

Polymers

Polymers are large molecules having high molecular mass (103 – 107 u). They are also called macromolecules.

Polymerisation is the process of formation of polymers from respective monomers.

Classification of polymers:

- (I) On the basis of source
- (i) Natural polymers: Found in plants and animals, e.g., proteins, cellulose, starch.
- (ii) Semi-synthetic polymers: Cellulose acetate (rayon), cellulose nitrate
- (iii) Synthetic polymers: Synthetic fibre → nylon 6, 6 Synthetic rubber → Buna-S
- (II) On the basis of structure
- (i) Linear polymers: High-density polythene, Polyvinyl chloride.
- (ii) Branched-chain polymers: Low-density polythene.
- (iii) Cross-linked or network polymers: They contain strong covalent bonds between various linear polymer chains, e.g., bakelite, melamine
- (III) On the basis of mode of polymerisation
- (i) Addition polymer: Polymers formed by repeated addition of monomers containing double or triple bonds Addition polymers formed from single monomeric species are called homopolymers. Addition polymers formed from two different monomeric species are called copolymers.
- (ii) Condensation polymers: Polymers formed by repeated condensation reaction between two different bi-functional or trifunctional monomers Condensation polymerisation involves elimination of small molecules such as water, alcohol, hydrogen chloride, etc.
- (IV) On the basis of molecular forces
- (i) Elastomers: Polymer chains are held together by the weakest intermolecular forces, e.g., buna N, buna S, neoprene
- (ii) Fibres: Possess strong intermolecular forces like H-bonding, e.g., nylon-6, 6, terylene
- (iii) **Thermoplastic polymers:** Possess intermolecular forces of attraction intermediate between elastomers and fibres, e.g. polythene, polystyrene, PVC
- (iv) Thermosetting polymers: Cross-linked or highly branched molecules, e.g., bakelite, ureaformaldehyde resins.

- **(V) On the basis of growth polymerisation** (Depending upon the type of polymerisation mechanism)
- (i) Chain-growth polymers
- (ii) Step-growth polymers

Types of polymerisation reactions:

- (I) Addition polymerisation or chain-growth polymerisation: Molecules of the same monomer or different monomers add together on a large scale to form a polymer.
- (a) Polytetrafluoroethene (Teflon): Chemically inert and resistant to attack by corrosive reagents. It is used for making oil seals and gaskets, and for non-stick-surface-coated utensils.

$$n \text{ CF}_2 = \text{CF}_2$$
 Catalyst $+ \text{CF}_2 - \text{CF}_2$ High pressure $+ \text{CF}_2 - \text{CF}_2$ Tetrafluoroethene

(b) Polyacrylonitrile: It is used as a substitute for wool in making commercial fibres as orlon or acrilan.

$$n \text{ CH}_2 = \text{CH CN} \xrightarrow{\text{Addition polymerisation}} \text{Peroxide catalyst} \qquad \text{CH}_2 - \text{CH}_{2n}$$
Acrylonitrile

(II) Condensation polymerisation or step-growth polymerisation: Involves a repetitive condensation reaction between two bi-functional monomers. This results in the loss of some simple molecules as water, alcohol, etc., and leads to the formation of high molecular mass condensation polymers.

(a) Polyamides

Nylon, 6, 6: Used in making sheets, bristles for brushes and in textile industry.

$$n \text{ HOOC } (CH_2)_4 \text{ COOH} + n \text{ H}_2\text{N } (CH_2)_6 \text{ NH}_2 \xrightarrow{553 \text{ K}} \left[\begin{array}{c} \text{H} & \text{H} & \text{O} & \text{O} \\ \text{I} & \text{I} & \text{II} & \text{II} \\ \text{N} - (CH_2)_6 - \text{N} - \text{C } (CH_2)_4 - \text{C} \end{array} \right]_n$$

$$\text{Nylon 6. 6}$$

Nylon 6: Used for the manufacture of tyre cords, fabrics and ropes

(b) Polyesters

Dacron: Used in blending with cotton and wool fibres and as glass-reinforcing materials in safety helmets.

$$n$$
HOH₂C — CH₂OH + n HOOC — COOH

Ethylene glycol Terephthalic acid

$$\begin{bmatrix}
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
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OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
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OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O & O \\
OCH_2 CH_2 - O - C & O \\$$

(c) Phenol-formaldehyde polymer: E.g., Bakelite Novolac, when heated with formaldehyde, undergoes cross linking to form bakelite, which is an infusible solid mass.

$$n$$
 CH_2OH
 H^+
 CH_2
 CH_2

Novolac, obtained on heating with formaldehyde, undergoes cross-linking to form an infusible solid mass called bakelite.

(d) Melamine-formaldehyde polymer: Used in the manufacture of unbreakable crockery.

Copolymerisation: Polymerisation involving more than one monomeric species.

Rubber (cis – 1, 4 – Polyisoprene): It is a natural polymer which possesses elastic properties. It is also termed as elastomer.

$$\begin{array}{c} H_3C \\ \sim \\ H_2C \end{array} \\ C = C \\ \begin{array}{c} H \\ CH_2 \end{array} \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \end{array} \\ C = C \\ \begin{array}{c} H \\ CH_2 \\ CH_2 \end{array} \\ CH_2 \\ CH_2$$

Linear polymer of isoprene (2-methyl-1, 3-butadiene)

Vulcanisation of rubber: Process of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373 K and 415 K.

Synthetic rubbers: Either homopolymers of 1, 3-butadiene derivatives, co-polymers of 1, 3-butadiene or its derivatives with another unsaturated monomer.

Preparation of synthetic rubbers

Neoprene: Used for manufacturing conveyer belts, gaskets and hoses.

Buna-N: It is resistant to the action of petrol, lubricating oil and organic solvents hence it is used for making oil seals, tank lining, etc.

$$n \text{ CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 + n \text{CH}_2 = \text{CH}$$

$$1,3\text{-Butadiene} \qquad \text{Acrylonitrile}$$

$$CN \\ Co-polymerisation \\ CH_2 - CH = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_1$$

Biodegradable polymers: One important class of biodegradable polymers are aliphatic polyesters. E.g., PHBV, nylon 2-nylon 6. They are used in speciality packaging, orthopaedic devices and in controlled release of drugs.

OH OH CH₃-CH-CH₂-COOH + CH₃-CH₂-CH-CH₂-COOH
$$\longrightarrow$$
 (O-CH-CH₂-C-O-CH-CH₂-C) \cap CH₃ O CH₂CH₃ O

3-Hydroxybutanoic acid

3-Hydroxypentanoic acid

PHBV