Polymers

POLYMERS

C1 **Polymer is formed from two words i.e. "poly" that means many and "mer" that means unit or part. Polymer also named as macromolecules because of heavy molecular mass.**

Monomer : The repeating structural units are derived from some simple and reactive molecules known as monomers.

Polymerisation : The process of formation of polymers from respective monomers is called polymerisation

for e.g. : $nCH_2 = CH_2 \xrightarrow{\text{polymerisation}} +CH_2 - CH_2+_n$

Ethene (monomer) — Polyethene (polymer)

Practice Problems :

1. **What are polymers ?**
2. **Explain the term polymer and monomer.**
3. **Define the term polymerisation.**

[Answers : (3) The process of formation of a high molecular mass macromolecules from one or more monomers by linking together a large number of repeating structural units through covalent bonds is called polymerisation]

C2 **Classification of Polymers :**

(a) **Classification based on source**

1. **Natural Polymer : These are found in plants and animals, for e.g., protein, starch.**
2. **Semi-synthetic polymers : Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate etc. are the usual examples of this sub category.**
3. **Synthetic Polymers : A variety of synthetic polymers as plastic, synthetic fibers (nylon 6, 6) etc.**

(b) **Classificaion based on structure of polymers**

1. **Linear Polymer : These polymers consist of long and straight chains for e.g., polyvinyl chlorides.**
2. **Branched chain polymer : These polymers contain linear chains having some branches e.g., polythene.**
3. **Cross linked or network polymer : These are usually formed from bi-functional and trifunctional monomers and contain strong covalent bonds between various linear polymer chains e.g., bakelite.**

(c) **Classification based on mode of polymerisation**

1. **Addition Polymers : Polymer is formed without being giving small molecules like H_2O, HCl etc. is called as addition polymer. Polymer formed from single monomer is known as homopolymer for e.g.** $nCH_2 = CH_2 \longrightarrow +CH_2 - CH_2+_n$.

Ethene — Polyethene

If polymers formed from two different monomers are termed as copolymers for e.g.,

$$nCH_2 = \underset{\text{1–3butadiene}}{CH - CH = CH_2} + nC_6H_5CH = \underset{\text{styrene}}{CH_2} \longrightarrow +CH_2 - CH = CH - CH_2 - CH_2 - \underset{C_6H_5}{CH}+_n$$

Butadiene-styrene copolymer (Buna-s)

2. **Condensation Polymers : The polymers are formed from monomers but with small eliminaion of molecules like water, alcohol, hydrogen chloride etc. for e.g.,**

$$nH_2N(CH_2)_6NH_2 + nHOOC(CH_2)_4COOH \longrightarrow +NH(CH_2)_6NHCO\,(CH_2)_4\,CO+_n + nH_2O$$

Nylon 6, 6

(d) Classification based on molecular forces :

1. Elastomers : These are rubber-like solids with elastic properties. These are held together by the weakest intermolecular forces. The weak binding forces permit the polymer 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 for e.g., Neoprene, Buna-N, Buna-S.

2. Fibres : Fibres are the thread forming solids which possess high tensile strength and high modulus. In this the bonding are strong like the hydrogen bond for e.g., nylon 6, 6, polyamides, polyester

3. Thermoplastic polymers : These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. The forces are inter mediate of elastomers and fibres. For e.g., polythene, polystyrene.

4. Thermosetting polymers : These polymers are cross linked is heavly branched molecules, which on heating undergo extensive cross linking in moulds and again become influsible. These cannot be reused for e.g., Bakelite, Urea-formaldehyde resine etc.

<u>Practice Problems :</u>

1. How are polymers classified on the basis of structure ?

2. Arrange the following polymers in increasing order of their intermolecular forces.

(i) Nylon 6, 6, Buna-S, Polythene.

(ii) Nylon 6, Neoprene, Polyvinyl chloride.

