Chemistry Notes for class 12 Chapter 15 Polymers

The word polymer has a Greek origin. which means many units (parts). Polymer is defined as a chemical substance of a high molecular mass formed by the combination of a large number of simple molecules, called monomers. e.g.,

$$n(CH_2=CH_2) \longrightarrow [-CH_2-CH_2-]_n$$

ethylene polyethylene

Polymerisation

The process by which the monomers get combined and transformed into polymers. is known as polymerisation.

 $n [Monomer] \rightarrow Polymer$

Difference between Polymers and Macromolecules

Polymers are also called macromolecules due to their large size but converse is not always true. A macromolecule mayor may not contain monomer units, e.g., chlorophyll ($C_{55}H_{72}O_5N_4Mg$) is a macromolecule but not a polymer since there are no monomer units present so we can conclude that all polymers are macromolecules while all macromolecules may not be polymers in nature.

Classification of Polymers Based on Source of Origin

(i) Natural polymers Those polymers which occur in nature. i.e., in plants or animals. are called natural polymers.

5.N.	Natural polymer	Occurrence Main reserve food of plants	
1.	Starch		
2.	Cellulose	Main structural material of plants	
3.	Proteins	Act as building blocks in animals.	
4.	Natural rubber	Occurs as latex (a colloidal dispersion of rubber in water) in the bark of many tropical trees, particularly from Heva Brasiliensis.	

(ii) **Synthetic polymers** The polymers which are prepared in the laboratory are known as synthetic polymers or man-made polymers, e.g., polythene, synthetic rubber, PVC, nylon-66, teflon, orlon etc.

(iii) **Semisynthetic polymers** Polymers obtained by making some modification in natural polymers by artificial means, are known as semi synthetic polymers, e.g., cellulose acetate (rayon), vulcanised rubber etc.

Classification of Polymers Based on Structure

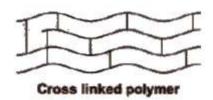


(i) **Linear polymers** These are the polymers in which the monomer units are linked to one another to form long linear chains. These linear chains are closely packed in space. The close packing results in high densities, tensile strength and high melting and boiling points. e.g., high density polyethene, nylon and polyesters are linear polymers.



Branched chain polymer

(ii) **Branched chain polymers** In such polymers, the monomer units are linked to form long chains with some branched chains of different lengths with source. As a result of branching, these polymers are not closely packed in space. Thus, they have low densities, low tensile strength as well as low melting and boiling points. Some common examples of such polymers are low density polyethene, starch, glycogen etc.



(iii) **Cross-linked polymers or network polymers** In such polymers, the monomer units are linked together to form three dimensional network. These are expected to be quite hard, rigid and brittle. Examples of cross linked polymers are bakelite, glyptal, melamine-formaldehyde polymer etc.

Classification of Polymers Based on Mode of Polymerisation

(i) **Addition polymers** The polymers formed by the polymerisation of monomers containing double or triple bonds (unsaturated compounds) are called addition polymers. Addition polymers have the same empirical formula as their monomers.

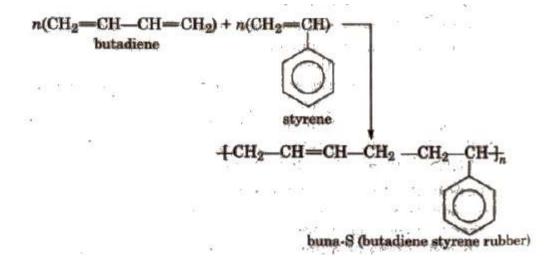
Addition polymers can further be classified on the basis of the types of monomers into the following two classes:

Homopolymers The polymers which are obtained by the polymerisation of a single type of monomer are called homopolymers.

$$n(CH_2 = CH_2) \longrightarrow (-CH_2 - CH_2)_n$$

ethene

Copolymers The polymers which are obtained by the polymerisation of two or more monomers are called copolymers



(ii) **Condensation polymers** The polymers which are formed by the combination of monomers with the elimination of small molecules such as water, alcohol, hydrogen chloride etc., are known as condensation polymers, e.g., nylon 6,6 is formed by the condensation of hexamethylene diamine with adipic acid.

