelite, Urea-formaldelyde resins
- 5. Addition Polymerisation or Chain Growth Polymerisation: Addition polymerisation is called chain growth polymerisation because it takes place through stages leading to increase in chain length and each stage produces reactive intermediates for use in next stage of the growth of chain. Most common mechanism for addition polymerisation reactions is free radical mechanism

# **Important Addition Polymers:**

Condensation Polymerisation or Step Growth polymerization: Polymerisation generally involves a repetitive condensation reaction between two bi-functional monomers. In condensation reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on. Since, each step produces a distinct functionalized species and is independent of each other, this process is also called as step growth polymerisation.

#### **Condensation Polymers:**

Terylene or Dacron: It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetate-antimony trioxide catalyst.

**Vulcanisation of rubber:** The process of heating a mixture of raw rubber with sulphur and an appropriate additive in a temperature range between 373 K to 415 K to improve upon physical properties like elasticity, strength etc.

## **Examples of synthetic rubber:**

Biodegradable Polymers: Polymers which are degraded by microorganisms within a suitable period so that biodegradable polymers and their degraded products do not cause any serious effects on environment.

# Examples of biodegradable polymer:

Commercially important polymers along with their structures and uses: