

Polymers : The term polymer is defined as very large molecules having high molecular mass $(10^3 - 10^7 u)$. These are also referred to as **macromolecules.** which are formed by joining of repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as monomers. The process of formation of polymers from respective monomers is called **polymerisation**.

Classification Based on Source

1. Natural polymers : These polymers are found in plants and animals. Examples are proteins, cellulose, starch, resins and rubber.

2. Semi-synthetic polymers : Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc.

3. Synthetic polymers : Plastic (polythene), synthetic fibers, and synthetic rubbers.

Classification Based on Structure of polymers

1. Linear polymers : High density polythene, polyvinyl chloride, etc.

2. Branched chain polymers : Low density polythene.

3. Cross linked or Network polymers : Bakelite, melamine.

Classification Based on Mode of Polymerisation 1. Addition polymers

The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, e.g., the formation of polythene from ethene and polypropene from propene. However, the addition polymers formed by the polymerisation of a single monomeric species are known as **homopolymers**, e.g., polythene.

n
$$CH_2 = CH_2 \rightarrow -(CH_2 - CH_2) - Homopolymer$$

Ethene Polythene

The polymers made by addition polymerisation from two different monomers are termed as **copolymers,** e,g., Buna-S, Buna-N, etc. $n CH_2 = CH - CH = CH_2 + nC_6H_5CH = CH_2 \rightarrow$

C₆H₅

 $-(CH_2-CH = CH_2 - CH_2 - CH_2 - CH_)_n$ 1,3-Butadiene Styrene Butadiene-styrene copolymer (Buna-S)

2. Condensation polymers

The condensation polymers are formed by repeated condensation reaction between two different bifunctional or tri-functional monomeric units. In these polymerisation reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc, take place. The examples are terylene (dacron), nylon 6, 6, nylon 6, etc. For example, nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid. n $H_2N(CH_2)_5NH_2 + nHOOC(CH_2)_4COOH \rightarrow$

 $[NH(CH_2)_6NHCO(CH_2)_4CO-]_n + nH_2O$ Nylong 6, 6

Classification Based on Molecular Forces 1. Elastomers

These are rubber - like solids with elastic properties. In these elastomeric polymers the polymer chains are held together by the weakest intermolecular forces. These 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. The examples are buna-S, buna-N neoprene, etc.

2. Fibres

Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

3. Thermoplastic polymers

These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibers. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

4. Thermosetting polymers

These polymers are cross linked or heavily branched molecules, which on heating undergo extensive crosslinking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldehyde resins, etc.

Classification Based on Growth Polymerisation

The addition and condensation polymers are nowadays also referred as chain growth polymers and step growth polymers depending on the type of polymerisation mechanism they undergo during their formation.

Types of Polymerisation Reactions

There two broad types of polymerisation reactions, i.e., the addition or chain growth polymerisation and condensation or step growth polymerisation.

Addition Polymerisation or Chain Growth Polymerisation

This mode of polymerisation leading to an increase in chain length or chain growth can take place through the formation of either free radicals or ionic species. However, the free radical governed addition or chain growth polymerisation is the most common mode.

1. Free radical mechanism

A variety of alkenes or dienes and their derivative are polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. For example, the polymerisation of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator. The sequence of steps may be depicted as follows.

Chain initiation steps

$$C_6H_5 - C - O - O - C - C_6H_5$$

Benzoyl peroxide Phenyl radical Chain propagating step

 $C_6H_5 - CH_2 - CH_2 + CH_2 = CH_2$ -

 $C_{6}H_{5} - CH_{2} - CH_{2} - CH_{2} - CH_{2}$ \downarrow $C_{6}H_{5} - (CH_{2} - CH_{2} - CH_{2} + nCH_{2})$

- CH₂ -

CH2 - CH2 - CH2 - C6H5

Chain terminating step

 $C_{6}H_{5} - (CH_{2} - CH_{2})_{n} CH_{2} - CH_{2}$

 $c_{eH_2} - cH_2 - cH_2 - cH_2$ **Dreparation of some important**

Preparation of some important addition polymers

 $C_{6}H_{5} + CH_{2} - CH_{2} + CH_{2}$

(a) Polythene : Two types

(i) Low density polythene:

It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K 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 branced 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 and manufacture of squeeze bottles, toys and flexible pipes.

(ii) 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 of 333 K 343 K and under a pressure of 6-7 atmospheres. High density polythhene (HDP) thus produced, consists of linear molecules and has a high density due to close packing. It is also chemically inert and more tougher. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

(b) Polytetrafluoroethene (Teflon)

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.

$$n CF_{2} = CF_{2} \xrightarrow{Catalyst} - [CF_{2} - CF_{2}]_{n}$$

Tetrafluoroethene Teflon
(c) Polyacrylonitrile

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

n CH₂ = CHCN
$$\xrightarrow{\text{Polymerisation}}$$
 -[CH₂ - CH]_n

Condensation polymerisation or Step Growth polymerisation

This type of polymerisation generally involves a repetitive condensation reaction between two bifunctional monomers. These polycondensation reactions may result in the loss of same simple molecules as water. alcohol, etc., and lead to the formation of high molecular mass condensation polymers.

In these reactions, the product of each step is again a bi-functional species and the sequence of condensation goes no. Since, each step produces a distinct functionalised species and is independent of each other, this process is also called as step growth polymerisation.

1. Polyamides

The condensation polymerisation of amines with dicarboxylic acids and also of amino acids and their lactams.

(a) Perparation of nylons (i) Nylon 6,6:

It is prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.

n HCOOC(CH₂)₄COOH + n H₂N(CH₂)₆NH₂

$$\xrightarrow{553 \text{ K}}$$
 $\xrightarrow{-}$ N (CH₂)₆-N-C(CH₂)₄-C $\xrightarrow{-}$
Nylon 6,6

Nylon 6,6 is used in making sheets, bristles for brushes and in textile industry,

(i) Nylon 6:

It is obtained by heating caprolactum with water at a high temperature.



Nylon 6 is used for the manufacture of type cords, fabrics and ropes.

2. Polyesters

These are the polycondensation products of dicarboxylic acids and diols. Dacron or terylene is the best known example of poyesters. It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetateantimony trioxide catalyst. Dacron fibre (terylene) is 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)

Phenol - formaldehyde polymers are the oldest synthetic polymers. The reaction starts with initial formation of o-and /or p-hydroxymethylphenol derivative, which further react with phenol to form compounds having rings joined to each other through $-CH_2$ groups. The initial product could be a linear product – **Novolac** used in paints.





Novolac

Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called **Bakelite.** It is used for making combs, phonograph records, electrical switches and handles of various utensils.



4. Melamine - formaldehyde polymer







NH₂

Melamine Fo Resin intermediate

Formaldehyde



It is used in the manufacture of unbreakable crockery.

Copolymerisation

Copolymerisation is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise and form a copolymer. The copolymer can be made not only by chain growth polymerisation but by step growth polymerisation also.

n
$$CH_2 = CH - CH = CH_2 +$$

Styrene
 $[CH_2 - CH = CH_2 - CH_2 - CH_2]_n$

Copolymers have properties quite different from homopolymers. For example, butadiene-styrene copolymer is quite tough and is a good substitute for natural rubber. It is used for the manufacture of autotyres, floortiles, footwear components, cable insulation etc.

Rubber

1.Natural rubber

It is also termed as elastomer. It is manufactured from rubber latex which is a colloidal dispersion of rubber in water. This latex is obtained from the bark of rubber tree.



The cis-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure. thus it can be stretched like a spring and exhibits elastic properties.

Vulcanisation of rubber:

The process consists of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373 K to 415 K. On vulcanisation, sulphur forms crosslinks at the reactive sites of double bonds and thus the rubber gets stiffened.

In the manufacture of tyre, 5% of sulphur is used as a crosslinking agent. The probable structures of valcanised rubber molecules are depicted below:



2. Synthetic rubbers

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. Thus, (synthetic rubbers are either homopolymers of 1,3-butadiene derivatives or copolymers of 1,3-butadiene or its derivatives with another unsaturated monomer.