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

$$-\{NH(CH_2)_6NHCO(CH_2)_4CO\}_{\overline{n}} + nH_2O$$

$$-(nylon 6.6)$$

Classification of Polymers Based on Molecular Forces

- 1. **Elastomers** These are rubber like solid polymers in which the polymer chains are held together by weakest intermolecular forces, e.g., natural rubber, buna-S, buna-N etc. The weak binding forces permit the polymers to be stretched. A few 'cross links' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber.
- 2. **Fibres** Fibres belong to a class of polymers which are thread-like and can be woven into fabrics. These are widely used for making clothes, nets, ropes, gauzes, etc. Fibres possess high tensile strength because the chains possess strong intermolecular forces such as hydrogen bonding. The fibres are crystalline in nature and have sharp melting points. A few examples of this class are nylon-66, terylene and polyacrylonitrile.

- 3. **Thermoplastics** These are linear polymers and have weak van der Waals' forces acting in the various chains. These forces are intermediate of the forces present in the elastomers and in the fibres. When heated, they melt and form a fluid which sets into a hard mass on cooling. Thus, they can be cast into different shapes by using suitable moulds, e.g., polyethene and polystyrene.

 (Plasticizers are high boiling esters or haloalkanes. These are added to I plastics to make them soft rubber like.J
- 4. **Thermosetting plastics** These are normally semifluid substances with low molecular masses. When heated, they become hard and infusible due to the cross-linking between the polymer chains. As a result, they also become three dimensional in nature. A few common thermosetting polymers are bakelite, melamine-formaldehyde resin and urea formaldehyde resin.

Types of Polymerisation

1. Chain Growth Polymerisation or Addition Polymerisation

It involves formation of reactive intermediate such as free radical, a carbocation or a carbanion. For this polymerisation monomers used are unsaturated compounds like alkenes; alkadienes and their derivatives. Depending upon the nature of the reactive species involved. chain growth polymerisation occurs by the following mechanisms:

- Free radical addition polymerisation
- Cationic polymerisation
- Anionic polymerisation
- (i) **Free radical addition polymerisation** The monomers used are generally monosubstituted alkenes. The most commonly used catalysts are benzoyl peroxide, hydrogen peroxide or t-butyl peroxide etc.

Mechanism The reaction involves the following steps

Step I Chain initiation step In this step, peroxide undergoes homolytic fission, e.g., benzoyl peroxide on heating produces phenyl initiator free radical.

Step II Chain propagation step The new free radical adds to another molecules of monomer to form a larger free radical.

$$\begin{array}{ccc} C_0H_5CH_2\dot{C}H_2 & \xrightarrow{CH_2=CH_2} & C_0H_5CH_2CH_2CH_2CH_2\\ & \xrightarrow{nCH_2=CH_2} & C_0H_5-(CH_2-CH_2)_n-CH_2-\dot{C}H_2 \end{array}$$

Step III Chain termination step There are three ways of chain termination: Coupling reaction, disproportionation reaction, chain transfer reaction. One mode of termination of chain is shown as under:

(ii) Cationic polymerisation It involves formation of carbocation which are generated by Lewis acids (like BF_3 , $AICI_3$, $SnCI_4$, etc.) and protonic acids such as H_2SO_4 , HF, etc.

Higher the stability of carbocation intermediate, more is the reactivity of monomers towards cationic addition polymerisation. It involves the following steps:

