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.

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

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

(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.

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

(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.

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

- **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**

$$(C_6H_5COO)_2 \longrightarrow 2(C_6H_5CO\dot{O}) \xrightarrow[-CO_2]{} 2\dot{C}_6H_5$$

$$\dot{C}_6H_5 + CH_2{=}CH_2 \longrightarrow C_6H_5CH_2{-}C\dot{H}_2$$

Step **II Chain propagating step**

$$C_6H_5{-}CH_2{-}C\dot{H}_2 + CH_2{=}CH_2 \longrightarrow$$

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

$$C_6H_5{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C\dot{H}_2$$

$$C_6H_5{-}(CH_2{-}CH_2)_n{-}CH_2{-}C\dot{H}_2$$

***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.

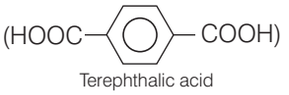
5. Some important **polymers and their monomers**

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

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

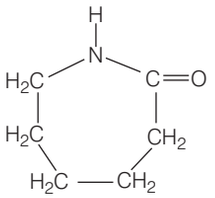
(iii) **Polymer** — Orlon or acrilan, polyacrylonitrile (PAN)
Monomer — Acrylonitrile [$CH_2{=}CH(CN)$]

(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

$$(CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle COOCH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_3)$$

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

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

$$CH_2{=}\underset{\displaystyle Cl}{\overset{|}{C}}{-}CH{=}CH_2$$

(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)

Practice Questions

1. The molecular mass of polymer is in the range of
(a) 10^{10} - 10^{15} u *(b)* 10^{3} - 10^{7} u
(c) 10^{6} - 10^{18} u *(d)* 10^{1} - 10^{3} u

2. To which category of polymers, cellulose derivatives belong to?
(a) Synthetic polymers *(b)* Semi-synthetic polymers
(c) Natural polymers *(d)* Branched polymers

3. Buna-S is a
(a) natural polymer *(b)* synthetic polymer
(c) semi-synthetic polymer *(d)* None of these

4. PVC is a
(a) linear polymer *(b)* branched polymer
(c) cross-linked polymer *(d)* None of these

5. What is full form of HDP?
(a) High density polythelene
(b) High density polythene
(c) High density polypropene
(d) High density polypropylene

6. Polymers containing linear chains having some branches are known as
(a) network polymers *(b)* branched polymers
(c) linear polymers *(d)* cross-linked polymers

7. Which one of the following is a network polymer?
(a) HDP *(b)* Bakelite
(c) LDP *(d)* Polyvinyl chloride

8. Buna-S is a copolymer of
(a) ethene and styrene *(b)* 1, 3-butadiene and ethene
(c) 1, 3-butadiene and styrene *(d)* ethene and propene

9. Rubber like solids with elastic properties are called
(a) elastomers
(b) fibres
(c) thermosetting polymers
(d) thermoplastic polymers

10. Polymer which contains strong intermolecular forces, e.g. hydrogen bonding is
(a) polystyrene *(b)* nylon-6,6
(c) teflon *(d)* natural rubber

11. The repeated addition of same monomer molecules having double or triple bonds is known as
(a) copolymer *(b)* elastomer
(c) homopolymer *(d)* fibre

12. Low density polythene is obtained through
(a) electrophilic addition
(b) free radical addition
(c) nucleophilic addition
(d) nucleophilic substitution

13. LDP is used in the insulation of electricity wires and manufacture of flexible pipes because
(a) it is chemically inert
(b) it is tough and flexible
(c) it is poor conductor of electricity
(d) All of the above

14. The type of polythene which is chemically inert and more tough and hard is
(a) HDP *(b)* LDP
(c) Both (a) and (b) *(d)* None of these

15. The commercial name of polyacrylonitrile is
(a) orlon (acrilan) *(b)* dacron
(c) bakelite *(d)* melamine

16. Nylon is an example of
(a) polyester *(b)* polysaccharide
(c) polyamide *(d)* polythene

17. $\left[\mathrm{NH(CH_2)_6NHCO(CH_2)_4CO}\right]_n$ is a
(a) homopolymer *(b)* condensation polymers
(c) addition polymer *(d)* thermosetting polymer

18. The monomers of dacron, a polyester is/are
(a) ethylene glycol *(b)* terephthalic acid
(c) caprolactam *(d)* Both (a) and (b)

19. Preparation of bakelite proceeds *via* reactions
(a) electrophilic addition and dehydration
(b) condensation and elimination
(c) nucleophilic addition and dehydration
(d) electrophilic substitution and dehydration

20. Among the following polymers, the phenol formaldehyde resin is
(a) teflon *(b)* bakelite
(c) melamine *(d)* buna-N

21. In natural rubber, few cross-links are introduced in between the chains. These chains help to
(a) make the rubber soft
(b) retract the original position after the force is released
(c) make the rubber hard
(d) None of the above

22. Which is the monomer of neoprene in the following?
(a) $CH_2=CH-C\equiv CH$
(b) $CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH$
(c) $CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2$
(d) $CH_2=CH-CH=CH_2$

23. Which polymer has 'chiral' monomer(s)?
(a) PHBV *(b)* Buna-N
(c) Nylon-6, 6 *(d)* Neoprene

24. Biodegradable polymer which can be produced from glycine and amino caproic acid is
(a) nylon-2-nylon-6 *(b)* PHBV
(c) buna-N *(d)* nylon-6, 6

25. Among the following, which polymer is used for making combs, electrical switches, handles of utensils and computer discs?
(a) Bakelite
(b) Glyptal
(c) Polystyrene
(d) PVC

ANSWERS

1. (b)	**2.** (b)	**3.** (b)	**4.** (a)	**5.** (b)	**6.** (b)	**7.** (b)	**8.** (c)	**9.** (a)	**10.** (b)
11. (c)	**12.** (b)	**13.** (c)	**14.** (a)	**15.** (a)	**16.** (c)	**17.** (b)	**18.** (d)	**19.** (d)	**20.** (b)
21. (b)	**22.** (c)	**23.** (a)	**24.** (a)	**25.** (a)					

Hints & Solutions

1. (*b*) The molecular mass of polymer is in the range of 10^3 -10^7 u. These are very large molecules having high molecular mass. Hence, these are also referred as macromolecules.

