



# POLYMERS



- \* Types of polymers
- \* Biodegradable Polymers
- \* Natural and Synthetic Rubber
- \* Commercially - Important Polymers

## TYPES OF POLYMERS

The word 'polymer' is coined from Greek words. 'Poly' means many and 'mer' means unit or part. Polymer is a giant molecule. It is also called complex molecule.

### 3.1.1

#### Introduction

*Polymer is a macromolecule formed from monomers joined by covalent bonds*

Polymer is a very large molecule having molecular mass in the order of  $10^3$  to  $10^7$ u. Polymer is also referred to as macromolecule which is formed by repeating structural units, on a large scale, joined by covalent bonds. The smallest unit that repeatedly combines to form the polymer is termed as monomer. The process of formation of polymer from respective monomers is called polymerisation.

Life began with and is still being maintained by polymers. The use of polymers in the manufacture of plastic cups, buckets, toys, packaging bags, automobile gears, tyres, electrical insulating materials and machine parts has revolutionised life style. Systematic study of polymer science and technology started as late as six decades ago, with the pioneering studies of Standing.

Common examples of polymers are plastics, rubbers, foams, fibres, proteins, nucleic acids, etc.

Polymers found in plants and animals are called natural polymers. Starch, cellulose, proteins, rubber, etc., are examples of natural polymers.

Man made polymers are called synthetic polymers. Plastics like polythene, neoprene rubber, gypal, synthetic fibres like terylene, nylon 6, nylon 6,6 etc., are examples of synthetic polymers.

Cellulose derivatives like rayon, cellulose nitrate, etc., are examples of semi-synthetic polymers. Rayons are used in packages, wrappings and photofilms. They are also called artificial silks. Pyroxylin, viscose rayon, acetate rayon and cuprammonium rayon are familiar semi-synthetic polymers.

Glass, polysiloxane, silicone rubber, etc., are inorganic polymers. cellulose, silk, leather, polythene, bakelite, etc., are organic polymers.

### 3.1.2

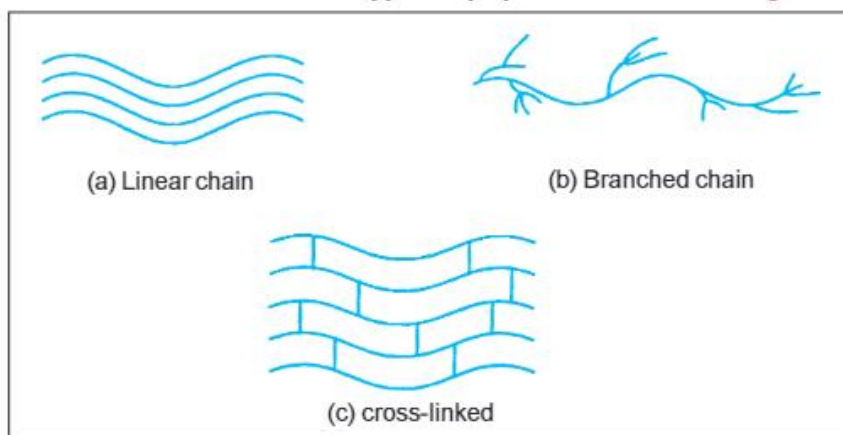
#### Classification

*Polymers with cross links are network polymers*

Polymers are classified into three types based on the structure. Linear polymers consist long and unbranched chains. High density polythene, polyvinyl chloride, etc., are examples of linear polymers. Polymers like low density polythene have linear chains having branches. These are called branched chain polymers. Polymers having cross links are called network polymers. They are usually formed from bifunctional or poly-functional monomers. They contain covalent bonds between long chains.



Bakelite, melamine, phenol-formaldehyde resin, etc., are examples of network polymers. Structures of these three types of polymers are shown in Fig 3.1.



**Fig 3.1 Structure of three types of polymers**

Based on mode of polymerisation, polymers are classified into two types, as addition polymers and condensation polymers.

Addition polymers are formed by the repeated addition of monomer molecules possessing multiple bonds. Formation of polythene from ethylene, PVC from vinyl chloride, polypropene from propylene, etc., are examples of addition polymerisation.

Condensation polymers are formed by the repeated condensation of monomer molecules possessing bifunctional or polyfunctional groups. Elimination of small molecules such as water, hydrogen chloride, alcohol, etc., take place during condensation.

Polymerisation of a single monomeric species is known as homopolymerisation and of two or more different monomeric species is known as copolymerisation. Polythene, polystyrene, isoprene rubber, etc., are homopolymers. Bakelite, terylene, buna-S rubber, etc., are copolymers.

Polymers are also classified based on molecular forces. The mechanical properties like elasticity, tensile strength, hardness, toughness, etc., are governed by intermolecular forces like van der Waals forces, dipolar forces and hydrogen bonds present in the polymer. These molecular forces bind polymer chains.

Rubber like solids with elastic properties are called elastomers. Polymer chains are held together in elastomers by weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. Natural rubber, neoprene rubber, buna-S rubber, buna-N rubber, etc., are elastomers.

Thread forming solids with high tensile strength and high modules are called fibres. Polymer chains are held together in fibres by stronger hydrogen bond forces and thus impart crystalline nature. Polyesters like terylene and polyamides like nylon 6,6 are examples of fibres.

Thermoplastic polymers possess intermolecular attraction forces intermediate between elastomers and fibres. These are linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. Polythene and polyvinyls are common thermoplastics.

Thermosetting polymers are heavily branched or cross linked polymers. On heating they under go extensive cross linking and become infusible. They cannot be reused. Bakelite and polysiloxanes are common thermosetting polymers.

Based on mode of reactions, polymers are classified into addition and condensation polymers

Homopolymer has single monomer and copolymer has two or more monomers

Thermosetting polymers become infusible on heating



*Polymers are also classified based on polarity and mechanism*

Polymers are also classified based on polarity and mechanism of polymerisation. Different classifications of polymers are summarised in Table 3.1.

**Table 3.1 Different classifications of polymers**

Basis for Classification	Nature of polymers	Common examples of polymers
Structure of polymers	Linear polymer Branched polymer Network polymer	Polythene, PVC. Low density polythene. Bakelite, Melamine.
Mechanism of polymerisation	Addition polymers Condensation polymers	Neoprene rubber, PVC. Terylene, Nylon 6,6, Bakelite.
Number of types of monomers used	Homopolymer Copolymer	Polythene, Neoprene rubber. Buna-S rubber, Bakelite, Nylon 6,6.
Molecular forces	Elastomers Fibres Thermoplastics Thermosetting	Buna rubber, Neoprene rubber. Polyesters, Polyamides. Polystyrene, Polyvinyls. Bakelite, Urea-HCHO resin.
Polarity	Cationic polymerisation  Anionic polymerisation	Polystyrene, Polyvinyl ether, Polyisobutene. Buna rubber, Polyisoprene, Polyacrylonitrile.

### 3.1.3

#### Polymerisation process

Depending upon the mechanism, polymerisation reactions are broadly classified into two types : Condensation or step growth polymerisation and addition or chain growth polymerisation.

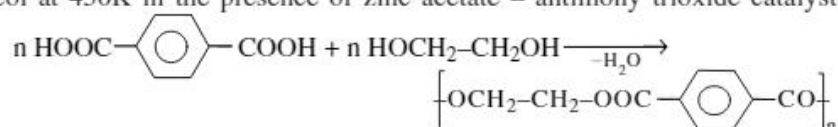
##### Condensation polymerisation

Condensation polymerisation takes place between molecules having polyfunctional groups. A condensation polymer is defined as a polymer in which the polymer unit contains fewer atoms than the number of atoms in all the monomer units from which the polymer is formed. The condensation occurs between molecules having polyfunctional groups and leads to the formation of high molecular mass polymer. The polymerisation reactions may result in the loss of some simple molecules like water, hydrogen halide, alcohol, etc.

The product of each step is again a polyfunctional group and the sequence of condensation goes on. Since, each step produces a distinct functionalised species and is independent of other, this process is also called step growth polymerisation.

Polyesters, polyamides, bakelite, melamine formaldehyde resin, etc., are important examples of step growth polymers.

Polyesters are the polycondensation products of diols and dicarboxylic acids. Terylene, also called dacron, is the best known example of polyester. It is a copolymer. It is manufactured by heating a mixture of terephthalic acid and ethylene glycol at 450K in the presence of zinc acetate – antimony trioxide catalyst.



*Polyesters and polyamides are step growth polymers*

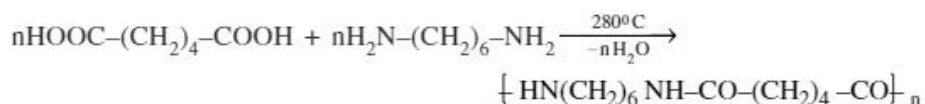


*Dacron is a polyester and Nylon 6,6 is a polyamide*

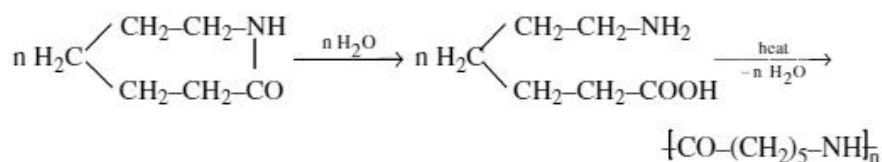
Dacron, also called terylene or PET, is water resistant and is used in blending with cotton and wool fibres. It is also used in safety belts and helmets.

Polyamides are polycondensation products of diamines and dicarboxylic acids. They are important examples of synthetic fibres and are termed as nylons.

Nylon 6,6 is prepared by the condensation of adipic acid with hexamethylene diamine under high pressure and at high temperature. Nylon 6,6 is a copolymer. It is used in textile industry and in making tyre cords, ropes, sheets, bristles for brushes, etc.



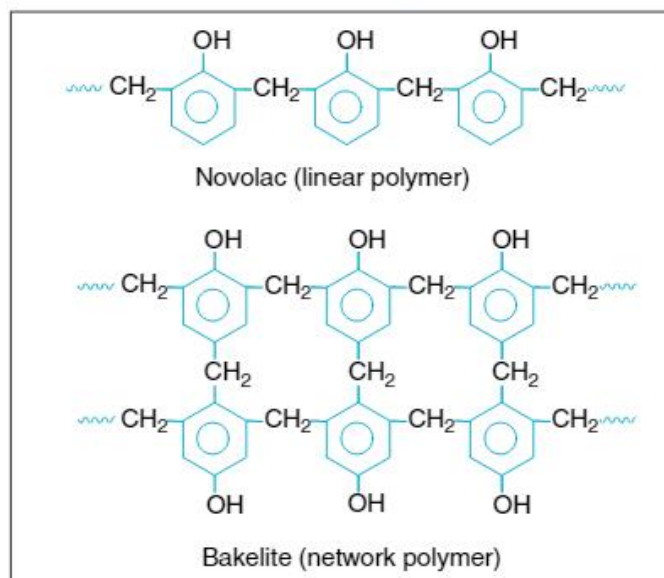
Nylon 6 is a condensation homopolymer. It is also called perlon L. It is obtained by heating caprolactum with water at 540K. It is used for the manufacture of fabrics, ropes and tyre cords.



Formaldehyde-phenol polymers are oldest known synthetic polymers. Condensation of phenol with formaldehyde in ether with base catalyst gives an initial product, a linear polymer, Novolac, which is used in paints. The reaction starts with the initial formation of o- and p-hydroxymethylphenol derivatives.

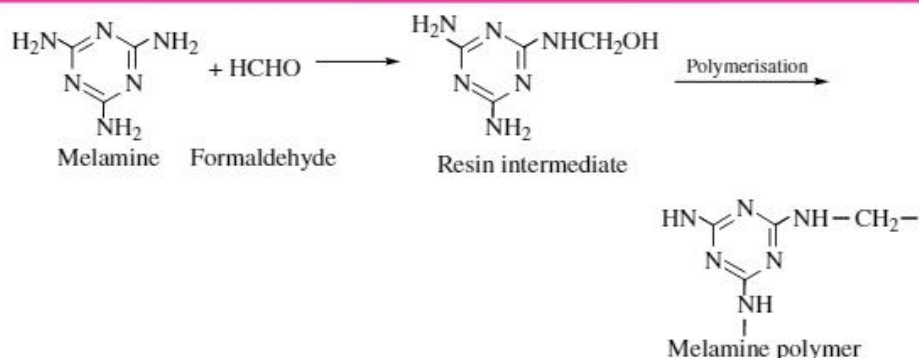
Novolac on heating with formaldehyde undergoes cross linking to give bakelite, which is an infusible solid mass shown in Fig 3.2.

*Novolac is a linear polymer. Bakelite is a cross linked polymer*



**Fig 3.2 Structures of Novolac and Bakelite**

Malamine formaldehyde polymer is formed by the condensation of formaldehyde and metamine. The reaction proceeds through a resin intermediate.



*Addition  
polymers are  
vinyl polymers  
and are also  
called chain  
growth polymers*

### Addition polymerisation

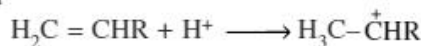
It is the process in which the molecules of same or different monomers add together on a large scale to form polymer. The monomers are unsaturated compounds like alkenes, alkadienes and their derivatives. They are also called vinyl polymers. The mode of polymerisation leading to an increase in chain length or chain growth can take place through the formation of either ionic species or free radicals.

### Ionic polymerisation

It is of two types based on the nature of ions used for the chain initiation. If a positive ion is used, the process is called cationic polymerisation. If a negative ion is used, the process is called anionic polymerisation.

**Cationic polymerisation :** Formation of a polyvinyl compound from its monomer is a simple example in which cation is a chain initiator. Lewis acids like  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{FeBr}_3$ ,  $\text{SnCl}_2$ , etc., are common chain initiators. Three steps are involved in cationic polymerisation.