Step I. Initiation Step

$$H_{2}SO_{4} \longrightarrow H^{+} + HSO_{4}^{-}$$

$$BF_{3} + H_{2}O \longrightarrow H^{+} + BF_{3}(OH^{-})$$

$$CH_{2} = C(CH_{3})_{2} + H^{+} \longrightarrow (CH_{3})_{3}C^{+}$$

$$carbocation$$

$$Step II. Propagation$$

$$(CH_{3})_{3}C^{+} + CH_{2} = C(CH_{3})_{2} \longrightarrow (CH_{3})_{3} - C - CH_{2}C^{+}(CH_{3})_{2}$$

$$\stackrel{nCH_{2} = C(CH_{3})_{2}}{\longrightarrow} (CH_{3})_{3}C - [CH_{2} - C(CH_{3})_{2}]_{n} - CH_{2} \cdot C^{+}(CH_{3})_{2}$$

$$Step III. Termination$$

$$(CH_{3})_{3}C[CH_{2} \cdot C(CH_{3})_{2}]_{n}CH_{2}C^{+}(CH_{3})_{2}]$$

$$\stackrel{-H^{+}}{\longrightarrow} (CH_{3})_{3}C[CH_{2} \cdot C(CH_{3})_{2}]_{n}CH_{2} = C(CH_{3})_{2}$$

(iii) **Anionic polymerisation** It involves formation of a carbanion, Steps involved in this process are

Step I Initiation Strong bases act as initiator.

$$\begin{array}{c} \text{KNH}_2 \longrightarrow \text{K}^+ + \text{NH}_2 \\ \text{CH}_2 = \text{CHCN} + \text{NH}_2 \longrightarrow \text{H}_2\text{N} - \text{CH}_2\text{CHCN} \\ \text{Carbanion} \\ \\ \text{Step II Propagation} \\ \text{H}_2\text{N CH}_2\text{CHCN} + n\text{CH}_2 = \text{CHCN} \\ \longrightarrow \text{H}_2\text{N} - \text{CH}_2 - \text{CH(CN)} - \text{CH}_2 \\ - \text{CHCN} + \text{CH}_2 - \text{CH(CN)} - \text{CH}_2 \\ \\ \text{-CHCN} + \text{CH}_2 - \text{CH(CN)} \\ \text{Step III Termination} \\ \text{H}_2\text{NCH}_2\text{CH(CN)} + \text{CH}_2\text{CHCN} \\ - \text{CH}_2\text{CHCN} - \text{CH}_2\text{CHCN} \\ - \text{CH}_2\text{CH(CN)} + \text{CH}_2\text{CHCN} \\ - \text{CH}_2\text{CH(CN)} + \text{CH}_2\text{CHCN} \\ - \text{CH}_2\text{CH(CN)} - \text{CH}_2\text{CH(CN)} \\ - \text{CH}_2\text{CH(CN)} \\ - \text{CH}_2\text{CH(CN)} - \text{CH}_2\text{CH(CN)} \\ - \text{CH}_2\text{CH(CN)} \\ -$$

Step Growth Polymerisation

Condensation polymerisation which occurs in a stepwise manner with elimination of some smaller molecules like H₂O, NH₃, HCI, ROH, etc., is concerned with step growth polymerisation, e.g., adipic acid and hexamethylenediamine phenol and formaldehyde etc., undergo step Growth Polymerisation.

Distinction Between Chain Growth Polymerisation and Step Growth Polymerisation

S.No.	Chain growth polymerisation	Step growth polymerisation		
It proceeds by a chain mech characterised by initiation, propagation and chain termination		hain it proceeds by an equilibrium step mechanism. The step growth process is usually much slower than chain growth polymerisation.		
2.	Only one repeating unit is added at a time.	Any two species present can react with elimination of some by product.		
3.	Reaction mixture contain only monomers, polymers and the growing chain.	All the molecular species are present at every stage of polymerisation.		

Molecular Mass of Polymers

The growth of the polymer chain depends upon the availability of the monomers in the reaction. Thus, the polymer sample contains chain of varying lengths and hence, its molecular mass is always expressed as an average molecular mass.

Number-Average Molecular Mass M_n

If N_1 molecules have molecular mass M_1 each, N_2 molecules have molecular mass M_2 each, N_3 molecules have molecular mass M_3 each and so on,

then,
$$M_n = \sum N_i M_i / \sum N_i$$

It is determined by osmotic pressure method.

Mass-Average Molecular Mass (\overline{M}_w)

Supposing, as before that N_1, N_2, N_3 etc., molecules have molecular mass M_1, M_2, M_3 etc., respectively,

then.

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

It is determined by light scattering and ultracentrifugation method.