Preparation of Synthetic Rubbers

1. Neoprene

Neoprene or polychloroprene is formed by the free redical polymerisation of chloroprene.



Chloroprene Neoprene 2-Chloro-1,3-butadiene

It has superior resistance to vegetable and mineral oils. It is used for manufacturing conveyor belts, gaskets and hoses.

$$CN_{2} = CH - CH = CH_{2} + n CH_{2} = CH$$

$$Copolymerisation$$

$$CN_{1}$$

$$CN_{2} = CH$$

$$CH_{2} - CH = CH - CH_{2} - CH_{2} - CH_{1}$$

1,3-butadiene Buna-N Acrylonitrile

2. Buna - N

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

Molecular mass of Polymers

The growth of the polymer chain during their synthesis is dependent upon the availability of the monomers in the reaction mixture. Thus, the polymer sample contains chains of varying lengths and hence its molecular mass is always expressed as an average. The molecular mass of polymers can be determined by chemical and physical methods.

Biodegradable Polymers

Aliphatic polysesters are one of the important classes of biodegradable polymers. Some important examples are given below:



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

PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs.

ОН	OH I
$CH_3 - CH - CH_2 - COOH + C$	$CH_3 - CH_2 - CH - CH_2 -$
$COOH \rightarrow \left(\begin{array}{c} O - CH = CH_2 - C \\ I \\ CH \end{array} \right)$	$C = O = CH = CH_2 = C$

3-Hydroxybutanoic acid 3 Hydroxypentanoic acid PHBV

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.

Polymers of Commercia Importance Some Other Commercially Important Polymers

	-		
Name of Pol _y mer	Monomer	Structure	Uses
Polypropene	Propene	Сн ₃ 	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	C_6H_5 $(CH_2-CH)_{1}$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride		Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyle Resin	(a) Urea (b) Frmaldehyde	$(+NH - CO - NH - CH_2)_{n}$	For making unbreakable cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid		Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde	$(H_2)^{O-H}$ $(H_2)^{O-H}$ $(H_2)^{O-H}$ $(H_2)^{O-H}$	For makingomb, electrical switches, handles of utensils and computer discs.



SOLVED PROBLEMS

Q.6

Sol.

Sol.

- Q.1 Explain the differences between Buna-N and Buna-S.
- Buna-N is a copolymer of 1,3-butadiene and Sol. acrylonitrile and Buna-S is a copolymer of 1,3butadiene and styrene.
- Q.2 Arrange the following polymmers in increasing order of their molecular forces. (i) Nylon-6,6 Buna-S, Polythene. (ii) Nylon-6, Neoprene, Polyvinyl chloride.
- (i) Buna-S< Polythene < Nylon-6,6 Sol. (ii) Neoprene < Polyvinyl chloride < Nylon-6
- D istiguish between the terms Q.3 homopolymer and copolymer and give an example of each.
- (i) Homopolymer: Traditional polymer formed Sol. bypolymerisation of monomers of the single substance is known as a homopolymer e.g., polythene formed from ethylene.

(ii) Copolymer: copolymer is a polymer that is formed bypolymerising two or more different monomers. e.g., Buna-S rubber is a copolymer of butadiene and styrene.

- How can youdiffrentiate between addition Q.4 and condensation polymerisation?
- Sol. (i) Addition polymerisation: In the process polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, e.g., the formation of polythene from ethane.

 $nCH_2 = CH_2 \rightarrow -[-CH_2 - CH_2 -]_n$ (ii) Condensation polymerisation: Is a process in which two or more bifunctional molecules undergo a series of condensation reactions with the elimination of some simple molecules and leading to the formation of polymers.

 $= \frac{1}{2} \frac{1}{2}$

Explain the term copolymerisation and Q.5 give two examples.

Sol. complymerisation is a process in which a mixture of more than one monomeric species is allowed to polymerise. The copolymer contains multiple untis of each monomer in the chain. The examples are (i) copolymer of 1,3butadiene and and acrylonitrile,

(i) n CH₂ = CH - CH = CH₂ + nC₆H₅CH = CH₂ \rightarrow 1,3-Butadiene styrene



What elastomers? Sol.