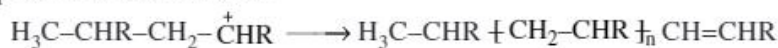
Step 1 : Chain initiation



Step 2 : Chain propagation



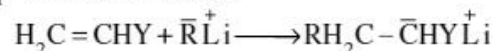
Step 3 : Chain termination



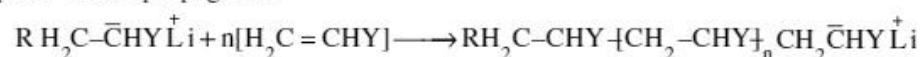
eg : polystyrene, polyvinylethers, polyisobutene, etc.

**Anionic polymerisation :** Formation of a vinyl compound can also be initiated by typical initiators like potassium amide, butyl lithium, etc. Anionic polymerisation involves two steps. A most striking aspect of anionic polymerisation is that the chain termination is absent.

Step 1 : Chain initiation



Step 2 : Chain propagation



Another example of anionic polymerisation is involving Lewis base,  $\text{NH}_2^-$  as catalyst.



eg : Buna type synthetic rubbers, polyacrylonitrile, polyisoprene, etc.

*Chain  
termination is  
absent in anionic  
polymerisation*



### Free radical polymerisation

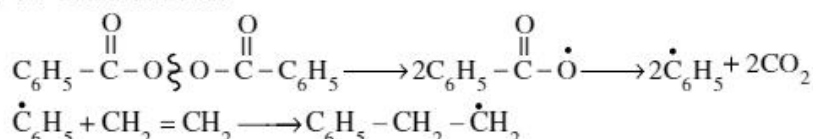
A variety of alkenes or dienes and their derivatives are polymerised in the presence of a free radical generating initiator like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide etc., acting as catalyst. Polymerisation of ethylene to polythene on heating a mixture of ethylene and a small amount of benzoyl peroxide is an example of free radical polymerisation.

The process starts with the addition of phenyl free radical formed from the peroxide to ethylene double bond generating a new and larger free radical. This is called chain initiation. The repetition of the reaction leads to the formation of bigger free radicals called chain propagation. Ultimately product free radical reacts with another free radical to give the polymerised product called chain termination.

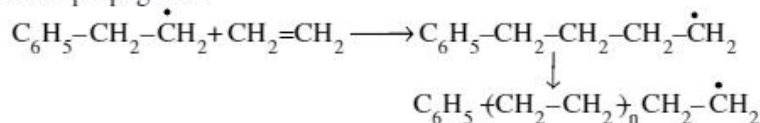
*Free radical polymerisation occurs in three steps in the presence of a peroxide*

In presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc., a variety of alkenes or alkydienes and their derivatives are polymerised. The sequence of various steps may be depicted as follows :

Step 1 : Chain initiation

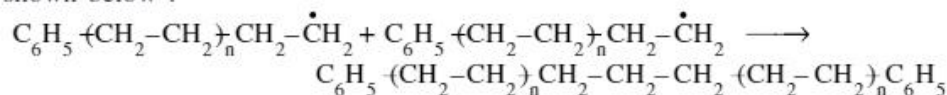


Step 2 : Chain propagation



Step 3 : Chain termination

For termination of the long chain, these free radicals can combine in different ways to form polythene. One of the possible modes of termination of chain is as shown below :




Types of chain polymerisation suitable for common monomers are summarised in Table 3.2.

**Table 3.2 Examples of few types of chain polymerisation**

S.No.	Monomer Type	Polymerisation Mechanism		
		Free Radical	Anionic	Cationic
1	Ethylene	+	–	+
2	Isobutylene	–	–	+
3	Dienes	+	+	–
4	Styrene	+	+	+
5	Vinylchloride	+	–	–
6	Vinyl ethers	–	–	+
7	Vinyl esters	+	–	–
8	Acrylonitrile	+	+	–



  
Polythene is  
most important  
addition polymer

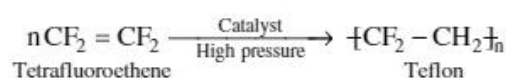
Polythene is most important addition polymer. Preparation of two types of polythene is given below :

**Low density polythene :** It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 to 570 K in the presence of traces of dioxygen or a peroxide initiator (catalyst). The low density polythene (LDP) obtained through the free radical addition and H-atom abstraction has highly branched structure. Low density polythene is chemically inert and tough but flexible and a poor conductor of electricity. Hence, it is used in the insulation of electricity carrying wires. It is used in manufacture of squeeze bottles, toys and flexible pipes.

**High density polythene :** It is formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler - Natta catalyst) at a temperature 333 K to 343 K and under a pressure of 6-7 atmospheres. High density polythene (HDP) thus produced, consists of linear molecules and has high density due to close packing. It is also chemically inert and more tough and hard. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

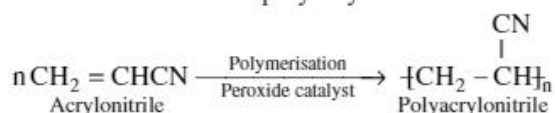
### Polytetrafluoroethene

Teflon is manufactured by heating tetrafluoroethene with a free radical or persulphate catalyst at high pressures. It is chemically inert and resistant to attack by corrosive reagents. It is used in making oil seals and gaskets and also used for non-stick surface coated utensils.



## Polycrylonitrile

The addition polymerisation of acrylonitrile in presence of a peroxide catalyst leads to the formation of polyacrylonitrile.

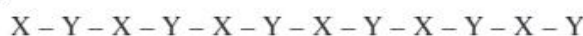


Polyacrylonitrile is used as a substitute for wool in making commercial fibres as orion of acrilan.

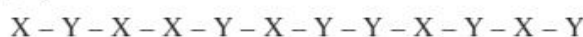
## Co-polymerisation

A high polymer consisting of two or more chemically different types of monomers is called a copolymer. A copolymer contains multiple units of each monomer in the same polymeric chain. Depending on the nature of distribution of two different monomers in the polymer chain, copolymers are four types.


- 1. Alternating copolymers :** The monomer units are in alternate positions in the polymer chain.



- 2. Random copolymers :** The monomer units are present at random positions in the polymer chain.



  
Teflon is poly  
tetrafluoroethene

  
Copolymers are  
four types based  
on distribution  
of monomers



$$(X - X - X) + (Y - Y - Y - Y - Y) + (X - X - X - X) +$$
$$\begin{array}{ccccccc} X & -X & -X & -X & -X & -X & -X \\ & | & & & & & | \\ & Y & & & & & Y \\ & | & & & & & | \\ & Y & & & & & Y \\ & | & & & & & | \\ & Y & & & & & Y \end{array}$$

**P.3.1** How are the polymers classified based on heat treatment?

Thermosetting polymers are condensation cross linked polymers. These become more hard on heating. They cannot be remoulded or reshaped, eg : Bakelite, terylene, urea - formaldehyde resin, etc.

**P.3.2** Is  $[\text{CH}_2 - \text{CHC}_6\text{H}_5]_n$  a homopolymer or a copolymer?

**P3.3** Alternating copolymers are commonest copolymers. Comment.

Buna type rubbers, on the other hand, are addition alternating copolymers.

**P.3.4**  $\text{Si}(\text{CH}_3)_2\text{Cl}_2$  is hydrolysed. What type of polymer is formed?

$$n \text{ HO}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{Si}}}-\text{OH} + \text{HO}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{Si}}}-\text{OH} \xrightarrow{-n\text{H}_2\text{O}} \text{HO}-\left[ \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{Si}}}-\text{O} \right]_n-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{Si}}}-\text{OH}$$

**P.3.5** A polymer is formed by the condensation of orthohydroxymethylphenol. Comment.

Norolac is used in paints.