3. What are natural and synthetic polymers ? Give two examples of each type.

4. Distinguish between the terms homopolymer and copolymer and given an example of each.

5. How do you explain the functionality of a monomer ?

6. Is $(NH - CHR - CO)_n$, a homopolymer or a copolymer ?

7. In which classes, the polymers are classified on the basis of molecular forces ?

8. How can you differentiate between addition and condensation polymerisation ?

9. Explain the term copolymerisation and give two examples ?

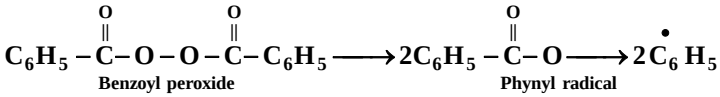
10. Define thermoplastics and thermosetting polymers with two examples of each.

[Answers : (1) (i) Linear polymers consist of long and straight chains. The examples are high density polythene (HDP), polyvinyl chloride, nylons, polyster, etc. (iii) Branched polymers contain linear chains having some branches. The examples are low density polythene (LDP), amylopectin, glycogen, etc. (iii) Cross linked polymers contain covalent bonds between various linear polymer chains. Bakelite, melmac (melamine-formaldehyde polymer), etc., are examples of such polymers. These are obtained from bifunctional monomers (2) Elastomers or rubbers have the weakest intermolecular forces of attraction followed by plastics while fibres have the strongest forces of attraction. Thus, the increasing intermolecular forces of attraction follows the order : Elastomer < Plastic < Fibre. (i) Buna-S, Polythene, Nylon 6, 6 (ii) Neoprene, Polyvinyl chloride, Nylon 6 (4) Homopolymer : Polymers whose repeating structural units are derived from only one type of monomer units are called homopolymer. For example, polythene, PVC, PAN, teflon, nylon 6, etc. Copolymers : Polymers whose repeating structural units are derived from different types of monomer molecules are copolymers. For example, Buna-S, nylon 6, 6, polyester, bakelite, melmac, etc. (5) Functionality means the number of bonding sites in a molecule. For example, the functionality of ethene, propene, styrene, acrylonitrile is one because such molecules can react at one site while that of 1, 3-butadiene, adipic acid, terephthalic acid, hexamehtylenediamine is two because they can bond at two positions with other molecules (6) It is a homopolymer (7) 1. Elastomers 2. Fibres 3. Thermoplastics and 4. Thermosetting polymers]

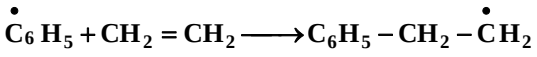
C3 Addition polymerisation or chain growth polymerisation :

1. Free radical mechanism :

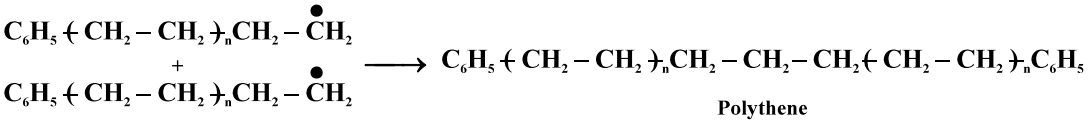
Chain initiation steps :



Benzoyl peroxide — Phynyl radical



Chain propagating step :



Polythene

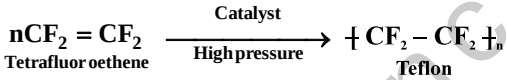
2. Preparation of some addition polymer :

(a) Polythene :

(i) Low density polythene (LDP) : It is obtained by polymerisation of ethene under high pressure of 1000 to 2000 atmospheres temperature of 350 K to 570 K in the presence of dioxygen or peroxide interior. They are chemically inert and tough but poor conductor of electricity.

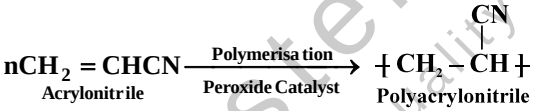
(ii) High density polythene : It is formed with catalyst triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmosphere. They consist of lienar molecules and has high density due to close packing. It is also chemically inert and more tougher and harder. It is used in buckets, dustbeens, bottles, pipes etc.