The polymers that haveelasticity like rubber, are referred to as elastomers. The polymer chain in elastomers are held together by weakest intermolecular forces.

Q.7 What is bipolymer?

Bipolymers are natural polymers that contain many different units, for examples: proteins and carbohydrates.

Q.8 Write the free radical mechanism for the polymerisation of ethaene.

The mechanism of chain growth polymerisation of ethene involves free mechanism as give below:

Step I : Chain initiating steps:





$$\begin{array}{c} O \\ \parallel \\ 2 C_6 H_5 - C - O \longrightarrow 2 C_6 H_5 \\ \hline Phenvl radical \end{array}$$

$$C_6H_5^+ + CH_2 = CH_2 \rightarrow 2C_6H_5 - CH_2 - CH_2^+$$

Q.9

Sol.

and

Step II : Chain propagating steps:		hardening on cooling. These plolymers possess
$C_6H_5 - CH_2 - CH_2 + CH_2 \longrightarrow C_6H_5CH_2 - CH_2 -$		intermolecular forces of attraction intermediate
$CH_2 - CH_2^{\bullet}$		between those of elastomers and fibres. Some
		common thermoplastics are polythene,
and so on		polystyrene, polyvinyl etc.
• С ₆ Н ₅ –(-		
$CH_2 - CH_2 \rightarrow_n - CH_2 - CH_2^{\bullet}$	Q.10	What is a biodegradable polymer? Give an
Step III : Chain propagating steps:		example of a biodegradable aliphatic
$C_6H_5 - (-CH_2 - CH_2 -)_n - CH_2 - CH_2^{\bullet} + C_6H_5 -$		polyster.
-(- CH ₂ - CH ₂ -)-n- CH ₂ - CH ₂ [•]	Sol.	biodegradable polymers: The polymers which
\longrightarrow C ₆ H ₅ -(- CH ₂ - CH ₂ -) _n - CH ₂ - CH ₂		degrade in the environment with time and called
-CH ₂ (- CH ₂ - CH ₂ -)-n- C ₆ H ₅		biopolymers or biodegradable polymers. They
		do not cause environmental problems.
Define thermoplastics and thermosetting		Structure: Biodegradable synthetic polymers
polymers with two examples of each.	1	are polymers which have same functional groups
(i) Thermoplastic polymers: These are the		as are present in biopolymers and lipids.
linear or slightly breached long chain molecules		Examples : Aliphatic polyesters, PHBV etc.
canable of repeatedly softening on heating and		

Q.11 give three differences between linear polymers and branched-chain polymers. Sol.

Linear Polymers	Branched-chain Polymers
 Have high milting points. Have high density. The tensile strength is high 	Have low melting points Have low density The tensile strength is low.
	Q.12 Differentiate between step growth chain growth reaction. Sol.
Step Growth	Chain Growth
1. It is a reaction in which monomer,	It is a reaction which involves a series of

1. It is a reaction in which monomer, having one or more double bonds, undergo repeated addition in a chain reaction.

Q.13 Is (-NH-CHR-CO-)n, a homopolymer or a copolymer?

Ans. $(-NH-CHR-CO-)_n$ is a homopolymer. It is formed by a single entity *capro lacutm*.

Q.14 Could a copolymer be formed in both addition and condensation polymerization or not? Explain with examples.

condensation reactions, between simple

monomers containing polar groups.

Ans. Yes, copolymer can be formed in both addition polymerization and condensation polymerization *Bakelite* is a condensation polymer of phenol and formaldehyde.
 Buna – S is an addition polymer of Butadiene and styrene.

Q.15 Write structure of a reagent used for initiating a free radical chain reaction. How does it act?

Ans. The reagent that is used for initiating a free radical chain reaction is *Tertiary butyl peroxide*. It decomposes under mild conditions to form *tert*. butoxide free radical, (CH₂)₃ CO.

$$(CH_3)_2 COOC(CH_3)_3 \xrightarrow{373-423 \text{ k}} 2CH_3 \xrightarrow{|}_{l_3} CH_2 = 0$$

The free radical add to monomer molecule to form a new free radical of larger size. Such repeated additions result in formation of polymer.