PoLydispersity Index

It is the ratio of the mass average molecular mass to the number average molecular mass

$$PDI = M_w / M_n$$

For natural polymers, PDI is usually equal to one which means that they are monodisperse. In other words, such polymers are more homogeneous. On the contrary, synthetic polymers generally have PDI > 1 which means that they are less homogeneous.

Polyolefins

These are obtained by the addition polymerisation of ethylene and its derivatives

1. Polythene

Polymer of ethylene or ethene.

(i) Low density polythene (LDP)

It is tough, flexible, transparent, chemically inert as well as poor conductor pf electricity. It has moderate tensile strength but good tearing strength.

It is used in the insulation of electricity carrying wires and manufacture of queeze bottles, toyes and flexible pipes.

(ii) **High density polyethylene** (HOP)

$$n(CH_2=CH_2) \xrightarrow{\begin{array}{c} 333-343 \text{ K} \\ \hline 6.7 \text{ atm} \\ \text{(Ziegler Natta} \\ \text{eatalyst)} \end{array}} \leftarrow CH_2-CH_2 \xrightarrow{}_{h}$$

It has high density due to close packing. It is also chemically inert and more tougher and harder.

It is used for making containers, house wares, bottles, toyes, electric insulation etc.

2. **Polystyrene** (Styrone)

The monomers are styrene molecules. It is thermoplastic. It is used for making toys, radio and TV cabinets

$$n \begin{bmatrix} \text{CH=-CH}_2 \\ \text{C}_6 \text{H}_5 \end{bmatrix} \xrightarrow{\text{(C}_2 \text{H}_5 \text{COO)}_2} \begin{bmatrix} \text{-CH--CH}_2 - \\ \text{C}_6 \text{H}_5 \end{bmatrix}_n$$

3. Polyvinylchloride (PVC)

$$n \begin{bmatrix} \text{CH}_2 = \text{CH}_2 \\ \text{Cl} \end{bmatrix} \xrightarrow{\text{Dibenzoyl}} \begin{bmatrix} -\text{CH}_2 - \text{CH} - \\ \text{Cl} \end{bmatrix}_{n}$$

$$\text{chloroethene}$$
(vinyl chloride)

It is used for making rain coats, toys, electrical insulation. It is hard and resistant to heat and chemicals.

4. Polypropylene (PP)

It is obtained by polymerising propylene in the presence of Ziegler-Natta catalyst.

$$n \begin{bmatrix} CH_3H \\ | & | \\ | & C = C \\ | & H \end{bmatrix} \xrightarrow{\text{Polymerisation}} \begin{bmatrix} CH_3H \\ | & | \\ | & C = C \\ | & H \end{bmatrix}$$

$$\text{propylene} \qquad \qquad \text{polypropylene (PP)}$$

Polytetrafluoroethene (Teflon)

It is chemically inert and resistant to attack by corrosive reagent. It is used in making oil seals, gaskets and also for non-stick surface coated utensils.

6. Polyacrylonitrile

$$n(\text{CH}_2 = \text{CHCN}) \xrightarrow{\text{Polymerisation}} - \text{CH}_2 - \text{CH}_{\frac{1}{n}}$$

$$\text{acrylonitrile} \xrightarrow{\text{(Peroxide catalyst)}} \text{polyacrylonitrile or orlon}$$

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

Polyamides

The polymers which contain an amide linkage in chain are known as pOlyamide, e.g., nylon-6, 6.

1. **Nylon-66**

It is obtained by the condensation of adipic acid and hexamethylenediamine with the elimination of water molecule

$$nH_2N(CH_2)_6NH_2 + nHO - C - (CH_2)_4 - C - OH - \frac{1}{nH_2O}$$
hoxamothylenediamine
$$H \quad H \quad O \quad O$$

$$- (CH_2)_6 - N - C - (CH_2)_4 - C \rightarrow_n$$

$$- (CH_2)_6 - N - C - (CH_2)_4 - C \rightarrow_n$$

The polyamides are identified by numbers. These numbers refer to the number of carbon atoms in diamine and in the dibasic acid. As in the above case, the carbon atoms are 6 in each case, therefore the product is described as nylon-66.

