

Class





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Unit 8

Polymers | Chemistry in Everyday Life

POLYMERS

INTRODUCTION

 Polymers are large molecules having high molecular mass (10³ – 10⁷ u) formed by chemical combination of a large number of relatively smaller molecules known as monomers.

- Monomers are linked to each other by covalent bonds and referred as polymerisation.
- All polymers are macromolecules but all macromolecules are not polymers.

CLASSIFICATION OF POLYMERS

Thermoplastics: Neither very strong nor very weak intermolecular forces. Do not have any cross-links between chains. Can be easily moulded on heating *e.g.*, polypropylene, polystyrene, etc.

Elastomers: Very weak intermolecular forces and possess elastic characters *e.g.*, natural rubber, buna-S, etc.

Fibres: Quite strong intermolecular forces like hydrogen bonds. Used for making fibres *e.g.*, nylon-6,6, polyacrylonitrile (orlon), etc.

Thermosetting plastics: Extensive cross-links are formed between polymeric chains on heating. They undergo permanent change *e.g.*, bakelite, resin, etc.

Natural polymers: Substances of natural origin, *i.e.*, found mainly in plants and animals *e.g.*, silk, enzymes, natural rubber, haemoglobin, starch, cellulose, proteins, etc.

Copolymers:

Addition polymers formed by two different monomeric units *e.g.*, Buna-S, Buna-N, etc.

Addition polymers: Formed by addition of monomers without elimination of byproducts.

Homopolymers: Addition polymers formed by the single monomeric units *e.g.*, polyethene, PVC, etc.

Condensation polymers: Formed by combination of monomers with elimination of simple molecules like water, alcohol, ammonia, etc. e.g., dacron, nylon-6,6, etc.

Based upon synthesis
POLYMERS

Based upon source or origin

Semisynthetic polymers: Derived by using natural polymers *e.g.*, vulcanised rubber, nitrocellulose, cellulose xanthate,

Linear polymers: Monomers are joined together to form straight chains *e.g.*, PVC, polystyrene, nylons, etc.

Branched chain polymers: Monomers are joined to form irregularly packed polymers having branched chains *e.g.*, amylopectin, glycogen, starch, etc.

Cross linked polymers: Initially formed linear polymer chains are joined together to form a three dimensional network structure e.g., bakelite, melamine formaldehyde resin (melmac), etc.

Synthetic polymers: Prepared in laboratory. Completely man-made polymers *e.g.*, teflon, dacron, synthetic rubber, nylon-6,6, etc.

Types of Polymerisation Reactions

Addition or Chain Polymerisation

• This type of polymerisation involves successive addition of monomer units to the growing chain having a reactive intermediate such as a free radical, a carbocation or a carbanion and leads to increase in chain length at each stages. Alkenes, conjugated dienes or any other unsaturated compounds polymerise by addition polymerisation.

Mechanism of free-radical polymerisation :

- Free-radical polymerisation is initiated by organic peroxide like benzoyl peroxide or other reagents such as azobis-isobutyronitrile which decomposes to give free radicals. Following steps are involved in the mechanism:
 - Chain initiation: Organic peroxides undergo homolytic fission to form free radicals.

$$R - C - O + O - C - R \longrightarrow \begin{bmatrix} O \\ || \\ R - C - O \end{bmatrix} \longrightarrow R + CO_2$$
 Organic peroxide Unstable

 Chain propagation: Free radical formed adds to a monomer molecule to form a new free radical.

$$R + CH_2 \rightarrow R - CH_2 - \dot{C}H_2$$

Addition of monomer molecules to growing free radical chain goes on till a long chain is formed.

$$\begin{array}{c} RCH_2\dot{C}H_2 + nCH_2 = CH_2 \\ \longrightarrow R + CH_2 - CH_2 - CH_2 - \dot{C}H_2 \end{array}$$

 Chain termination: The termination of the long chain radicals usually occurs by radical coupling or disproportionation reactions.