- Q.16 Write the mode of free radical polymerization of an alkene?
- **Ans.** In polymerization of alkenes the reactive intermediate is free radical (In) i.e., initiator

Initiator +
$$CH_2 = CH_2 \xrightarrow{in} In - CH_2 \rightarrow CH_2 \xrightarrow{CH_2 = CH_2} In - CH_2 - CH_2 \rightarrow CH_$$

- Q.17 Write structures of monomers used for getting the following polymers?
- a. PVC b. Teflong c. PMMA Ans. (a) $CH_2 = CHCI$ (Vinyl chloride)
 - **(b)** $CF_2 = CF_2$ (tetrfluoroethylene) CH_3

 H_3

(c) $CH_2 = COOCH_3$ (Methylmethaacrylate).

- Q.18 Why should one always use purest monomer in free radical polymerization?
- **Ans.** If impurities are present in the monomer of a free radical polymerization process, then such impurities may combine with free radical and may slow down or even stop the polymerization process.
- Q.19 How does the presence of carbon tetrachloride influence the course of vinylic free radical polymerization? Explain with an example.
- Ans. The presence of CCl₄ in the course of vinylic free radical polymerization, initiates a new polymerization chain and thereby forms a new polymer as depicted below





In presence of CCl_4 , styrene polymerizes to form polystyrene of lower average molecular mass which also contains one chlorine.

The highly unreactive free radical formed CCl₃ which terminates the chain reaction. Such compounds are called *Chain transfer reagents*.

Q.20 Explain how does 1, 3 – butadiene polymerize by different routes?

Ans. 1, 3 – Butadiene polymerizes by following different routs.

(*i*) **1**, **4** – **Polymerization**. When polymerization occurs at C – 1 and C – 4 of butadiene, an unbranched polymer I formed from an alkene having a double bond at each of its carbons by different groups and hence exist either as *trans* – polybutadiene or *cis* – polybutadiene or as a mixture of these





(*ii*) **1**, **2** – **Polymerization**. It can undergo polymerization at C – 1 and C – 2 to yield the polymeric product i.e., polyvinyl polythene. The double bonds in these initial polymers can be linked, by further treatment with chemicals, to modify their properties. These reactions form the basis of formation of rubbers.

Q.21 Why does styrene undergo anionic polymerization easily?

Ans. Styrene undergoes *anionic polymerization* easily because C_6H_5 group is styrene is electron with drawing. It involve the following steps.

In it an *anionic initiator* such as *potassium amide* or n - butyl *lithium* add up to the double bond of styrene to form a **carbanion**.

$$\stackrel{+}{\operatorname{KNH}}_{2} + \stackrel{+}{\operatorname{CH}}_{2} \stackrel{=}{\overset{-}{\operatorname{CH}}}_{1} \xrightarrow{H_{2}N-\operatorname{CH}}_{2} \stackrel{-}{\underset{L_{6}}{\overset{-}{\operatorname{CH}}}}_{1} \xrightarrow{H_{2}N-\operatorname{CH}}_{2} \stackrel{-}{\underset{C_{6}}{\overset{-}{\operatorname{CH}}}}_{1}$$

This is chain initiation step.

In the *chain propagation step* this carbanion adds to the double bond and the process goes on getting repeated to form a *polymeric carbanion*.

In the **chain terminating step**, the reaction may be terminated by the *addition of an acid*.

- Q.22 Why is cationic polymerization preferred in case of vinylic monomers containing electron donating groups?
- Ans. Cationic polymerization is preferred case of vinylic monomers containing donating groups, because a cationic initiater will add on to the double bond and would produce a cationic intermediate for propagating the addition chain procees. In the presence of an acid (which gives H⁺), the acid adds on the double bond of vinylic monomer to form a cation. On further addition to the double bon of various monomers, a bigger cation is formed and sequence propagates the chain to the polymeric cation. The chain termination occure by loss of proton. Various steps involved are shown below.

