

POLYMERS

Topic: 1

CLASSIFICATION OF POLYMERS, TYPES OF POLYMERIZATION TECHNIQUES, RUBBER – NATURAL AND SYNTHETIC

LONG ANSWER QUESTIONS

1. What is polymerisation? Give examples to different kind of polymerization.

Ans: Carothers, Mark and Flory classified the polymers into two categories based on the mechanism of polymerisation.

- a) Addition polymerisation (or) chain growth polymerisation.
- b) Condensation polymerisation (or) step growth polymerisation.

a) **Addition polymerisation:** Addition polymers are formed by the combination of monomers without the elimination of some byproduct molecules.

Alkene, Alkadienes and their derivatives are used as monomer in the formation of addition polymers. Addition polymerisation can take place through the formation of either free radical (or) ions such as carbanions (or) carbocations.

Addition polymerisation reaction is very rapid and takes place in 3 steps (a) chain initiation (b) chain propagation (c) chain termination.

Addition polymerisation divided into 2 types.

- 1) Ionic polymerisation
- 2) free radical polymerisation.

1) Ionic polymerisation: The Addition polymerisation that takes place due to Ionic intermediate is called Ionic Addition polymerisation.

Based on the nature of ions used for the initiation process Ionic polymerisation classified into 2 types

- i) Cationic polymerisation
- ii) Anionic polymerisation

i) **Cataionic polymerisation:** Cationic polymerisation is initiated by an acid (Lewis Acids such as BF_3 , AlCl_3 , FeCl_3 , SnCl_4 , H_2SO_4 , HF in presence of small amount of H_2O).

E.g. Isobutylene – Butyl rubber, polystyrene. Polyvinyl ether

ii) **Anionic polymerisation:** Anionic polymerisation is initiated by anion (may be base (or) nucleophiles such as n-butyl lithium (or) Potassium amide)

Monomer, containing e^- withdrawing groups like phenyl ($-\text{C}_6\text{H}_5$). Nitrile ($-\text{CN}$) etc. undergo anionic addition polymerisation.

E.g. Polystyrene, Poly acylonitrile

b) Condensation polymerisation: Condensation polymers are any kind of polymers formed through a condensation reaction, releasing small molecules as by-products such as water or methanol, as opposed to addition polymers which involve the reaction of unsaturated monomers.

Ex: Types of condensation polymers include polyamides, polyacetals and polyesters

c) Free radical polymerisation: Free radical polymerization is a method of polymerization by which a polymer is formed from the successive addition of free radical building blocks. Free radicals can be formed via a number of different mechanisms usually involving separate initiator molecules. Following creation of free radical monomer units, polymer chains grow rapidly with successive addition of building blocks onto free radical sites.

Ex: Polyethylene and polypropylene are manufactured by this process.

d) Copolymerization: A heteropolymer or copolymer is a polymer derived from two (or more) monomeric species, as opposed to a homopolymer where only one monomer is used. Copolymerization refers to methods used to chemically synthesize a copolymer.

Ex: Commercially relevant copolymers include ABS plastic, SBR, Nitrile rubber, styrene-acrylonitrile, styrene-isoprene-styrene (SIS) and ethylene-vinyl acetate.

2. Write a note on condensation polymerization and addition polymerization.

a) Condensation polymerization: Condensation polymerization, a form of step-growth polymerization, is a process by which two molecules join together, resulting loss of small molecules which is often water. The type of end product resulting from a condensation polymerization is dependent on the number of functional end groups of the monomer which can react.

Monomers with only one reactive group terminate a growing chain, and thus give end products with a lower molecular weight. Linear polymers are created using monomers with two reactive end groups and monomers with more than two end groups give three dimensional polymers which are cross linked.

Polyester is created through ester linkages between monomers, which involve the functional groups carboxyl and hydroxyl (an organic acid and an alcohol monomer).