Properties and uses

Nylon-66 is a linear polymer and has very high tensile strength. It shows good resistance to abrasion. Nylon-66 is usually fabricated into sheets. It is used in bristles for brushes and in textile

2. **Nylon-6**

Nylon-6 is obtained by heating caprolactam with water at a high temperature.

Resins

1. Phenol-Formaldehyde Polymer

(Bakelite and Related Polymers)

These polymers are obtained by the condensation reaction of phenol with formaldehyde in the presence of either acid or a base catalyst. The reaction involves the formation of methylene bridge at ortho, para or both ortho and para positions. A linear or cross linked material is obtained depending upon the condition of reaction.

Bakelite is used for making combs, photograph records, electrical switches etc. Soft bakelites with low degree of polymerisation are used as binding glue for laminated wooden plants, in varnishes and lacquers.

2. Melamine-formaldehyde Resin

It is a copolymer formed by the polymerisation of melamine (which is a heterocyclic triamine) and formaldehyde as follows:

Properties and Uses

It is very hard and tough. It has assumed great importance these days particularly in making crockery. They do not break even when droped from a height.

3. Urea-formaldehyde Resin

$$\begin{array}{c} \text{NH}_2 - \text{C} - \text{NH}_2 + 2\text{HCHO} \xrightarrow{\text{Heat}} \\ \text{HOCH}_2 - \text{NH} - \text{C} - \text{NH} - \text{CH}_2\text{OH} \\ & \downarrow \text{Polymerisation} \\ & (-\text{CH}_2 - \text{NH} - \text{C} - \text{NH} - \text{CH}_2 -)_n \\ & \text{urea-formaldehyde resin} \end{array}$$

4. Natural Rubber

Natural.rubber is a coiled linear 1, 4-polymer of isoprene.

$$CH_3$$
 $CH_2 = C - CH = CH_2$
isoprene

In the polymer chain of natural rubber, the residual double bonds are located between C_2 and C_3 of the isoprene unit. All these double bonds have cis configuration, and thus natural rubber is cis-1,4-polyisoprene.

$$CH_3$$
 H CH_2 $CH_$

A section of the polymeric chain of natural rubber

In the natural rubber, there is no polar substituent. The only intermolecular forces are van der Waals' type. The cis-configuration gives the polymeric chain of natural rubber a coiled structure. As a result, it can be stretched by the application of a force. When the force is removed, the chain returns back to its original coiled shape.

Natural rubber is soft and sticky. It can be used only in the temperature range 10°C-50°C. At higher temperature, it becomes soft and at low temperature, it becomes brittle. It has high water absorption capacity. It is attacked by oxidising agents and organic solvents. As such, it cannot be used very extensively for commercial puposes.

Vulcanisation of Rubber

The properties of natural rubber can be modified by introducing -S-S- polysulphide crosslinks in its structure. This process of introducing -S-S- crosslnks in the structure of natural rubber by heating with sulphur at 110°C is called vulcanisation of rubber.

Vulcanisation is carried out by adding sulphur (3-5%) and zinc oxide to the rubber, and then heating the object at about 110°Cfor about 20-30 minutes. Zinc oxide accelerates the rate of vulcanisation. Vulcanisation introduces polysulphide (-S-S-) bonds between the adjacent chains. These crosslinks tend to limit the motion of chains relative to each other.

5. Neoprene

Polymer formed by polymerisation of chloroprene is neoprene or synthetic rubber.

$$n(\mathrm{CH}_2 = \mathrm{C} - \mathrm{CH} = \mathrm{CH}_2) \ \longrightarrow \ -[\mathrm{CH}_2 - \mathrm{C} = \mathrm{CH} - \mathrm{CH}_2]_{\overline{b}}$$

It is used for the manufacturing conveyers belts, gasket and hoses.

