Chapter_15

Polymers

1. Polymers can be defined as compounds of high molecular mass (10^3-10^7u) formed by combination of large number of small molecules. These small molecules which constitute the repeating units in a polymer are called monomer units, e.g. polythene, nylon-6, 6.

2. Classification of polymers

- *Classification based on source*
  - (i) **Natural polymers** are found in plants and animals e.g. proteins.
  - (ii) **Semi-synthetic polymers** like cellulose derivative as cellulose acetate (rayon) and cellulose nitrate, etc.
  - (iii) **Synthetic polymers** like plastic, synthetic rubber (Buna-S).
- *Classification based on structure*
  - (i) **Linear polymers** are long and straight chain, e.g. high density polythene.
  - (ii) **Branched chain polymers** contain chain having some branches e.g. low density polythene.
  - (iii) **Cross-linked polymers** are formed by bi-functional and trifunctional monomers, contain covalent bonds between linear polymeric chains.
- *Classification based on mode of polymerisation*

(i) **Addition polymers** formed by repeated addition of monomer molecules possessing double or triple bonds e.g. polythene.

Addition polymer are of two types. *These are as follows :*

(a) **Homopolymers** are those addition polymers in which single monomeric species is involved in their formation. e.g. polythene.

$$n\underset{\text{Ethene}}{CH_2{=}CH_2} \longrightarrow \underset{\text{Polythene}}{-(CH_2-CH_2)_n-}$$

(b) **Copolymers** are those addition polymers in which two different monomeric species are involved in their formation. The process is called copolymerisation e.g. Buna-S.

$$n\underset{\text{1,3-butadiene}}{CH_2{=}CH{-}CH{=}CH_2} + n\underset{\text{Styrene}}{C_6H_5CH{=}CH_2} \longrightarrow$$

$$\underset{\text{Buna -S}}{-(CH_2-CH=CH-CH_2-CH_2-\underset{C_6H_5}{\underset{|}{C}}H)_n-}$$

(ii) **Condensation polymers** are formed by repeated condensation reaction between two different bifunctional or trifunctional monomeric units. e.g. nylon-6,6.

- *Classification based on molecular forces*

(i) **Elastomers** are rubber-like solids with elastic properties. These polymers have the weakest intermolecular forces, which permit the polymer to be stretched. A few 'cross-links' are introduced in between the chains, through which the polymer regain its original position after the force is released, e.g. vulcanised rubber, buna-S, buna-N, neoprene, etc.

$$\underset{\text{Neoprene}}{-(-CH_2-\underset{Cl}{\underset{|}{C}}=CH-CH_2-)_n-}$$

(ii) **Fibres** have strong intermolecular forces like hydrogen bonding or dipole-dipole interactions. They are useful in making fibres as their molecules are long and thread-like. They possess high tensile strength, high modulus and less elasticity. These strong forces also lead to close packing of chains and imparts crystalline nature. e.g. nylon-6,6, (polyamides), terylene (polyester), etc.

(iii) **Thermoplastic polymers** are those polymers in which intermolecular forces are intermediate between those of elastomers and fibres. They are linear or slightly branched long molecules which are capable of repeatedly softening on heating and hardens on cooling. e.g. polystyrene, polythene, PVC, etc.

$$\underset{\text{(PVC)}}{-(CH_2-\underset{Cl}{\underset{|}{C}}H)_n-}$$

- **Thermosetting polymers** are cross-linked or heavily branched molecules, which on heating undergo extensive cross-linking and become infusible. Once they get set, they cannot be reshaped and reused. e.g. bakelite, urea-formaldehyde resins, etc.

3. Types of Polymerisation Reactions

The two types of polymerisation reactions are as follows :

Addition polymerisation Here, the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The most common mode of addition polymerisation is free radical mechanism.