Nylon is another common condensation polymer. It can be manufactured by reacting di-amines with carboxyl derivatives. In this example the derivative is a di-carboxylic acid, but di-acyl chlorides are also used. Another approach used is the reaction of di-functional monomers, with one amine and one carboxylic acid group on the same molecule:



General chemical structure of one type of condensation polymer

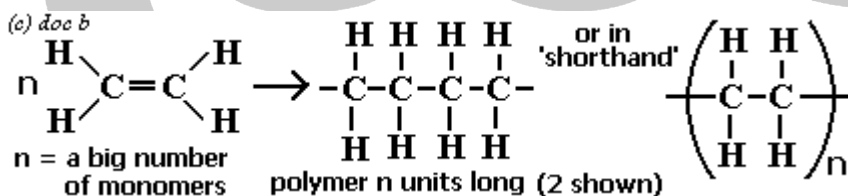
The carboxylic acids and amines link to form peptide bonds, also known as amide groups. Proteins are condensation polymers made from amino acid monomers. Carbohydrates are also condensation polymers made from sugar monomers such as glucose and galactose. Condensation polymers, unlike addition polymers, may be biodegradable. The peptide or ester bonds between monomers can be hydrolysed by acid catalysts or bacterial enzymes breaking the polymer chain into smaller pieces.

Ex: The most commonly known condensation polymers are proteins, fabrics such as nylon, silk, or polyester.

b) **Addition Polymerisation: Chain growth polymerization** is a polymerization technique where unsaturated monomer molecules add on to a growing polymer chain one at a time. It can be represented with the chemical equation:



where n is the degree of polymerization.



"Chain growth polymerization" and **addition polymerization** (also called **polyaddition**) are two different concepts. In fact polyurethane polymerizes with addition polymerization (because its polymerization does not produce any small molecules, called "condensate"), but its reaction mechanism is a step-growth polymerization.

3. Discuss the structure of natural rubber.

Ans: Natural rubber, also called **China rubber** or **caoutchouc**, is an elastomer (an elastic hydrocarbon polymer) that was originally derived from latex, a milky colloid produced by some plants. The plants would be 'tapped', that is, an incision made into the bark of the tree and the sticky, milk colored latex sap collected and refined into a usable rubber. The purified form of natural rubber is the chemical poly isoprene, which can also be produced synthetically. Natural rubber is used extensively in many

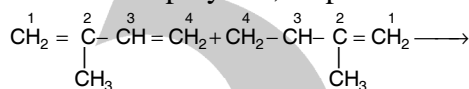
applications and products, as is synthetic rubber. It is normally very stretchy and flexible and extremely waterproof.

- **Natural rubber:** Rubber is a naturally occurring polymer. It is obtained as latex from rubber tree, shrubs and vines.
- Latex is a emulsion of polyhydrocarbon droplets in a aq. solution. Latex contain 35% rubber.
- Rubber present in latex is coagulated by the addition of CH_3COOH (or) HCOOH
- Rubber trees are found in India, Malaysia, Indonesia, Ceylon, South America.
- **Structure rubber:** E.F of rubber C_5H_8
- On strong heating it gives CO_2 , H_2O , SO it contains C, H.

- When heated in absence of air (or) O_2 gives isoprene $(\text{CH}_2 = \underset{\text{CH}_3}{\overset{\text{CH}_2}{\text{C}}} - \text{CH})$. So natural

rubber is the polymer of isoprene.

- It is a linear polymer, isoprene unit are joined head to – tail by 1, 4 links.



- $-(\text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{C}}{=}} \text{CH} - \text{CH}_2 - \text{CH}_2 - \underset{\text{CH}_2}{\overset{\text{CH}}{=}} \text{C} - \text{CH}_3)_n$
- X-ray studies indicate that in natural rubber isoprene units are arranged in cis form
- It contain 11,000 to 20,000 isoprene units with molecular wt. 13,0000 to 34,0000

4. How are polymers classified?

Ans: CLASSIFICATION OF POLYMERS:

- Polymers are classified in a number of ways as
 - 1) Classification based on source of availability.
 - 2) Classification based upon structure.
 - 3) Classification based upon molecular forces.
 - 4) Classification based upon mode of synthesis.

1) Based on the source the polymers again classified as

a) Natural polymers b) synthetic polymers

a) Natural polymers: The polymers obtained from nature (plants and animals) are called Natural polymers. Ex. Starch, cellulose, Natural rubbers, proteins, Nucleic acid (DNA, RNA), cotton, silk, wool)

b) Synthetic Polymers: The polymers which are prepared in the laboratories are called synthetic polymers

E.g. Polyethylene, polyvinylchloride (pvc), Nylon, Teflon, Bakelite, Terylene etc.