**P.3.6** Classify the following as addition and condensation polymers : teryline, bakelite, polythene and PVC.

**Solution** Teryline, polythene and polyvinylchloride are addition polymers.  
Backlite is a condensation polymer.



**P.3.7** What are plastics and plasticisers?

**Solution** Substances like polythene and polyvinyls are commonly called plastics. They are usually addition vinyl polymers. They are familiar for their flexibility and softness.  
Substances added to plastics to impart viscosity, flexibility and other properties to the finished products are called plasticisers.



**P.3.8** Arrange the polymers in increasing order of their intermolecular forces.

(a) Nylon 6,6 ; Buna-s and Polythene

(b) Nylon 6 ; Neoprene and PVC

**Solution** Increasing order of intermolecular forces is given as,

(a) Buna-s < Polythene < Nylon 6,6

(b) Neoprene < Polyvinylchloride < Nylong 6

### EXERCISE - 3.1.1

1. Define the terms monomer and polymer.
2. What are polymers? How are they formed?
3. How do you classify polymers based on their structure? Give examples.
4. Give the classification of polymers based on intermolecular forces.
5. Give one example each for synthetic and semi-synthetic polymers.
6. Give one example each for linear and branched chain polymers.
7. What are cross linked (or network) polymers? Give example.
8. What are elastomers? Give example.
9. What are fibres? Give example.
10. What are natural and synthetic polymers? Give two examples of each type.
11. What are LDP and HDP? How are they formed?
12. What are addition polymers, condensation polymers, homopolymers and copolymers? Give examples.
13. How do you classify co-polymers into four types?
14. Explain copolymerization with an example.
15. Write examples of few types of chain polymerisation.
16. How do you explain the functionality of a polymer?
17. What is teflon? Write its special property?
18. Discuss the mechanism and catalysts used in ionic polymerisation and free radical polymerisation.



## NATURAL AND SYNTHETIC RUBBER

Rubber is a polymer which is capable of returning to its original length, shape or size, after being stretched or deformed. It is a common example of elastomer. It is the oldest natural polymer used by man kind. Rubber is chemically a polydiene.

## 3.2.1

## Natural rubber

*Rubber latex is an emulsion of polyhydrocarbons in aqueous solutions*

South Americans called rubber 'caoutchoue', meaning to weep. Joseph Priestley named the solid material as rubber, because it is used to erase pencil marks.

Natural rubber is obtained from a variety of shaubs and vines called rubber trees. The plants yield a milky suspension known as latex. Latex is an emulsion of negatively charged polyhydrocarbon particles in an aqueous solution. It contains 30-40% rubber, which is coagulated using acetic acid or formic acid. This crude rubber is refined by masticating and then compounding by the addition of necessary agents.

The raw natural rubber is a soft and sticky mass. It is insoluble in aqueous solutions, but soluble in petrol, benzene, carbon disulphide, etc. It has low tensile strength and breaks when too much stretched.

The empirical formula of natural rubber is  $C_5H_8$ . It is a hydrocarbon as it burns in air finally to give carbon dioxide and water. In the absence of air, heating rubber produces isoprene. Isoprene is chemically 2-methyl-1,3-butdiene.

Ozonolysis experiments on natural rubber suggested that the isoprene units are joined head-to-tail by 1,4-links. In the 1,4-link formation, the residual double bonds are rearranged between  $C_2$  and  $C_3$  of each isoprene unit. X-ray studies of Bunna established that rubber is composed of long chain isoprene units arranged in the 'cis' form as shown in Fig 3.3. The 'trans' form is called gutta percha.

The weight average molecular weight of rubber is in between 1,30,000 to 3,40,000. Natural rubber has no polar groups and hence the intermolecular forces are limited only to van der Waals forces. Rubber has a coiled structure and it can be stretched like a spring.

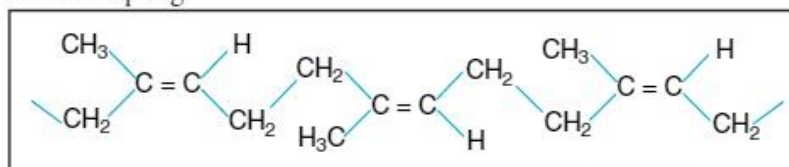


Fig 3.3 Natural rubber (cis-1,4-polyisoprene)

## 3.2.2

## Vulcanisation of rubber

*Heating a mixture of rubber and sulphur is called Vulcanisation*

Natural rubber is brittle at low temperature ( $< 283K$ ) and becomes soft at high temperature ( $> 335K$ ). It shows high capacity to water absorption, low elasticity and is readily abrasive. These properties of rubber are not suitable for its use as automobile tyres and tubes. Good year found that these physical properties of rubber can be improved by adding sulphur to hot rubber. This process is called vulcanisation

Vulcanisation was originally performed by heating a mixture of raw rubber and sulphur at  $373 - 415K$ . This process can be accelerated by adding catalysts like zinc oxide, zinc stearate, etc. On vulcanisation, sulphur forms cross links at the respective sites of double bonds and thus rubber gets stiffened. In the manufacture of tyre rubber, generally 5% of sulphur is used for vulcanisation.



Vulcanisation leads to develop cross links. The possible structures of vulcanised rubber are shown in Fig 3.4. Cross links may be formed at double bonded carbon atoms or at the allylic  $-\text{CH}_2-$  groups.

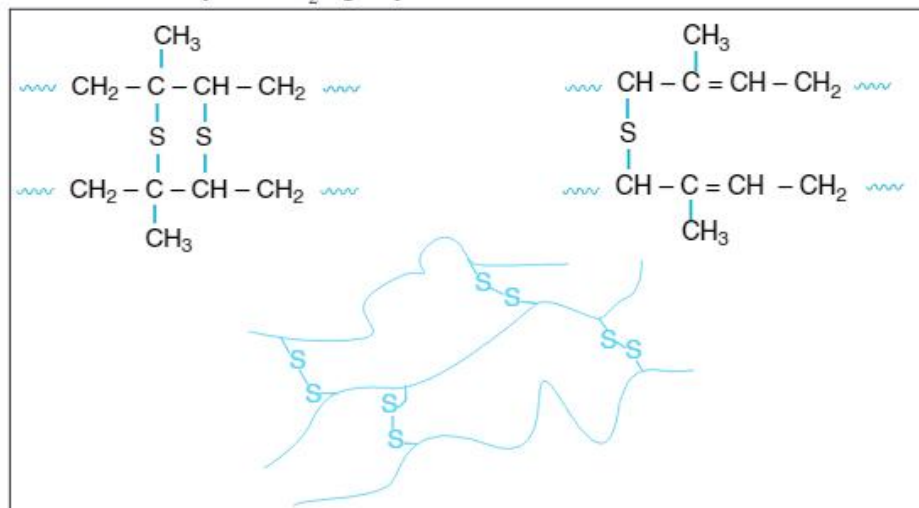


Fig 3.4 Cross links formed by sulphur on vulcanisation

*Rubber gets stiff due to cross links during vulcanisation*

When the proportions of sulphur are increased, rubber can be hardened. If the amount of sulphur is 45% used in vulcanisation, rubber sets to a non-elastic hard material known as ebonite. Due to cross links during vulcanisation, rubber gets stiff. The intermolecular movement of rubber coils is prevented. Vulcanised rubber has excellent physical properties like elasticity, high resistance to chemical oxidation, minimum tendency to absorb water and low solubility in organic solvents.