6. Buna-N

It is a copolymer of buta-I, 3-diene and acrylonitrile. It is formed as follows

$$n ext{ CH}_2 = ext{CH} = ext{CH} = ext{CH}_2 + n ext{ CH} = ext{CH}_2$$

buta-1,3 diene

 CN

acrylonitrile

Polymerisation

 $CH_2 - CH = CH - CH_2 - CH - CH_2 \rightarrow_n$

(buna-N)

Properties and Uses

It is insulator in nature and is used for making conveyor belts and printing rollers.

Polyesters

The polymers which contain an ester linkage are known as polyester, e.g., dacron.

1. Polymethylmethacrylate (PMMA)

It is prepared by the polymerisation of methylmethacrylate in the presence of suitable organic peroxide.

$$n \begin{bmatrix} \text{CH}_3 \\ \text{CH}_2 = \text{C} - \text{COOCH}_3 \end{bmatrix} \xrightarrow{\text{Organic peroxide}} \begin{bmatrix} \text{CH}_3 \\ -\text{CH}_2 - \text{C} \\ \text{COOCH}_3 \end{bmatrix}_{\text{methylmethacrylate}}$$

The polymer is known by several commercial names such as lucite, acrylite, plexiglass and perspex.

Properties and uses

It is a hard and transparent polymer and is quite resistant to the effect of light, heat and ageing. It is used, in the manufacture of unbreakable lights, protective coatings, dentures, and in making windows for aircrafts.

2. Glyptal

It is a polyester having crosslinks. It is a thermosetting plastic. It is obtained by condensation of ethylene glycol and phthalic acid or glycerol and phthalic acid.

$$nHO-CH_2-CH_2-OH+n$$

$$ethylene glycol$$

$$phthalic scid$$

$$-O-CH_2-CH_2-O-C$$

$$glyptal$$

$$Heat$$

$$-nH_2O$$

$$O$$

$$O$$

$$C$$

$$G$$

When its solution in a suitable solvent is evaporated, it leaves a tough but non-flexible film. It is, therefore, used in the manufacture of paints and lacquers.

3. Terylene (Dacron)

It is a condensation product of ethylene glycol and terephthalic acid.

Polymerisation is carried out at 420 to 460 K in the presence of catalyst mixture of zinc acetate and antimony trioxide.

Properties and uses

Terylene is highly resistant to the action of chemical and biological agents. Its fibres are quite strong and durable. It can also be blended with wool or cotton to obtain fabrics of desired composition.

Terylene is used in the manufacture of a variety of clothes such as terycot, terywool and terysilk as a result of blending with other yerns. It is also used for preparing magnetic recording tapes, conveyer belts, aprons for industrial workers etc.

Biopolymers and Biodegradable Polymers

Synthetic polymers are mostly non-biodegradable i.e., it is very difficult to dispose off the polymeric waste, e.g., polythene bags.

Nature has provided us a variety of polymers which can be produced by the biological systems in plants and animals. These are called biopolymers, e.g., polysaccharides, proteins, nucleic acids, etc. In the biological system, these polymers decompose or hydrolyse in the Presence of different enzymes. This means that they are biodegradable.

Aliphatic polyesters are the common examples of biodegradable Polymers.

It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.

$$\begin{array}{c} \text{OH} & \text{OH} \\ \text{CH}_3-\text{CH}-\text{CH}_2\text{COOH} + \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2\text{COOH} \longrightarrow \\ \text{3-hydroxybutanoic acid} & \text{3-hydroxypentanoic acid} \\ \\ -\text{O-CH-CH}_2-\text{C}-\text{O-CH-CH}_2-\text{C} \\ \text{CH}_3 & \text{O} & \text{C}_2\text{H}_5 & \text{O} \\ \end{array} \right]_n$$

2. Nylon-2-Nylon-6

It is an alternating polyamide copolymer of glycine (H_2N-CH_2-COOH) and amino caproic acid [$H_2N(CH_2)$ ₅COOH] and is biodegradable.

Some More Impotant Polymers

- 1. Saran is a copolymer of vinyl chloride and Isused for wrapping food materials.
- 2. ASS rubber is a copolymer of acrylonitrile, buta-1, 3-diene and styrene.
- 3. Bubble gum contains styrene butadiene rubber.