Radical coupling:

$$2R(CH_2CH_2)_nCH_2\dot{C}H_2 \longrightarrow$$

 $R(CH_2CH_2)_nCH_2CH_2CH_2CH_2(CH_2CH_2)_nR$
Disproportionation :

$$2R + CH_2CH_2 \rightarrow_n CH_2 \stackrel{\cdot}{C}H_2 \longrightarrow$$

$$R + CH_2CH_2 \rightarrow_n CH = CH_2$$

$$+ R + CH_2CH_2 \rightarrow_n CH_2CH_3$$

Mechanism of cationic addition polymerisation:

 Initiated by the use of strong Lewis acids such as HF, AlCl₃, H₂SO₄, etc.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

 $H^+ + CH_2 = CH_2 \longrightarrow CH_3 - CH_2^+$

The carbocation thus formed undergoes addition with several monomers and finally the chain is terminated by combination with a negative ion or loss of a proton *e.g.*, polyvinyl ether, polyisobutylene, polystyrene, etc. Alkenes containing electron donating groups polymerise preferably under this polymerisation.

Mechanism of anionic addition polymerisation:

 Initiated by strong bases such as NaNH₂, C₄H₉Li, Grignard reagent, etc.

$$\begin{array}{c} \overbrace{B^- + \operatorname{CH}_2 = \operatorname{CH}_2 \longrightarrow B - \operatorname{CH}_2 - \operatorname{CH}_2} \\ \operatorname{Carbanion} \end{array}$$

The carbanion thus formed undergoes addition with number of monomers and finally terminates. *e.g.*, polymerisation of acrylonitrile, vinyl chloride and methyl methacrylate, etc. Alkenes containing electron withdrawing groups polymerise preferably under this polymerisation.

Condensation or step growth polymerisation:

 Condensation polymerisation involves the reaction of polyfunctional molecules to give macromolecules with the loss of simple molecules like water, carbon dioxide, etc. For example,

$$n \text{HOOC} \longrightarrow \text{COOH} + n \text{HO}(\text{CH}_2)_2 \text{OH} \longrightarrow$$
Terephthalic acid Ethylene glycol
$$= \left\{ \text{OC} \longrightarrow \text{CO} - \text{O} - (\text{CH}_2)_2 - \text{O} \right\}_n + n \text{H}_2 \text{O}$$
Terylene or Dacron

Copolymerisation

• It is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise to form a copolymer. Copolymers can be prepared by both chain growth and step growth polymerisation *e.g.*, butadiene-styrene copolymer.

$$nCH_2 = CH - CH = CH_2 + \bigcup_{\text{Styrene}} CH = CH_2$$

$$+ CH_2 - CH = CH - CH_2 - CH - CH_2 + \bigcup_{\text{Styrene}} CH_$$

SOME IMPORTANT ADDITION AND CONDENSATION POLYMERS

Addition Polymers

LDPE

- Highly branched polymer.
- Low density (0.92 g/cm³), low melting point (384 K).
- Transparent, moderate tensile strength.
- Chemically inert, tough but flexible.
- Used for packaging, insulation and manufacturing squeeze bottles, pipes, toys, etc.

HDPE

- Linear molecules, closely packed.
- High density (0.97 g/cm³), high melting point (403 K).
- Translucent
- Chemically inert, quite harder, greater tensile strength.
- Used for manufacturing containers, housewares and pipes, etc.

Teflon

- Chemically inert and resistant to attack by corrosive reagents.
- Teflon coating undergoes decomposition at temperature above 300 °C.
- Used for non-stick surface coated utensils.

Condensation Polymers

Nylon 6,6

- Prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.
- It is used in textile industry.

Bakelite

- Infusible solid mass.
- Cross-linking polymer.
- Formed when novolac undergoes heating with formaldehyde.
- Used for handling of various utensils.

RUBBER



Natural rubber

It is a linear 1, 4-addition polymer of isoprene and have *cis*-configuration of all double bonds thus, known as *cis*-1, 4-polyisoprene.

- It is insoluble in water, dilute acids and alkalies but soluble in organic solvents like benzene, petrol, etc.
- It has low elasticity and tensile strength.
- It shows high water absorption capacity.
- It has weak intermolecular van der Waals' forces.

Vulcanisation of rubber

It is the process of heating natural rubber with sulphur at a temperature of 373-415 K. Sulphur cross-links makes the rubber hard, tough with greater tensile strength.