2) Based on the structure polymers are classified as (a) linear polymer (b) Branched chain polymer (c) cross-linked polymer

a) Linear polymer : In linear polymer the monomeric units are linked together to form linear chain.

E.g. Polyethylene, Nylon, polyester etc.

b) Branched chain polymer : In branched chain polymers the monomeric units are joined to form long chains with side chains (or) Branches of different length. E.g. Glycogen, starch, L.D.P.E. etc.

c) cross-linked polymer: In cross linked polymers the monomer units are cross linked together to form a three dimensional Network. E.g. Bakelite, melamine-formaldehyde Resin polystyrene-Butadiene.

3) Based on the molecular forces polymers are classified as a) Thermoplastic b) Thermosetting
c) Elastomers d) Fibres

a) Thermoplastics: Thermoplastics are the polymers which soften on heating and harden on cooling reversibly.

E.g. Polyethylene, polystyrene, pvc, Teflon, Nylon, sealing wax.

b) Thermosetting: Thermosetting plastics are the polymers which undergo permanent change on heating (irreversible)

E.g. Bakelite, Polyester, Polysiloxanes.

c) Elastomers : Elastomers are the polymers which possess elastic character.

E.g. Natural rubber

d) Fibres : Fibres are polymers in which the chains are held by intermolecular forces like H-bond, Dipole-dipole interaction.

E.g. Nylon, poly Acrylonitrile

4) Based on the mode of synthesis polymer are classified as

a) Addition polymers b) condensation polymers

a) Addition polymers: A polymer formed by direct addition of repeated monomer without the elimination of by product molecules are called Addition polymer.

E.g. Polyethylene, polypropylene, pvc, Teflon, orlon, Neoprene, pvp (polyvinyl pyrolidone)

b) Condensation polymers: A polymer formed by the condensation of two (or) more monomers with the elimination of simple molecule like H₂O, NH₃, HCl, alcohol etc. are called condensation polymer.

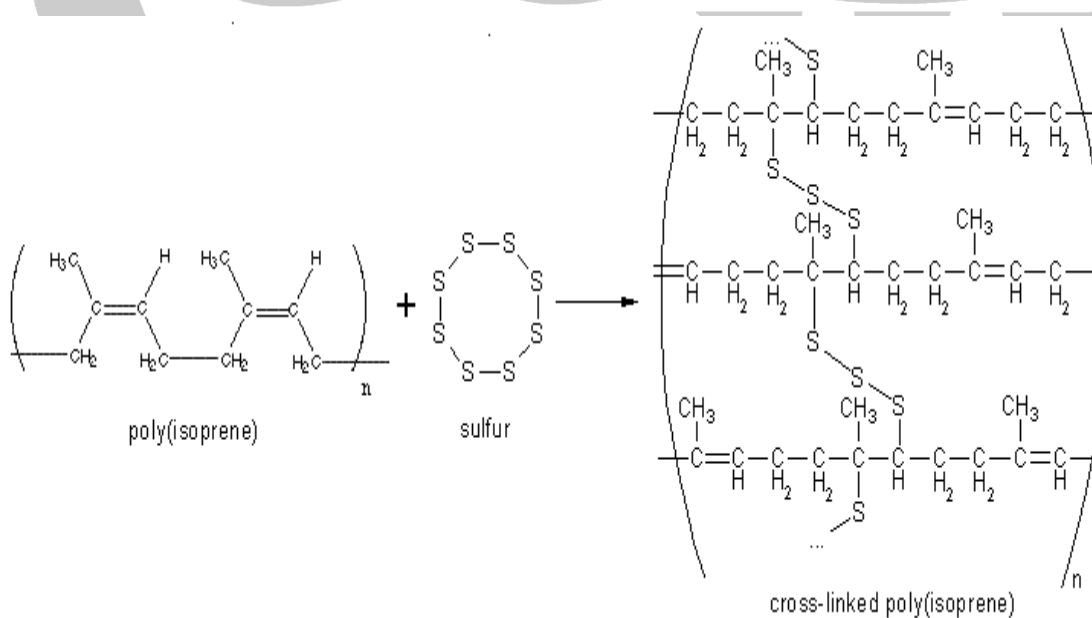
E.g. Terylene, Bakelite, Alkyl Resin, Nylon 6, 6.

Leather, cellulose, Rayon etc. are the example of organic polymer and Glass (Silicone rubber) is the example of inorganic polymers.