(b) Polytetrafluoroethene (Teflon) : It is chemically inert and resistant to attack by corrosive reagents. It is used in making oil seals, gas kets and for used in making non-stick surface coated utensils.



Tetrafluor oethene — Teflon

(c) Polyacrylonitrile : It is used as substitute for wool in making commercial fibres.



Acrylonitrile — Polyacrylonitrile

Practice Problems :

1. Write the free radical mechanism for the polymerisation of ethene.

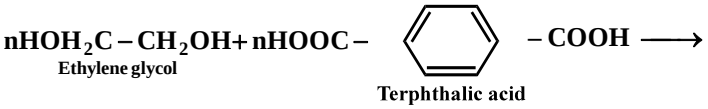
2. Write the name and structure of one of the common initiators used in free radical addition polymerisation.

[Answers : (2) Benzoyl peroxide]

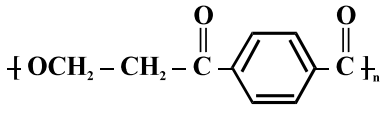
C4 Condensation polymerisation or step growth polymerisation :

example of condensation polymerisation is

(i)



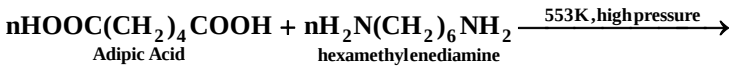
Ethylene glycol — Terphthalic acid

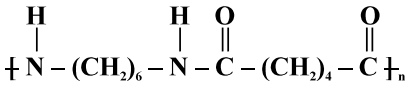


Terylene or Dacron

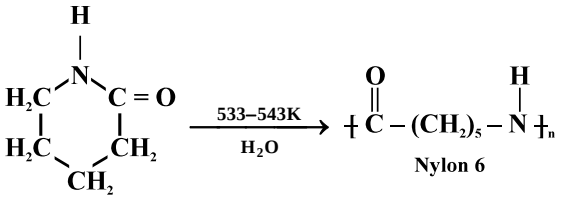
(ii) Polyamide :

(a) Nylon 6, 6 : It is used in making sheets, bristles for brushes and in textile industry.



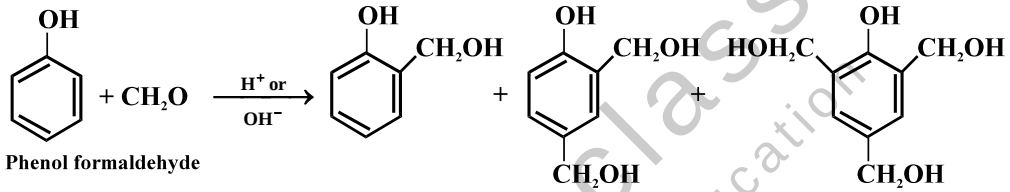


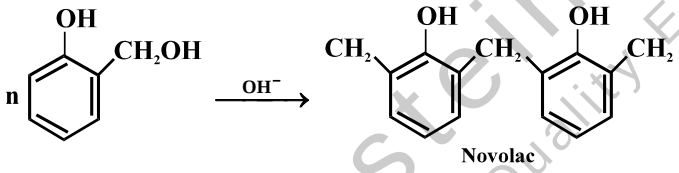
(b) Nylon 6 : It is used for manufacture of tyre cords, fabrics and ropes.



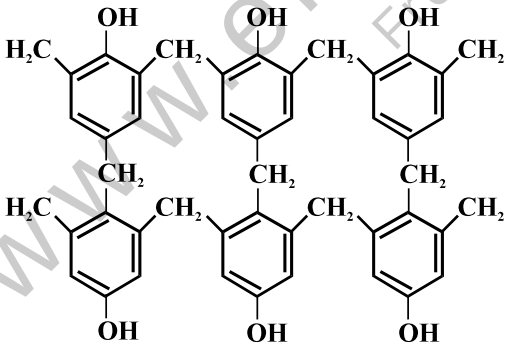
2. Polysters : These are the polycondensation products of dicarboxylic acids and diols for eg., Dacron, which given earlier.