- 4. Epoxy resins are used In making adhesives such as analdite, etc. These are the copolymer of epichlorohydrin and bisphenol-A.
- 5. Thikol is another variety of synthetic rubber which is a copolymer of ethylene chloride and sodium tetrasulphide (Na_2S_4) .
- 6. Dynells a copolymer of vinyl chloride and acrylonitrile and is used for making human hair wigs.
- 7. Silk Is a thread like natural polymer which is obtained from cocoons of sllk worms. It is a natural polyamide fibre.
- 8. Thermocol Is a foamed plastic obtained by blowing air through molter polystyrene or polyurethane.
- 9. Superglue is a polymer of methyl α -cyanoacrylate and is obtained by anionic polymerisation of monomer.



CBSE Class-12 Chemistry Quick Revision Notes Chapter-15: 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 are called monomers.

• Polymerization:

The process of formation of polymers from respective monomers is called polymerization

• Classification of Polymers:

- A. Based on source of availability, it is classified into
- a) Natural polymers: Polymers obtained from nature, mostly plants and animals. Examples Cellulose, starch, etc.
- b) Synthetic polymers: Polymers prepared in laboratory. Examples Teflon, Nylon 6,6, Synthetic rubber (Buna S) etc.
- c) Semi synthetic polymers: Polymers derived from naturally occurring polymers by carrying out chemical modifications. Examples Rayon (cellulose acetate), cellulose nitrate, etc.
- B. Based on the structure of polymer, it is classified into
- a) Linear polymers: Polymer consists of long and straight chains. Examples High density polythene, polyvinyl chloride, etc.
- b) Branched chain polymers: Polymers contains linear chains having some branches. Examples Low density polythene
- c) 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.
- C. 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.
- D. Based on Molecular forces, it is classified into
- a) Elastomers: Polymer chains are held together by weakest intermolecular forces. Polymers are rubber like solids with elastic properties. Examples Buna S,

Buna - N, Neoprene

- b) 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.
- c) 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.
- d) 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
- 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

• Steps involved in addition polymerisation:

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

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.

$$C_{6}H_{5} - CH_{2} - CH_{2} + CH_{2} = CH_{2} \rightarrow C_{6}H_{5} - CH_{2} - CH_{2} - CH_{2} - CH_{2} \rightarrow C_{6}H_{5} - (CH_{2} - CH_{2})_{n} - CH_{2} - CH_{2}$$

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:

$$C_{6}H_{5} - (CH_{3} - CH_{2})_{n} - CH_{2} - \overset{*}{C}H_{2} \\ \xrightarrow{*} C_{6}H_{5} - (CH_{2} - CH_{2})_{n} - CH_{2} - CH_{2}$$

• Important Addition Polymers:

a) Low density polythene (LDP)

$$nCH_2 = CH_2 \xrightarrow{350-570k/1000 \text{ to } 2000 \text{ atm traces of O}_2} \to (CH_2 - CH_2)_n$$
 Ethene

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

b) High density polythene(HDP)

$$nCH_2 = CH_2 \xrightarrow{333-343k/6-7 \text{ atm zieglar Natta catalyst}} (CH_2 - CH_2)_n$$

$$Ethene$$

$$Polythene$$

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

c) Polytetrafluoroethene (Teflon)

$$nCF_2 = CF_2 \xrightarrow{catalyst/High \text{ pressure}} (CF_2 - CF_2)_n$$

$$Tetrafluoroethene$$

$$Teflon$$

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

d) Polyacrylonitrile

$$nCH_{2} = CHCN \xrightarrow{Polymerisation/Peroxide \text{ catalyst}} (CH_{2} - CN)_{n}$$

$$Acrylonitrile \xrightarrow{Polymerisation/Peroxide \text{ catalyst}} (CH_{2} - CN)_{n}$$

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

- Condensation Polymerisation or Step Growth polymerization:
 - Polymerisation generally involves a repetitive condensation reaction between two bifunctional monomers. In condensation reactions, the product of each step is again a bifunctional 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:
 - 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.