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

Ans: Uncured natural rubber is sticky, deforms easily when warm, and is brittle when cold. In this state, it is a poor material when a high level of elasticity is required. The reason for inelastic deformation of un-vulcanized rubber can be found in its chemical structure: rubber is composed of long polymer chains. These chains can move independently relative to each other, which lets the material change shape. Natural rubber contains double bonds which provide reactive sites for cross linking when reacted with sulfur. The CH₂ groups present after double bond are called allyl groups which are very reactive and participate in cross linking process.

Crosslinking introduced by vulcanization prevents the polymer chains from moving independently. As a result, when stress is applied the vulcanized rubber deforms, but upon release of the stress, the article reverts to its original shape.



Vulcanized material is less sticky and has superior mechanical properties. A vast array of products is made with vulcanized rubber including tires, shoe soles, hoses, and hockey pucks. The process is named after Vulcan, Roman god of fire..

6. Write the modes of anionic and cationic polymerisations.

Ans: Addition polymerisation divided into 2 types.

- a) Ionic polymerisation
- b) Free radical polymerisation.

Ionic polymerisation:

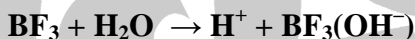
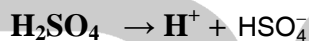
The Addition polymerisation that takes place due to Ionic intermediate is called Ionic Addition polymerisation.

Based on the nature of ions used for the initiation process Ionic polymerisation classified into 2 types

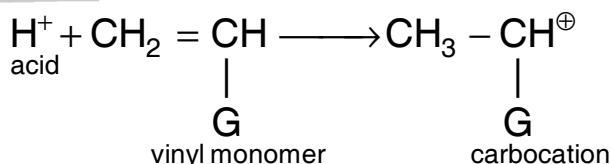
- a) Cationic polymerisation
- b) Anionic polymerisation

a) Cationic polymerisation: Cationic polymerisation is initiated by an acid (Lewis acids such as BF_3 , AlCl_3 , FeCl_3 , SnCl_4 , H_2SO_4 , HF in presence of small amount of H_2O).

E.g. Isobutylene – Butyl rubber, polystyrene. Polyvinyl ether.

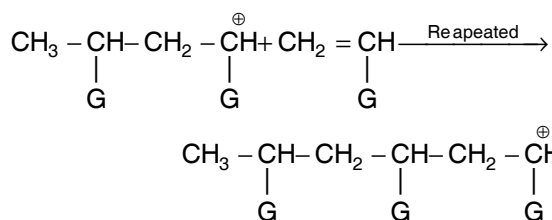
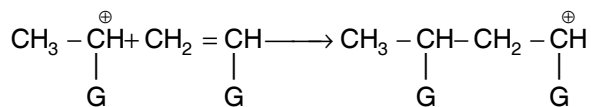


1) Chain initiation: Proton (H^+) add to C – C double bond of alkene to form stable carbocation.

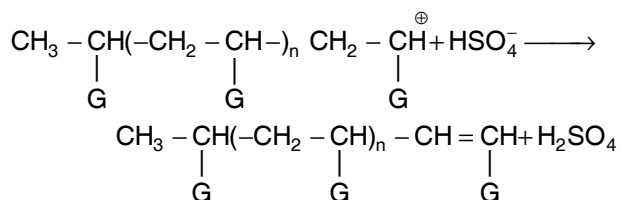


(G = e^- donating group, + I effect)

2) Chain propagation: Carbocation add to the C – C double bond of another monomer molecule to form new carbocation.



3) Termination: Reaction is terminated by combination of carbocation with negative ion (or) by loss of proton

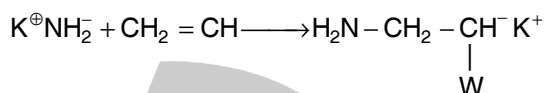


b) Anionic Polymerization: Anionic polymerisation is initiated by anion (may be base (or) nucleophiles such as n-butyl lithium (or) Potassium amide)

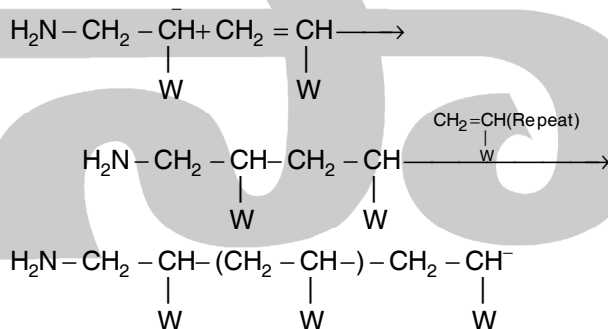
Monomer, containing e^- withdrawing groups like phenyl ($-\text{C}_6\text{H}_5$). Nitrile ($-\text{CN}$) etc. undergo anionic addition polymerisation.