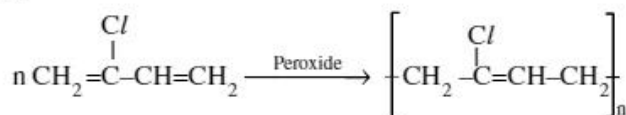
### 3.2.3

#### Synthetic rubber

Any polymer which is capable of getting stretched almost to double the length and which is also vulcanisable as in the case of natural rubber is called synthetic rubber. As soon as the external stretching force is released, it returns to original size and shape. Natural and synthetic rubber resemble in their properties. Both rubbers undergo vulcanisation.

Synthetic rubbers are two types. They may be homopolymers of derivatives of 1,3-butadiene. They may be copolymers of 1,3-butadiene with another unsaturated hydrocarbon derivative.

Neoprene is homopolymer. It is an example of synthetic rubber and is called polychloroprene. It is formed by the free radical polymerisation of 2-chloro-1,3-butadiene, in the presence of a peroxide catalyst. Neoprene has superior resistance to vegetable and mineral oils. It is used for the manufacture of belts, gaskets and hoses.

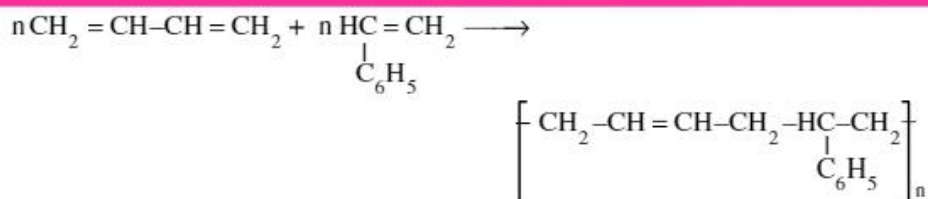


Buna rubbers are copolymers. Buna-S rubber is obtained by the copolymerisation of 1,3-butadiene and styrene. It is called styrene butadiene rubber (SBR) and is denoted as GRA. It is used in making automobile tyres and foot-wear.

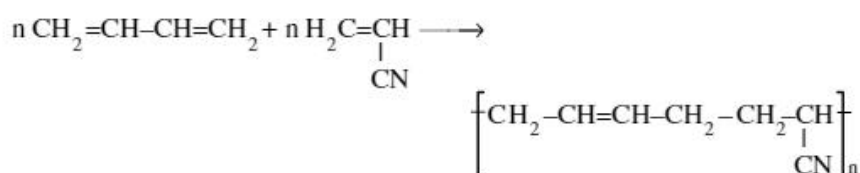
*Neoprene is formed by the free radical polymerisation of chloroprene*

*Buna-S and buna-N rubbers are copolymers*





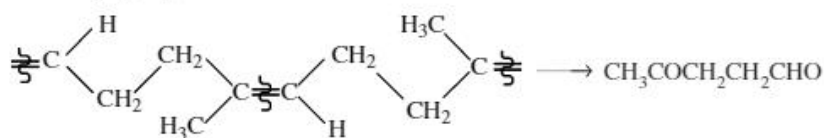
Buna-N rubber is obtained by the copolymerisation of 1,3-butadiene and acrylonitrile. It is denoted as GRN. It is resistant to action of petrol, oil and organic solvents. It is used in making oil seals, tank linings and hoses/pipes.



**P.3.9** What is the ozonolysis derivative of natural rubber?

**Solution** Natural rubber is cis-polyisoprene.

Ozonolysis of polyisoprene gives 4-oxopentanal. The double bonds cleave during ozonolysis to give carbonyl groups.



**P.3.10** What are the differences between buna-S and buna-N rubbers?

**Solution** Both buna - S and buna - N are synthetic rubbers.

Buna - S rubber is a copolymer of 1, 3 - butadiene and styrene.

Buna - N rubber is a copolymer of 1, 3 - butadiene and acrylonitrile.

There is a slight difference in the position of side chain in these rubbers.



**P.3.11** Why the natural rubber is elastic?

**Solution** Intermolecular forces in rubber are weaker van der Waals forces. These forces are further weakened because of all cis configurations about double bonds do not let the polymer chains come closer enough for an effective attraction.

As a consequence the rubber molecule cannot be present as a straight chain and exists in coiled structure. Hence natural rubber is elastic and can be stretched like a spring.



**P.3.12** Write the order of intermolecular forces in neoprene, nylon 6 and PVC.

**Solution** Increasing order of intermolecular forces is : neoprene < polyvinylchloride < nylon 6.

Neoprene rubber is cis-1,4-polychloroprene. It has very weak van der Waals forces.

Van der Waals forces are relatively stronger in polyvinylchloride, because of the presence of halogen atoms.

Nylon 6 is a polyamide and hence van der Waals forces are even stronger.



**EXERCISE - 3.1.2**

1. How is natural rubber isolated from vines and shaubs?
2. Write on the structural elucidation of natural rubber.
3. What is vulcanisation of rubber?
4. How are the physical properties of rubber improved by vulcanisation process?
5. What is the cross linking agent used in tyre rubber?
6. Discuss the preparation and uses of synthetic rubbers.
7. Write the main differences between buna-N and buna-S.

**BIODEGRADABLE POLYMERS**

The living systems are constituted of many polymers. Carbohydrates, proteins, nucleic acids, etc., are a few of such essential polymers for life.

**3.3.1****Carbohydrates and proteins**

Carbohydrates are also known as saccharides. Our food is mainly constituted by carbo-hydrates. They burn in the body to provide the necessary energy to work. Clothing materials like cotton and rayon are made of carbohydrates. Wood and plant fibres are also carbohydrates. Carbohydrates, thus provide the basic amenities of life.

*Polysaccharides are biopolymers*

Carbohydrates which do not undergo hydrolysis are called monosaccharides. Disaccharides yield two monosaccharides upon hydrolysis.

Oligosaccharides yield three to ten monosaccharides upon hydrolysis. Polysaccharides yield large number of mono-saccharides. Polysaccharides are considered as biopolymers.

*Amino acids in a protein form peptide linkages*

Proteins are biopolymers of amino acids and are present in all living cells. Enzymes and hormones are constituted by proteins.

All proteins undergo hydrolysis to give amino acids. The amino acids in a protein form a peptide linkage, the linkage formed between amine group of one amino acid molecule and carboxylic group of another molecule. The linkage is shown as  $\text{-NH-CO-}$ .

**3.3.2****Biodegradable polymers**

Many polymers are quite resistant to the natural degradation process and are thus responsible for the accumulation of polymeric solid waste materials. Thmanagement of these solid wastes created acute environmental problems. These polymeric wastes remain undergraded for quite a long time.