- On vulcanisation, sulphur forms cross-links at the reactive site of double bonds and thus, the rubber get stiffened.
- Some additives like carbon black, zinc oxide, etc. are used to improve wearing properties.

Synthetic rubber

It is obtained by polymerising certain organic compounds which may have properties similar to rubber and some additional desirable properties. These are also vulcanised. For example, neoprene, styrene butadiene rubber (SBR), thiokol, silicones, polyurethane rubber.

The trans-isomer of polyisoprene i.e. gutta percha is synthetic rubber and considered to be non-elastic.

Neoprene

It is a polymer of chloroprene. It is superior due to its stability to aerial oxidation and its resistance to vegetables and mineral oils.



Nitrile rubber or Buna-N

It is a polymer of buta-1,3-diene and acrylonitrile. It is resistant to the action of petrol, lubricating oil and organic solvents, etc.

SOME IMPORTANT POLYMERS

Polymer	Structure of monomer(s)	Structure of polymer	Uses
Polythene	CH ₂ =CH ₂	$+CH_2-CH_2+_n$	As insulator, packing material, household and laboratory ware.
Polystyrene	CH=CH ₂	$\begin{bmatrix} -CH-CH_{\frac{1}{2}} \\ -CH-CH_{\frac{1}{2}} \end{bmatrix}_{n}$	As insulator, wrapping material, household articles and toys maker.
Polyvinyl chloride (PVC)	CH ₂ =CHCl	$\begin{bmatrix} CH_2 - CH \end{bmatrix}_n$	In manufacture of raincoats, hand bags, leather clothes and vinyl flooring.
Polytetrafluoro - ethylene (PTFE) or Teflon	CF ₂ =CF ₂	$+CF_2-CF_2+_n$	As lubricant, insulator and making cooking wares.
Polyacrylonitrile (PAN) or Orlon	CH ₂ =CH-CN	$\begin{bmatrix} \operatorname{CH}_2 - \operatorname{CH} \\ \vdots \\ \operatorname{CN} \end{bmatrix}_n$	In making synthetic fibres and wool.
Butyl rubber	$CH_2 = C$ CH_3 CH_3	$ \begin{array}{c} $	Used in place of natural rubber in industry.
Neoprene	CH ₂ =C-CH=CH ₂ Cl	$ \begin{bmatrix} CH_2 - C = CH - CH_2 \\ CI \end{bmatrix}_n $	As insulator, making conveyor belts and printing rollers.
Styrene Butadiene Rubber (SBR) or (Buna-S)	CH=CH ₂ and CH ₂ =CH-CH=CH ₂	$ \begin{array}{c c} -CH_2-CH-CH_2-CH=CH-CH_2 \end{array} $	In making automobile tyres, floor tiles, cable insulation and footwear.
Nitrile rubber (Buna-N)	CH ₂ =CHCN and CH ₂ =CH-CH=CH ₂	$\begin{bmatrix} CH - CH_2 - CH_2 - CH = CH - CH_2 \\ CN \end{bmatrix}_n$	In making oil seals, hose-pipes and tank linings.
Nylon-6 (Perlon-L)	HNO	$\begin{bmatrix} C - (CH_2)_5 - N \\ \parallel & \parallel \\ O & H \end{bmatrix}_n$	In making carpets, ropes and tyre cords.
Nylon-6, 6	HOOC—(CH ₂) ₄ —COOH and H ₂ N—(CH ₂) ₆ —NH ₂	+CO-(CH2)4-CONH-(CH2)6-NH+n	Synthetic fibres, fishing nets, ropes and tyre industries.
Terylene (Dacron)	HOOC—O—COOH and HOCH ₂ CH ₂ OH	$-\left[O-CH_2-CH_2-O-C-\left(\begin{array}{c}O\\I\\I\\C\end{array}\right)-\begin{array}{c}O\\I\\I\\I\\I\\I\\I\\I\\I\\I\\I\\I\\I\\I\\I\\I\\I\\I\\I\\I$	Synthetic fibres, safety belts, tyre cords and tents.
Bakelite (Phenol- formaldehyde resin)	OH and HCHO	CH_2 CH_2 CH_2	In making gears, protective coatings and electric fittings.