E.g. Polystyrene, Poly acrylonitrile

1) Chain initiation:



2) Chain propagation:

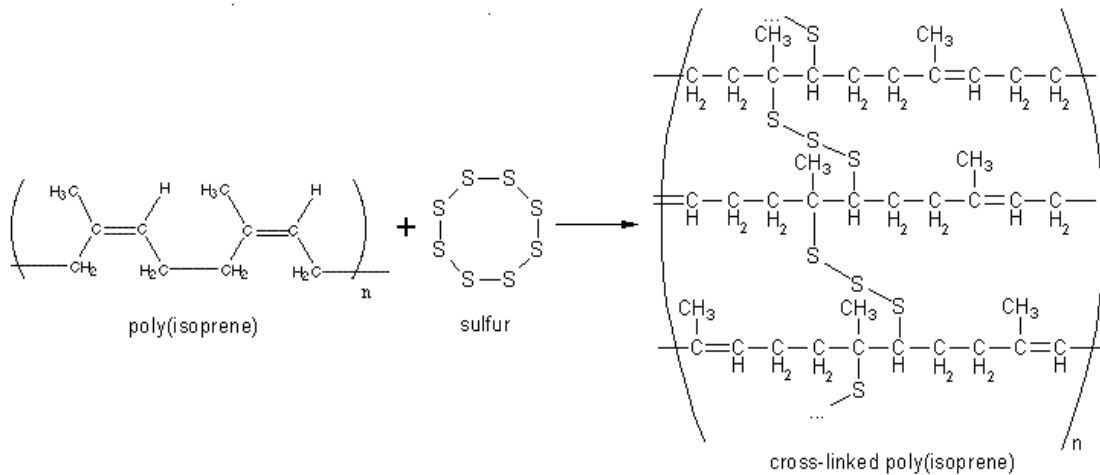


Anionic polymerisation has no chain termination reaction.

7. What is vulcanization? Write the consequences of vulcanisation of rubber.

Ans: Vulcanization or **vulcanization** is a chemical process for converting rubber or related polymers into more durable materials via the addition of sulfur or other equivalent "curatives." These additives modify the polymer by forming cross links (bridges) between individual polymer chains. Vulcanized material is less sticky and has superior mechanical properties. A vast array of products are made with vulcanized rubber including tires, shoe soles, hoses, and hockey pucks. The process is named after Vulcan, Roman god of fire. Hard vulcanized rubber is sometimes sold under the brand names ebonite or vulcanite, and is used to make hard articles such as bowling balls and saxophone mouth pieces.

Uncured natural rubber is sticky, deforms easily when warm, and is brittle when cold. In this state, it is a poor material when a high level of elasticity is required. The reason for inelastic deformation of un-vulcanized rubber can be found in its chemical structure: rubber is composed of long polymer chains. These chains can move independently relative to each other, which lets the material change shape. Cross linking introduced by vulcanization prevents the polymer chains from moving independently. As a result, when stress is applied the vulcanized rubber deforms, but upon release of the stress, the article reverts to its original shape.



With natural rubber, large amounts of sulfur, as well as high temperatures and long heating periods are necessary and one obtains an unsatisfactory crosslinking efficiency with unsatisfactory strength and aging properties. Only with vulcanization accelerators can the quality corresponding to today's level of technology be achieved. The multiplicity of vulcanization effects demanded cannot be achieved with one universal substance; a large number of diverse additives, comprising the "cure package," are necessary.

The combined cure package in a typical rubber compound consist of sulfur together with an assortment of compounds that modify the kinetics of crosslinking and stabilize the final product. These additives include accelerators, activators like zinc oxide and stearic acid and antidegradants. The accelerators and activators are catalysts. An additional level of control is achieved by retarding agents that inhibit vulcanization until some optimal time or temperature. Antidegradants are used to prevent degradation of the vulcanized product by heat, oxygen and ozone.