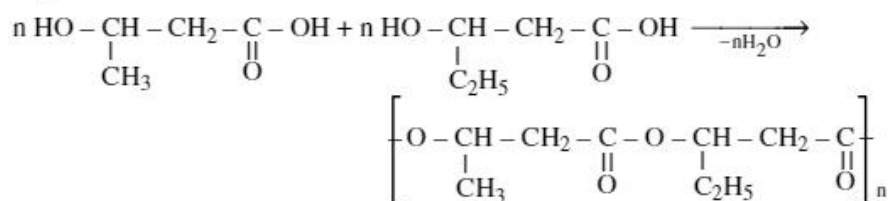
In view of the problems created by the polymeric solid wastes and of the general awareness, certain new biodegradable polymers have been designed, synthesised and developed. These polymers have functional groups that are mostly present in biopolymers and lipids. They may degrade quickly in living systems by enzymatic chemical reactions like oxidation or hydrolysis.



*Aliphatic polyesters are biodegradable polymers*

Aliphatic polyesters are one of the important classes of biodegradable polymers. The condensation reaction between carboxylic acids and alcohols was utilised by Carothers to prepare polyesters. Polyamides are also prepared in a similar way.

Poly  $\beta$ -hydroxy butyrate-co- $\beta$ -hydroxy valerate is a biodegradable polymer and is known as PHBV. This polymer undergoes bacterial degradation in the environment. It is obtained by copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



The physical properties of PHBV change according to the relative amounts of the two hydroxy carboxylic acids used in the preparation. Excess amounts of hydroxy butanoic acid makes the polymer tougher, while excess amounts of hydroxypentanoic acid makes the copolymer more flexible.

PHBV is of immense utility in the field of medicine for making capsules. When the drug is put in the capsule of PHBV, it is released only when the polymer is degraded. It is also used in speciality packaging and in orthopaedic devices.

*Polyglycolic acid, polylactic acid are examples of biodegradable polyesters*

Polyglycolic acid and polylactic acid are homopolymers of the polyester type. These polymers are prepared by the condensation of the monomers 2-hydroxyethanoic acid and 2-hydroxypropanoic acid respectively. Both these polymers are biodegradable esters. Now these polyesters are commercially used for post operative sutures.

Nylon 2 – nylon 6 is an alternating polyamide. It is also a biodegradable polymer. It is obtained by the copolymerisation of glycine and aminocaproic acid. Threads and fibres used as sutures are prepared from it, as it is degraded by bacteria.



**P.3.13** Write the main differences between the structures of starch and cellulose.

**Solution** 100 to 3000 D-glucose units are joined by  $\alpha$  1, 4-glycoside linkages and also  $\alpha$  1, 6-cross links in starch.

300 to 2500 D-glucose units are joined by  $\beta$  1, 4-glycoside linkages in cellulose. Cellulose has packed arrangement of chains. Hence, it is stiff and hard.



**P.3.14**  $\text{CH}_3\text{CHO} + \text{HCN} \longrightarrow \text{X} \xrightarrow{\text{H}_3\text{O}^+} \text{Y}$ .

Which type of polymer is formed from the organic compound Y?

**Solution** X = acetaldehyde cyanohydrin.

Y = lactic acid.

Hydrolysis of compound X, acetaldehyde cyanohydrin with a dilute mineral acid gives compound Y, lactic acid.

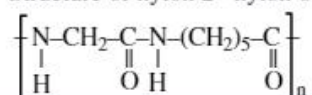
The condensation homopolymer of lactic acid is called polylactic acid. It is a polyester and is a biodegradable polymer.



**P.3.15** Suggest the structure of nylon 2–nylon 6.

**Solution** Nylon 2–nylon 6 is a biodegradable polymer. It is an alternating copolymer obtained by the condensation of glycine and amino caproic acid. It is chemically a polyamide.

Structure of nylon 2– nylon 6 is given as :



### EXERCISE - 3.1.3

1. Write a note on the classification of carbohydrates. Mention the important poly-saccharides.
2. Discuss a polypeptide and its linkages.
3. What is the need of biodegradable polymers? Write examples.
4. Discuss the preparation and uses of biodegradable polyesters.

## COMMERCIALLY IMPORTANT POLYMERS

Polymers find many important applications in every day life. Use of many metals and alloys is replaced by some polymers.

### 3.4.1 Important synthetic polymers

Polythene is almost attached in day to day life especially in the form of packages, carry bags and house hold articles. Natural as well as synthetic rubbers are familiar for their use in automobile tyres, foot wear, printing rollers and oil seals. Artificial silk, a cellulose derivative, is familiar in four different rayons.

PVC, teflon, PMMA, PET, nylon, bakelite, glyptal are some of the very important commercial polymers to mention.

Commercially important polymers are listed in Table 3.3 and Table 3.4 along with their respective monomers, structures and important uses.

### 3.4.2 Molecular weights

The number of monomeric units per polymer molecule varies from sample to sample. Thus polymer sample contains chains of varying length.

The molecular mass of a given polymeric chemical substance does not remain constant as in the case of simple chemical substances. Hence molecular weight of a polymer is expressed in terms of average value. The statistical average is taken in several types. Some of these types to mention are listed.

Number average molecular weight,  $\overline{M}_n$ ;

Weight average molecular weight,  $\overline{M}_w$ ;

Atomic number average molecular weight,  $\overline{M}_z$  and

Viscosity average molecular weight,  $\overline{M}_v$ .

Let the number of particles of mass  $M_1$  be  $N_1$ , mass  $M_2$  be  $N_2$ , etc., in a given polymer.

The total mass of the polymer sample =  $N_1M_1 + N_2M_2 + \dots = \sum_{n=1}^{\infty} N_nM_n$

*Molecular weight  
of polymers are  
taken as  
statistical  
averages*



Table 3.3 Commercially important addition polymers\*

Name of the polymer (type)	Constituent monomer	Structure of the polymer	Important properties of the polymer	Application of polymer in common life
Low density polythene (homopolymer)	Ethylene $H_2C = CH_2$	$\text{-(CH}_2\text{-CH}_2\text{)}_n$	Density is low (LDPE)	Pipes, water lines, insulation in cables.
High density polythene (homopolymer)	Ethylene $H_2C = CH_2$	$\text{-(CH}_2\text{-CH}_2\text{)}_n$	Density is high (HDPE)	Toys, household articles, laboratory apparatus.
Polyvinyl chloride or PVC (homopolymer)	Vinyl chloride $H_2C = \underset{\text{Cl}}{\underset{ }{CH}}$	$\left[ \text{CH}_2 - \underset{\text{Cl}}{\underset{ }{CH}} \right]_n$	Resistant to acids and bases. Insoluble in water, alcohols and petroleum ether	Adhesives, coatings, fibres, cheap plastic cables and pipes.
Polyvinylbenzene or polystyrene (homopolymer)	Vinyl benzene $H_2C = \underset{C_6H_5}{\underset{ }{CH}}$	$\left[ \text{CH}_2 - \underset{C_6H_5}{\underset{ }{CH}} \right]_n$	Poor resistant to weather. Becomes yellow in air.	Moulded containers, TV cabinets, toys, foamed plastics, insulating material.
Polytetrafluoro ethylene or Teflon (homopolymer)	Tetrafluoro ethylene $F_2C = CF_2$	$\text{-(F}_2\text{C - CF}_2\text{)}_n$	Resistant to acids, bases and organic solvents. Strength is unchanged with temperature	Cooking ware, lubricant, electrical insulator.
Polypropylene (homopolymer)	Propylene $H_2C = \underset{CH_3}{\underset{ }{CH}}$	$\left[ \text{H}_2\text{C} - \underset{CH_3}{\underset{ }{CH}} \right]_n$	Relatively stiff and hard	Pipes, cables, fibres, toys and ropes.
*Neoprene (homopolymer), buna -S and buna -N (copolymers) rubbers are also addition polymers. Their preparation and uses are given under synthetic polymers.				