Steps involved in free radical polymerisation of ethene are

***Step* I Chain initiation step**

$$(C_6H_5COO)_2 \longrightarrow 2(C_6H_5C\dot{O}O) \xrightarrow[-CO_2]{} 2\dot{C}_6H_5$$

$$\dot{C}_6H_5 + CH_2{=}CH_2 \longrightarrow C_6H_5CH_2-\dot{C}H_2$$

Step **II Chain propagating step**

$$C_6H_5-CH_2-\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow$$

$$\downarrow (n\text{-}1)CH_2{=}CH_2$$

$$C_6H_5-CH_2-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$C_6H_5-(CH_2-CH_2)_n-CH_2-\dot{C}H_2$$

***Step* III Chain terminating step**

$$2C_6H_5(CH_2-CH_2)_nCH_2-\dot{C}H_2 \longrightarrow$$

$$C_6H_5(CH_2-CH_2)_nCH_2CH_2CH_2CH_2$$

$$(CH_2-CH_2)_nC_6H_5$$

- **Condensation polymerisation** involves a repetitive condensation reaction between two bi-functional monomers.

4. **Copolymerisation** involves the polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise and form a copolymer.

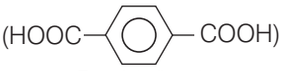
5. Some important **polymers and their monomers**

(i) **Polymer** — Polythene
Monomer— Ethene ($CH_2 = CH_2$)

(ii) **Polymer** — Teflon
Monomer— Tetrafluoroethylene ($CF_2 = CF_2$)

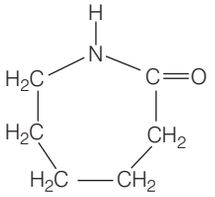
(iii) **Polymer** — Orlon or acrilan, polyacrylonitrile (PAN)
Monomer — Acrylonitrile [$CH_2 = CH(CN)$]

(iv) **Polymer** — Terylene or dacron.
Monomers — Ethylene glycol ($CH_2OH—CH_2OH$),



Terephthalic acid

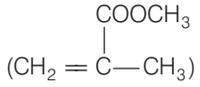
(v) **Polymer** — Nylon-6 or perlon
Monomer — Caprolactam



(vi) **Polymer** — Nylon-6,6
Monomers— Adipic acid [$HOOC(CH_2)_4COOH$] and hexamethylene diamine [$H_2N(CH_2)_6NH_2$]

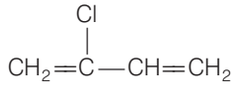
(vii) **Polymer** — Bakelite
Monomer — Formaldehyde (HCHO) and phenol (C_6H_5OH)

(viii) **Polymer** — PMMA [Polymethyl methacrylate]
Monomer — Methyl methacrylate



(ix) **Polymer** — Cellulose
Monomer — β-D-glucose.

(x) **Polymer** — Neoprene or synthetic rubber
Monomer — Chloroprene



(xi) **Polymer** — Buna-S
Monomer — Buta-1,3-diene ($CH_2 = CH—CH = CH_2$), styrene ($C_6H_5—CH = CH_2$)

(xii) **Polymer** — Buna-N
Monomer — Buta-1,3-diene ($CH_2=CH—CH=CH_2$) , acrylonitrile ($CH_2=CH—CN$)

6. **Natural rubber** is *cis* polyisoprene, a polymer of isoprene (2-methylbuta-1,3-diene).

7. **Vulcanisation** is the heating of natural rubber with sulphur and an appropriate additive at a temperature range between 373 K to 415 K. Sulphur forms cross-links at the reactive sites of the double bond and thus, rubber gets stiffened, i.e. becomes less sticky and plastic, more resistant to swelling in organic liquids and has enhanced elasticity. Physical properties of rubber can be improved by vulcanisation.

8. Rubber made with 1-3% sulphur is soft and stretchy and is used in making rubber bands and rubber made with 5% sulphur is more rigid and is used in the manufacture of tyres for automobiles etc.

   It is also used in making footwears, battery boxes, foam mattresses, balloons, toys, etc.

   Main constituent of bubble gum is styrene-butadiene (Buna-S) copolymer.

9. **Biodegradable polymers** are those polymers which get decomposed by themselves over a period of time due to environmental degradation by bacteria.
   e.g. PHBV(Poly β -hydroxy butyrate-co-β-hydroxy valerate)