(i) Chain Initiation Step

(ii) Chain Propagation Step

 $\begin{array}{cccc} H_{3}C - \stackrel{\bullet}{\underset{CH_{3}}{\leftarrow}} H & + & CH_{2} = CH & - & \rightarrow & H_{3}C - CH - CH_{2} - \stackrel{\oplus}{\underset{CH_{3}}{\leftarrow}} H \\ & & & I \\ & & & I \\ & & & CH_{3} & & CH_{3} \end{array} \xrightarrow{} \begin{array}{c} H \\ & & I \\ & & I \\ & & & I \end{array}$

(iii) Chain Termination Step

$$\begin{array}{c} H_{3}C-CH- \begin{bmatrix} CH_{2}-CH \\ I \\ CH_{3} \end{bmatrix}_{n} \xrightarrow{C} CH_{2}-CH \\ \vdots \\ CH_{3} \end{bmatrix}_{n} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3}-CH \\ \vdots \\ CH_{3} \end{bmatrix}_{n} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3}-CH \\ \vdots \\ CH_{3} \end{bmatrix}_{n} \xrightarrow{C} CH_{2}-CH \\ \vdots \\ CH_{3} \\ CH_{3$$

- Q.23 Will you prefer to polymerize acrylonitrile under anionic or cationic polymerization conditions? Explain your choice.
- **Ans.** In this case **cationic polymerization** will be preferred. Since it contains an electron releasing group (-CN) so cationic polymerization will be facilitated.
- Q.24 Elaborate the structure of natural rubber.

$$CH_3$$

 $H_2C = C - CH = CH_2$ (isoprene)

Ans. The monomer of natural rubber is *isoprene*. The structure of natural rubber may be shown as

- **Q.25 Depict** a free radical mode of addition polymerization of isoprene.
- Ans. Free Radical Mode of Addition Polymerization of Isoprene. It is given below

$$\dot{\hat{\mathbf{R}}}_{\text{(initiator)}} + \mathbf{CH}_2 = \underbrace{\mathbf{C}-\mathbf{CH}}_{l} = \mathbf{CH}_2 \xrightarrow{} \mathbf{R}-\mathbf{CH}_2 \xrightarrow{} \mathbf{CH}_2 \xrightarrow{} \mathbf{CH}_2$$





Q.26 How do double bonds in rubber molecules influence their structure and reactivity?

Ans. More the number of double bonds less will the rubber be reactive. This is due to greater inter
 – molecular forces of attraction between the monomers.

They are very tough and possess high abrasion resistance, high load bearing capacity and are used in the manufacture of auto tyres. They are also used for floor tiles, footwear components, cable insulation etc.

Power by: VISIONet Info Solution Pvt. Ltd Website : www.edubull.com Mob no. : +91-9350679141

Q.27 How does vulcanization change the Ans. character of natural rubber?

Ans. After vulcanization the rubber acquires properties such as excellent elasticity, low water absorption tendency, resistance to oxidation and organic solvents.

On **vulcanization** (*i.e.*, heating natural rubber with sulphur at 373 - 415 K), sulphur establishes cross links at reactive sites (e.g., $-CH_2-$, alpha to double bond). Because of this the rubber gets stiffened and the intermolecular movement of rubber spring is prevented resulting in the change in physical characteristics of rubber.

- Q.28 Why are the numbers 66 and 6 put in the name nylon 66 and nylon 6?
- Ans. In Nylon 66 the number 6, 6 indicate that it is formed from two monomers each containing 6 carbon atoms.

In Nylon – 6 the number 6 indicates that it is formed from a monomer containing 6 carbon atoms.

Q.29 Illustrate with equations, how is Dacron obtained fro mcaprolactam?



Q.30 How is bakelite formed? Explain the reactions with equations.

Ans. Bakelite is formed by the condensation of *phenol* and *formaldehyde* in the presence of acid or base.

The reaction starts with initial formation of O - and / or p - hydroxymethylphenol derivatives, which further react with phenol to form compounds where rings are joined to each other with - CH₂ - groups. The initial product could be the linear product*novolac*.