The total number of particles of polymer =  $N_1 + N_2 + \dots = \sum_{n=1}^{\alpha} N_i$

The number average molecular weight of the polymer, ( $\overline{M}_n$ ) :

$$\overline{M}_n = \frac{\sum_{n=1}^{\alpha} N_i M_i}{\sum_{n=1}^{\alpha} N_i} = \frac{N_1 M_1 + N_2 M_2 + \dots}{N_1 + N_2 + \dots} Z$$

The fraction of total mass multiplied by the molecular weight of  $N_1$  particles, we get the partial mass contributed as,  $N_1 M_1^2 / \sum_{n=1}^{\alpha} N_i M_i$ .

Similar expressions of partial masses of particles  $N_2, N_3$ , etc., are obtained.

The weight average molecular weight of the polymer, ( $\overline{M}_w$ ) :



Table 3.4 Commercially important condensation polymers\*

Name of the polymer (type)	Constituent monomer(s)	Structure of polymer (important property)	Application in common life
Nylon 6,6 (copolymer)	Adipic acid $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ Hexamethylene diamine $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$	$[\text{HN}(\text{CH}_2)_6\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO}]_n$ (Stiff fibrous nylon)	Textiles, tyre making tyre cards, ropes, sheets, bristles for brushes
Nylon 6 or perlon L (homopolymer)	Caprolactum $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}$	$[\text{NH}-(\text{CH}_2)_5-\text{CO}]_n$ (High electrical resistance, antiabusive)	Textiles, tyre cords, ropes
Terylene or Decron or (PET) Polyethylene terephthalate (copolymer)	Terephthalic acid $\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$ Ethylene glycol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	$[\text{OC}-\text{C}_6\text{H}_4-\text{COOCH}_2-\text{CH}_2-\text{O}]_n$ (Resistant to water, but attacked by NaOH)	Ropes, tents, safety belts, tyre cords
Bakelite (copolymer)	Phenol $\text{C}_6\text{H}_5\text{OH}$ Formaldehyde $\text{HCHO}$	$[\text{C}_6\text{H}_4(\text{OH})\text{CH}_2]_n$ (Cures under pressure and bonds layer firmly)	Gears, protective coatings, laminations
Melamine-formaldehyde (copolymer)	Melamine $\text{H}_2\text{N}-\text{C}_6\text{H}_3(\text{NH}_2)_3$ Formaldehyde $\text{HCHO}$	$[\text{HN}-\text{C}_6\text{H}_3(\text{NH})_2-\text{NH}-\text{CH}_2]_n$ (Stiff and hard material)	Unbreakable crockery

\*Polylactic acid (homopolymer), PHBV and nylon-2,6 (copolymers) are also condensation polymers. Their preparation and uses are given under biodegradable polymers.

*Molecular weights of polymers are determined by measuring osmotic pressure*

$$\overline{M}_w = \frac{\sum_{i=1}^{\alpha} N_i M_i^2}{\sum_{i=1}^{\alpha} N_i M_i}$$

$$\overline{M}_w = \frac{N_1 M_1^2 + N_2 M_2^2 + \dots}{N_1 M_1 + N_2 M_2 + \dots}$$

**Determination of molecular weights :** Number average molecular weight can be determined chemically by end-group analysis or physically by the use of any colligative property.



A solution of polymer, one gram per litre is prepared. A series of solutions of known concentration (C) are prepared from the above solution by suitable dilution. The osmotic pressure ( $\pi$ ) of solutions is measured.

The value of  $\pi/C$  is plotted against C. A straight line plot is obtained. It is extrapolated and  $(\pi/C)$  at zero concentration is noted as  $(\pi/C)_0$ .

$$\left(\frac{\pi}{C}\right)_0 = RT \frac{1}{M_n} \quad (\text{or}) \quad \bar{M}_n = RT \left(\frac{C}{\pi}\right)_0$$

The weight average molecular weight of a polymer depends on the weight of the polymer in a given volume of polymer solution. Such molecular weights are determined by scattering of light or by viscosity measurement.

Both  $\bar{M}_n$  and  $\bar{M}_w$  have no units. The ratio between weight average and number average molecular weights is called polydispersity index (PDI).

The value of PDI for polymers ranges in between 1 and 1.5. Polymers with uniform length of the polymeric chains have PDI equal to unity, since  $\bar{M}_w = \bar{M}_n$ . Polymers with PDI of near unity can be synthesised.

*Ratio of mass and number average molecular weights is called polydispersity index (PDI)*

**P.3.16** How is PTFE familiar commercially ?

**Solution** PTFE is polytetrafluoroethylene, also called teflon. It is a polyfluorocarbon.

Mechanical strength of PTFE remains unchanged over a wide range of temperature. Hence it is used in non stick cook ware. It is resistant to acids, bases, organic and inorganic substances. Hence it is used as corrosion resistant coating.

**P.3.17** A vinyl polymer is a life saving substance as blood plasma. Write the empirical and structural formula of its monomer.

**Solution** The polymer which saves life as blood plasma is polyvinyl pyrrolidone. Its monomer is N-vinyl pyrrolidone.

The empirical formula of the monomer is  $C_6H_9NO$ .

The structural formula is  $H_2C=CH-N-CO \begin{matrix} | \\ H_2C-CH_2 \end{matrix} > CH_2$

**P.3.18** Write the names of monomers in the polymer,  $\{NH-(CH_2)_6-NH-CO-(CH_2)_4-CO\}_n$

**Solution** Adipic acid  $HOOC-(CH_2)_4-COOH$  and hexamethylene diamine  $H_2N-(CH_2)_6-NH_2$  are the monomers.

Copolymers of these two monomers is called Nylon 6,6.

**P.3.19** 30% molecules of a polymer have a molar mass of 30,000. 40% have 40,000 and rest have 60,000. Calculate the average molecular mass and PDI of the polymer.

**Solution** Number average molecular mass,  $(\bar{M}_n) = \frac{30 \times 30000 + 40 \times 40000 + 30 \times 60000}{30 + 40 + 30} = 43,000$

Weight average molecular mass,  $(\bar{M}_w) = \frac{30(30000)^2 + 40(40000)^2 + 30(60000)^2}{30 \times 30000 + 40 \times 40000 + 30 \times 60000} = 46,279$

Polydispersity index (PDI) =  $\frac{\bar{M}_w}{\bar{M}_n} = \frac{46,279}{43,000} = 1.08$





**P.3.20** What are the similarities and differences between Nylon 6 and Nylon 6,6 ?

**Solution**

Both Nylon 6 and Nylon 6,6 are condensation polymers of the type polyamides.