3. Phenol : Formaldehyde polymer

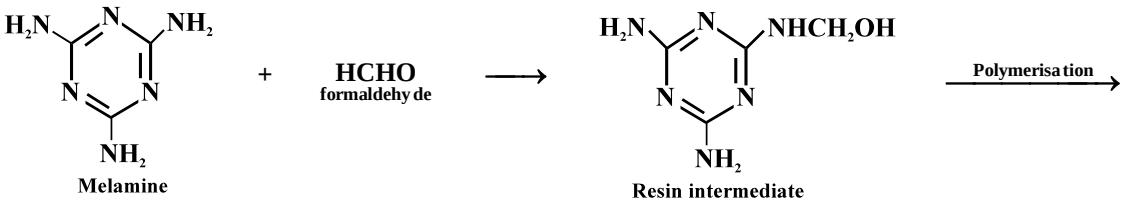


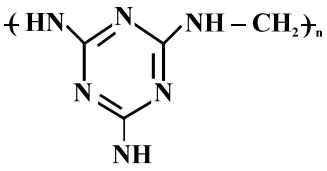


After heating Novolac with formaldehyde then it convert into bakelite.



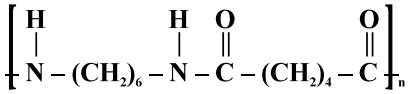
4. Melamine-formaldehyde polymer :

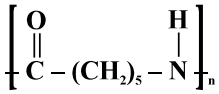




Practice Problems :

1. Write the names of monomers of the following polymers :

(i) 

(ii) 

(iii) $+CF_2 - CF_2+_n$

2. Classify the following as addition and condensation polymers : Terylene, Bakelite, Polyvinyl chloride, Polythene.

3. Write the monomers used for getting the following polymers :

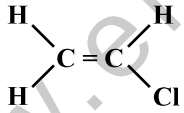
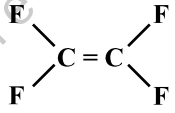
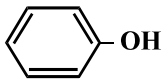
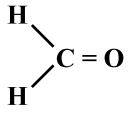
(i) Polyvinyl chloride **(ii)** Teflon

(iii) Bakelite

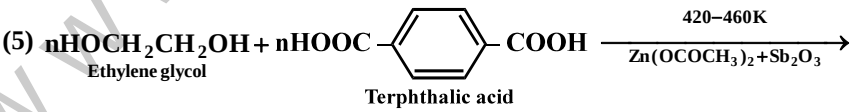
4. What are the monomeric repeating units of Nylon-6 and Nylon-6, 6 ?

5. How is dacron obtained from ethylene glycol and terephthalic acid ?

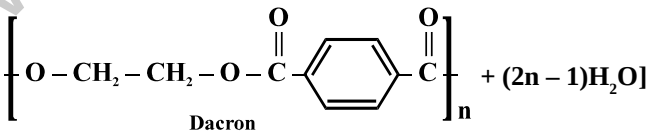
[Answers : (1) (i) Hexamethylenediamine ($H_2N - (CH_2)_6 - NH_2$) and adipic acid ($HOOC - (CH_2)_4 - COOH$) (ii) Caprolactam (iii) Tetrafluoroethene ($F_2C = CF_2$) (2) (Addition polymers : Polyvinyl chloride and bakeline. Condensation polymers : Terylene and bakelite

(3) (i)  **(ii)**  **(iii)**  **and** 

Vinyl chloride | Tetrafluoroethene | Phenol | Formaldehyde

(5) 