$$nHOOC(CH_{2})_{4}COOH + nH_{2}N(CH_{2})_{6}NH_{2} \xrightarrow{553K/High \text{ pressure}} [N - (CH_{2})_{6} - N - C(CH_{2})_{4} - C]_{n}$$

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

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

a) 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.

n HOH₂C - CH₂OH + n HOOC
$$\longrightarrow$$
 COOH \longrightarrow COCH₂-CH₂-C \longrightarrow C \longrightarrow Ethylene glycol (Ethane-1, 2 - diol) Terephthalic acid (Benzene-1,4 - di

It is used to crease resistant 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.

$$OH \longrightarrow OH \longrightarrow CH_2OH \longrightarrow CH_2OH \longrightarrow CH_2OH \longrightarrow CH_2OH$$

$$CH_2OH \longrightarrow CH_2OH \longrightarrow CH_2OH \longrightarrow CH_2OH$$

$$OH \longrightarrow CH_2OH \longrightarrow CH_2OH \longrightarrow CH_2OH$$

$$OH \longrightarrow CH_2OH$$

b) Novolac on heating with formaldehyde forms Bakelite

$$CH_2$$
 CH_2 CH_2

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

$$\begin{array}{c} \xrightarrow{\text{Polymerisation}} & \left\{\begin{array}{c} \text{HN} \swarrow \text{N} \\ \text{N} \swarrow \text{N} \end{array}\right\}_{\text{NH}} \text{NH-CH}_2 \quad \left\{\begin{array}{c} \\ \\ \end{array}\right\}_{\text{n}}$$

It is used in the manufacture of unbreakable crockery

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.

Sulphur cross links in vulcanised rubber

Classification of 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.

$$\begin{array}{c} H_3C \\ \hline \\ --H_2C \end{array} \\ C = C \\ \hline \\ CH_2 \\ CH_2 \\ \hline \\ CH_2 \\ CH_2 \\ \hline \\ CH_2 \\$$

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.

• Examples of synthetic rubber:

A) Neoprene or polychloroprene

$$nCH_2 = C - CH = CH_2 \xrightarrow{Polymerisation} [CH_2 - C = CH - CH_2]_n$$

$$2-chloro-1, 3-butadiene$$
Neoprene

It is used for manufacturing conveyor belts, gaskets and hoses

B) Buna - N

$$nCH_{2} = CH - CH = CH_{2} + nCH_{2} = CN \xrightarrow{Copolymerisation} [CH_{2} - CH = CH - CH_{2} - CH_{2} - CH_{2}]_{n}$$

$$Acrylonitrile$$

$$Acrylonitrile$$

$$Buna-N$$

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

C) Buna - S

$$nCH_2 = CH - CH = CH_2 + nC_6H_5CH = CH_2 - \longrightarrow [CH_2 - CH = CH - CH_2 - CH_2 - CH]_n$$

$$Styrene \qquad (Buna-S)$$

$$(Buna-S)$$

- 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:
 - a) Poly β -hydroxybutyrate co- β -hydroxy valerate (PHBV):

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

3-Hydroxybutanoic acid 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)

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

$$A \min o \text{ capronic acid}$$

$$A \min o \text{ capronic acid}$$

• Commercially important polymers along with their structures and uses:

Name of	Monomer	Structure	Uses
Polymer			
Polypropene	Propene	CH ₃	Manufacture of
		$(CH_2 - CH)_n$	ropes, toys,
		2 ""	pipes,
			fibres, etc.
Glyptal	(a) Ethylene	(OCH₂-CH₂OOC CO) _n	Manufacture of
	glycol		paints and
	Manufacture of	$\langle \overline{\Diamond} \rangle$	lacquers
	(b) Phthalic		
	acid		
Polystyrene	Styrene	C_6H_5	As insulator,
		$(CH_2 - CH)_n$	wrapping
		- "	material,
			manufacture
			of toys, radio
			and
			television
			cabinets
Polyvinyl	Vinyl chloride	Cl 	Manufacture of
chloride		$(CH_2 - CH)_n$	rain
(PVC)			coats, hand
			bags, vinyl
			flooring, water
			pipes