Nylon 6 is a homopolymer of caprolactum. Nylon 6,6 is a copolymer of hexamethylene diamine and adipic acid.



**P.3.21** What is teflon ? Write its applications.

**Solution**

Teflon is polytetrafluoroethylene. It is a homopolymer of tetrafluoroethylene.

Teflon is used in non-stick cooking ware, as lubricant and also as electrical insulator.

### EXERCISE - 3.1.4

1. Write the structures and uses of polythene, PVC, teflon, polystyrene and polymethyl methacrylate.
2. Mention two synthetic polymers prepared using formaldehyde. Write their structures and uses.
3. Discuss on the molecular masses of polymers?
4. How are the molecular masses of polymers experimentally determined?
5. What is the significance of PDI of a polymer?



1.	Polymer is a giant molecule having molecular mass in the order of $10^3$ to $10^7$ u.
2.	Polymerisation is a process in which repeating structural units, on a large scale, joined by covalent bonds.
3.	Common examples of polymers are plastics, rubbers, fibres, proteins, nucleic acids, etc.
4.	Polymers found in plants and animals are called natural polymers. Man made polymers are called synthetic polymers.
5.	Based on the structure, polymers are three types : linear, branched and net work polymers.
6.	Addition polymers are formed by the repeated addition of monomer molecules possessing multiple bonds.
7.	Condensation polymers are formed by the repeated condensation of monomer molecules possessing polyfunctional groups.
8.	Polymerisation of a single monomeric species is known as homopolymerisation and of two or more different monomeric species is known as copolymerisation.
9.	Natural rubber is obtained from a milky suspension of rubber tree, called latex. Latex is an emulsion of negatively charged polyhydrocarbon particles in water.
10.	Natural rubber is cis-1,4-polyisoprene. The trans form is called gutta percha.
11.	Vulcanisation is a process of heating raw rubber and sulphur at 373 - 415 K. Sulphur forms cross links and rubber gets stiffed.



12. Neoprene rubber is formed by the free radical homopolymerisation of 2-chloro-1,3-butadiene.
13. Buna rubbers are examples of co-polymers. Buna-S is obtained from 1,3-butadiene and styrene and buna-N from 1,3-butadiene and acrylonitrile.
14. Carbohydrates like starch and cellulose are natural biopolymers. They are called polysaccharides.
15. Proteins are natural polypeptides and give amino acids upon hydrolysis.
16. PHBV, polyglycolic acid, polylactic acid and nylon 2-nylon 6 are examples of biodegradable polymers
17. Polythene is most familiar commercial polymer. It is almost attached in day to day life in the form of packages, carry bags and house hold articles.
18. Nylon 6 and nylon 6,6 are condensation polymers of the type polyamides.
19. Decron and gypstal are condensation polymers of the type polyesters.
20. The ratio of weight average molecular mass and number average molecular mass of a polymer is called polydispersity index. Index of unity denotes uniform length of polymer chains.

### EXERCISE - 3.2

1. How are polymers classified based on heat treatment?
2. Write the differences between homopolymers and copolymers.
3. What are condensation polymers and addition polymers?
4. Natural rubber is polymer of 2-methyl-1,3-butadiene. Discuss the type of addition and orientation of monomers linked together.
5. How does the property of rubber change upon vulcanisation?
6. What are the different methods of classification of carbohydrates?
7. Discuss the attractive forces that stabilise secondary and tertiary structures.
8. Glycine and glycolic acid are separately used for preparing biodegradable polymers. Discuss.
9. Mention the reasons for acute environmental problems of using synthetic solid polymers?
10. What are the monomers used in preparing bakelite? Write the speciality of bakelite.
11. Mention the monomers used in the preparation of the following polymers. Write their important uses. (a) polyvinyl pyrrolidone, (b) polyacrylonitrile and (c) dacron.
12. How are silicon polymers obtained? Mention their important properties.
13. What is polydispersity index? Write its importance in understanding average molecular masses.
14. Which among neoprene, polythene, nylon 6,6 and polyvinylchloride has highest extent of intermolecular forces? Why? (Ans : Nylon 6,6)
15. Bakelite polymer is hard and stiff. Why?



16. A sample of polymer contains 200 molecules of molecular mass  $10^3$  each; 300 molecules have  $10^4$  each and 500 molecules have  $10^5$  each. Calculate polydispersity index of polymer. (Ans : 1.6)
17. Glyptal is a condensation polymer between substances 'X' and 'Y'. 'X' is ethylene diol. Which hydrocarbon on oxidation yields the compound 'Y'? (Ans : o-Xylene)
18. How biodegradable polymers are important, in view of disposal problems ?
19.  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{COCH}_3 \xrightarrow{\text{KMnO}_4, \text{KOH}} \text{X} \xrightarrow{\text{H}_3\text{O}^+} \text{Y (organic acid)}$ .  
Describe the polymerisation occurs between Y and 1, 2-ethandiol. (Hint : Terylene)
20. Phenol on condensation with excess 'X' in alkali medium gives bakelite. Ozonolysis of which hydrocarbon produces 'X'? (Ans : Ethene)
21.  $\text{A} \xleftarrow{1,4\text{-trans addition}} \text{CH}_2 = \overset{\text{CH}_3}{\underset{|}{\text{C}}} - \text{CH} = \text{CH}_2 \xrightarrow{1,4\text{-cis addition}} \text{B}$   
What are major differences between the polymeric substances A & B?
22. 1,4-Addition of but-1,3-diene occurs during the polymerisation in the presence of a familiar catalyst. Give the composition of catalyst. (Ans : Ziegler-Natha Catalyst,  $(\text{C}_2\text{H}_5)_3\text{Al} + \text{TiCl}_4$ )
23. Beckmann's rearrangement of an organic compound 'X' gives another compound 'Y'. 'Y' is the monomer of a homopolymer 'Z'. If the compound X is  $\text{C}_6\text{H}_{10}=\text{NOH}$ , predict the compound Z. (Ans : Nylon-6)
24. Orlon is the homopolymer of 'X' obtained by the addition of HCN on a hydrocarbon 'Y' in the presence of cuprous catalyst. Oxidation of 'Y' with Baeyer's reagent gives 'Z'. If terylene is obtained by the condensation of 'Z' with terephthalate, what is Y? (Ans :  $\text{C}_2\text{H}_4$ )
25.  $2\text{HC}\equiv\text{CH} \xrightarrow[\text{NH}_4\text{Cl}]{\text{Cu}_2\text{Cl}_2} \text{X} \xrightarrow{\text{HCl}} \text{Y}$ . What rubber is obtained from 'Y'? (Ans : Neoprene)
26. The properties of PHBV change according to the relative amounts of the two hydroxy carboxylic acids used in the preparation. Justify.
27. 40% of the polymeric molecules have a molecular mass 30,000. If x % and y % of the molecules of the same polymer have molecular masses 20,000 and 60,000 respectively with a PDI of 1.2037, calculate the ratio x and y. (Ans : 1:1)