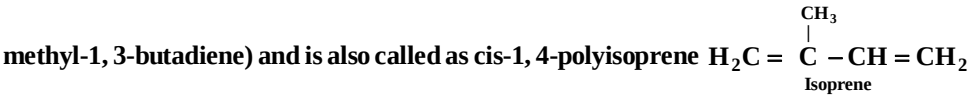
Ethylene glycol | Terphthalic acid

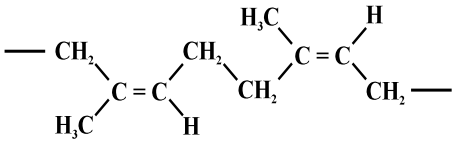


Dacron

C5 Rubber :

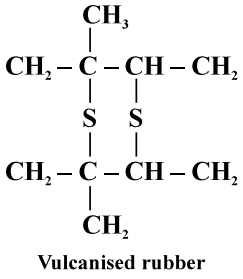
1. Natural Rubber : It is manufactured from rubber later which is a colloidal disperssion of rubber inwater. Natural rubber may be considered as a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as cis-1, 4-polyisoprene





Vulcanisation of rubber :

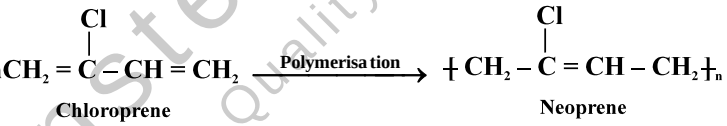
To improving the physical properties, vulcanisation is carried out. This process consist of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373 K to 415 K.



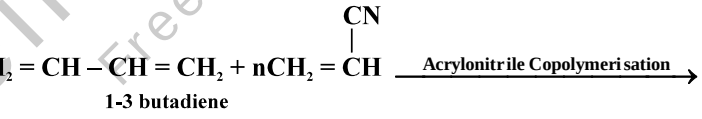
2. Synthetic rubber : Synthetic rubber is any vulcanisable rubber like polymer, which is capable of getting stretched to twice its length. However, it returns to its original shape and size as soon as the external stretching force is released.

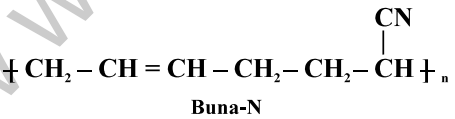
Preparation of synthetic rubbers :

(a) Neoprene :



(b) Buta-N :





Practice Problems :

1. Explain the difference between Buna-N and Buna-S.

2. How does the presence of double bonds in rubber molecules influence their structure and reactivity ?

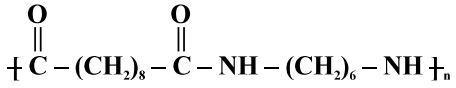
3. Discuss the main purpose of valcanisation of rubber.

4. Write the names and structures of the monomers of the following polymers :

(i) Buna-S (ii) Buna-N (iii) Dacron (iv) Neoprene

5. Identify the monomer in the following polymeric structures :

(i)



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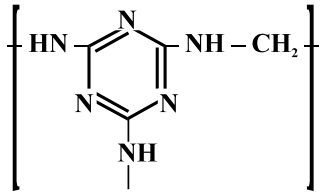
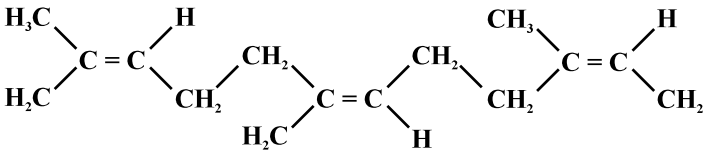


[Answers : (1) Both are copolymers. Buna-N is a copolymer of 1, 3-butadiene and acrylonitrile while Buna-S is a copolymer of 1, 3-butadiene and sytrene (2) Natural rubber is cis-polyisoprene and is obtained by 1, 4-polymerisation of isoprene units.