2. (*b*) Cellulose derivatives such as cellulose acetate and cellulose nitrate are semi-synthetic polymers.

3. (*b*) Buna-S is a synthetic polymer, also known as man-made polymer.

4. (*a*) PVC (Polyvinyl chloride) is linear polymer as it contains long and straight chains.

5. (*b*) HDP stands for high density polythene. It is a linear polymer.

6. (*b*) Polymers containing linear chains having some branches are known as branched polymers.
It is represented as,


Branched polymer

7. (*b*) Bakelite is a network or cross-linked polymer as it contains several covalent bonds between various linear polymer.

8. (*c*) Buna-S is a copolymer of 1, 3-butadiene and styrene. The reaction involved is as follows :

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

$$\longrightarrow -\left(CH_2-CH=CH-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2\right)_n-$$

Buna-S

9. (*a*) Elastomers are rubber like-solids with elastic properties like-neoprene, buna-S, buna-N, etc.

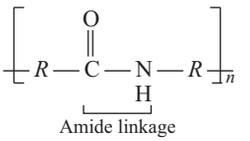
10. (*b*) Nylon-6,6 contains strong intermolecular forces like H-bonding. These strong forces lead to close packing of chains and impart crystalline nature.

11. (*c*) The repeated addition of same monomer molecules having double or triple bonds is known as homopolymer.

13. (*c*) Low density polythene (LDP) is used in the insulation of electricity wires and manufacture of flexible pipes and squeeze bottles because it is chemically inert, tough, flexible and poor conductor of electricity.

14. (*a*) The type of polythene which is chemically inert and more tough and hard is HDP (High Density Polythene). It consist of linear molecules and have high density.

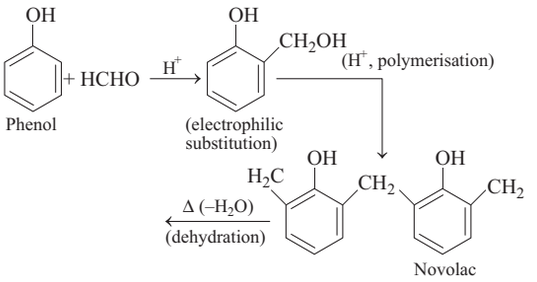
16. (*c*) Nylon is an example polyamide containing amide linkages $-(-CONH-)-$. It is prepared by condensation copolymerisation of diamines with dicarboxylic acids or by condensation polymerisation of lactam.


Amide linkage

17. (*b*) $-(-NH(CH_2)_6NHCO(CH_2)_4CO-)_n$ is obtained by the condensation of hexamethylene diamine and adipic acid. It is a copolymer.

18. (*d*) The monomers of dacron are ethylene glycol and terephthalic acid. It is manufactured by heating a mixture of glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetate-antimony trioxide catalyst.

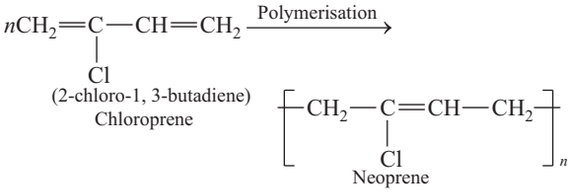
19. (*d*) Preparation of bakelite proceeds *via* electrophilic substitution and dehydration reactions. It is shown below:



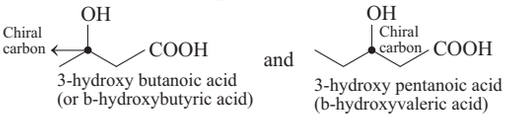
20. (*b*) Bakelite is the phenol-formaldehyde resin.
It is obtained by heating novolac with formaldehyde.

21. (*b*) In natural rubber, few cross-links are introduced in between the chains, which help the polymers to retract the original position after the force is released.

22. (*c*) Option (c) is a monomer of neoprene, i.e chloroprene. Chemically, it is 2-chlorobutane-1, 3-diene. It is obtained by free radical polymerisation of chloroprene. Complete reaction is as follows :



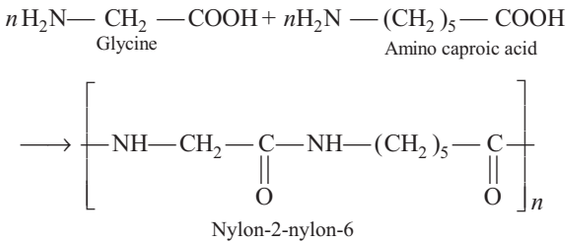
23. (*a*) PHBV, (Poly 3- hydroxybutyrate -co-3-hydroxyvalerate) is a copolymer of



In both monomers, there is one chiral centre (shown by dark spot).

∴ Polymer contains chiral monomers.

24. (*a*) Nylon-2- nylon-6 is the biodegradable polymer that can be produced from glycine (containing two carbon atoms) and aminocaproic acid or 6-aminohexanoic acid (containing six carbon atoms). Reaction involved is as follows :



It is a biodegradable polyamide copolymer.

25. (*a*) Bakelite polymer is used for making combs, electrical switches, handles of utensils and computer discs.