On further heating with formaldehyde *novolac* undergoes cross – linking to form an infusible solid, this polymer is called *bakelite*

Thermoplastic Polymers	Thermosetting Polymers	
1. In them the intermolecular forces at attraction are	1. In them the intermolecular forces of attraction are	
intermediate between those of elastomers and fibres.	maximum.	
2. On heating they become soft.	2. In them the intermolecular forces at	
3. In them there are no cross – linkages e.g.	3. In them cross –linkages exist <i>e.g.</i> , <i>bakelite</i> .	
polyethylene, polystyrene.		





Q.31 Explain the differences between polyacrylates and polyesters.

Ans.

Q.32 What is PHBV?

Ans. PHBV stands for *poly* – *hydroxybutyrate* – CO β – *hydroxy valerate*. It is a copolymer of 3 – hydroxbutanoic acid and 3 – hydroxypentanoic acid I nwhich monomer units are connected by ester linkages. It is represented by







EXERCISE-I

UNSOLVED PROBLEMS

- **Q.1** How do you explain the functionality of a monomer?
- **Q.2** Define the term polymerisation.
- **Q.3** Is $-(-NH -CHR -CO -)_n$ a homopolymer or copolymer?
- Q.4 In which classes, the polymers are classified on the basis of molecular forces?
- Q.5Write the monomers used for getting the following polymers?
(i) Polyvinyl chloride(ii) Teflon(iii) Bakelite.
- **Q.6** Write the name and the structure of one of the common initiators used in free radical addition polymerisation.
- **Q.7** How does the presence of double bonds in rubber molecules influence their structure and reactivity?
- **Q.8** Discus the main purpose of vulcanisation of rubber.
- Q.9 What are the monomeric repeating units of Nylon-6 and Nylon-66?
- Q.10Write the names and structures of the monomers of the following polymers:
(i) Buna-S(ii) Buna-N(iii) Docron(iv) Neoprene.
- **Q.11** Identify the monomer in the following polymer structures.



- **Q.12** How is decron obtained from ethylene glycol and terephthalic acid?
- **Q.13** How is bakelite formed? Explain the reactions with equations.
- **Q.14** Waht is Buna-S ? How it is synthesised?
- **Q.15** Differentiate between Nylon-6 and Nylon-66.



E	XERCISE-II BO	DARC	PROBLEMS
Q.1	Write the modes of free radical polymerisation of an alkene.	Q.10	Write the structures of monomers used and use of each of the following polymers:
Q.2	Differentiate between addition and condensation polymer based on mode of		(a) Teflon (b) Buna-N
	polymerisation. Give one example of each type.	Q.11	What are biodegradable polymers ? Give two examples.
Q.3	What is meant by copolymerisation ? Give an example of such a polymer?	Q.12	Draw the structure of the monomer of each of the following polymers (i) Polywinyl chloride (PVC)
Q.4	How is bakelite made and what is its major use? Why is bakelite a thermosetting polymer?		(ii) Nylon-6
Q.5	Differentiate between a homopolymer and a copolymer. Give one example of each type.	Q.13 Q.14	Write the monomers of polythene and teflon. What does the designation '6, 6' mean in the
Q.6	Write the names and structures of monomer used for getting the following polymers:		
	(i) PVC (ii) PMMA	Q.15	Draw the molecular structures of the monomersof(i) PVC(ii) Teflon
Q.7	How are polymers classified on the basis of forces operating between their molecules ? Which of these classes does nylon-6,6 belong?	Q.16	What do '6,6' indicate in the name nylon-6,6?
Q.8	Write the structures of monomers used in the preparation of : (a) Teflon (b) PMMA.	Q.17	Is $(CH_2-CH)_n$ a homopolymer or a copolymer ?
Q.9	(a) How does vulcanisation change the character of natural rubber?(b) Why are the numbers 6,6 and put in the names of nylon-6,6 and nylon-6?	Q.18	Define thermoplastic and thermosetting polymers. Give one example of each. OR What is a biodegradable polymer ? Given an example of a biodegradable alignatic polyecter