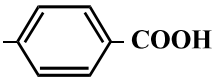


These cis-configuration at double bonds does not allow the polymer chains to come closer for effective interactions and hence intermolecular forces are quite weak. As a result, natural rubber, i.e., cis-polyisoprene has a randomly coiled structure and hence shows elasticity (3) Natural rubber has following disadvantages (i) It is soft and sticky at high temperature and brittle at low temperatures. Therefore, rubber is generally used in a narrow temperature range (283 - 335 K) where its elasticity is maintained. (ii) It has a large water absorption capacity, has low tensile strength and low resistance to abrasion. (iii) It is not resistant to the action of organic solents. (iv) It is easily attacked by oxygen and other oxidising agents. To improve the properties of natural rubber, it is valcanised by heating it with about 5% sulphur at 373 K - 415 K. Vulcanised rubber has obtained excellent elasticity over wide range of temperature. It has low water absorption tendency, is resistant to the action of organic solvent and oxidising agents

(4) (i) Buna – S : $\underset{\text{1,3–Butadiene}}{CH_2 = CH - CH = CH_2}$ **and** $\underset{\text{Styrene}}{C_6H_5 - CH = CH_2}$

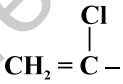
(ii) Buna – N : $\underset{\text{1,3–Butadiene}}{CH_2 = CH - CH = CH_2}$ **and** $\underset{\text{Acrylonitrile}}{CH_2 = CH - CN}$

(iii) Dacron – : $\underset{\text{Ethylene glycol}}{HO - CH_2 - CH_2 - OH}$ **and**



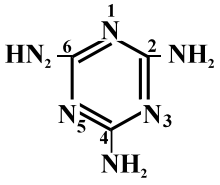
Terephthalic acid

(iv) Neoprene :



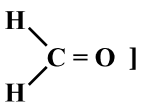
Chloroprene or 2-chloro-1, 3-butadiene

(5) (i) $\underset{\text{Decanoic acid or Sebacic acid}}{HOOC - (CH_2)_8 - COOH}$ **and** $\underset{\text{Hexamethylenediamine}}{H_2N - (CH_2)_6 - NH_2}$ **(ii)**



2, 4, 6-Triamino-1, 3, 5-triazine

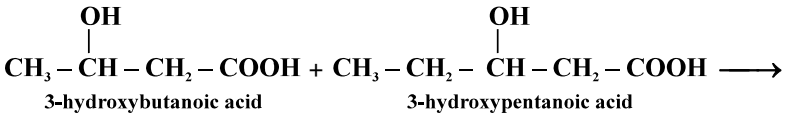
and



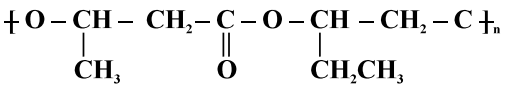
Formaldehyde

C6 Biodegradable Polymers :

1. Poly β-hydroxybutyrate-co-β-hydroxy valerate (PHBV)



3-hydroxybutanoic acid 3-hydroxypentanoic acid



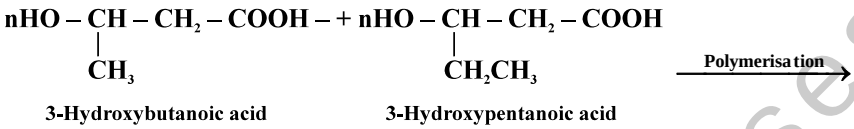
PHBV

2. Nylon 2-nylon 6 : It is formed by glycine ($H_2N - CH_2 - COOH$) and amino acid [$H_2N(CH_2)_5COOH$]. It is polyamide copolymer.

Practice Problems :

1. What is a biodegradable polymer ? Give an example of a biodegradable aliphatic polyester.

[Answers : (1) Polymers which disintegrate over a period of time in environmental degradation by bacteria are called biodegradable polymers. An example of biodegradable aliphatic polyester is PHBV, i.e., Poly-β-hydroxybutyrate-co-β-hydroxyvalerate. It is obtained as under :



3-Hydroxybutanoic acid 3-Hydroxypentanoic acid