SHORT ANSWER QUESTIONS

1. Explain what synthetic polymers are.

Ans: Synthetic Rubber: Synthetic polymers are either homopolymer of 1,3 butadiene (or) copolymer in which one of the monomer is 1,3 butadiene (or) it derivative. It undergoes vulcanisation like natural rubber.

Some common examples of synthetic rubber. Neoprene, styrene-butadiene rubber (SBR), silicones, polyurethane rubber etc.

2. How are polymer classified based on molecular forces?

Ans: Based on the molecular forces polymers are classified as a) Thermoplastic b) Thermosetting

c) Elastomers d) Fibres

a) Thermoplastics: Thermoplastics are the polymers which soften on heating and harden on cooling reversibly.

E.g. Polyethylene, polystyrene, pvc, Teflon, Nylon, sealing wax.

b) Thermosetting: Thermosetting plastics are the polymers which undergo permanent change on heating(irreversible)

E.g. Bakelite, Polyester, Polysiloxanes.

c) Elastomers : Elastomers are the polymers which possess elastic character.

E.g. Natural rubber

d) Fibres : Fibres are polymers in which the chains are held by intermolecular forces like H-bond, Dipole-dipole interaction.

E.g. Nylon, poly Acrylonitrile

3. How are polymers are Classified Based on Structure of Polymers?

1. Linear polymers

These polymers consist of long and straight chains. The examples are high density polythene, polyvinyl chloride, etc.

2. Branched chain polymers

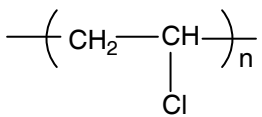
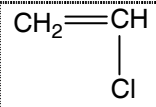
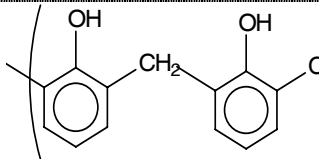
These polymers contain linear chains having some branches, e.g., low density polythene.

3. Cross linked or Network polymers

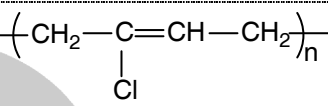
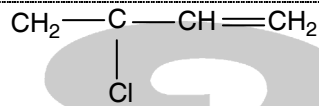
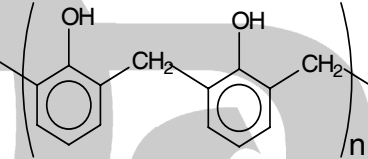
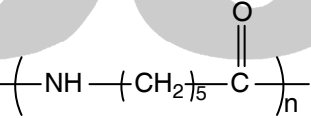
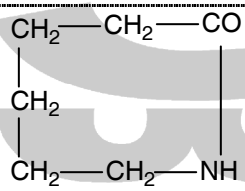
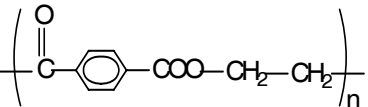
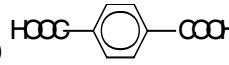
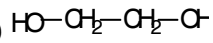
These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains. Eg: Bakelite, melamine, etc.

4. Mention the type of polymerisation involved in the formation of the following polymers – a) Bakelite b) PVC c) Polyethene.

S.NO.	Name of polymer	Structure	Monomer	Type of polymerisation
1.	Polythene	$\left(\text{CH}_2-\text{CH}_2\right)_n$	$\text{CH}_2=\text{CH}_2$ (ethylene)	Cationic addition polymerisation

2.	Polyvinyl chloride(PVC)		 Vinyl chloride	Manufacture raincoats, hand bags, cheap plastic for cable insulation
3.	Bakelite		C ₆ H ₅ OH (phenol) HCHO (formaldehyde)	For making gears protective coating and electrical fitting

5. Mention the structures and name of the monomers used in preparing the following polymers – a) Bakelite b) Nylon c) Terylene d) Neoprene.

S.NO.	Name of polymer	Structure	Monomer
1.	Neoprene		
2.	Bakelite		C ₆ H ₅ OH (phenol) HCHO (formaldehyde)
3.	Nylon-6 (or) Perlon L		
4.	Polyethylene Terephthalate (PET) (or) Terylene (or) Dacron		1)  2) 

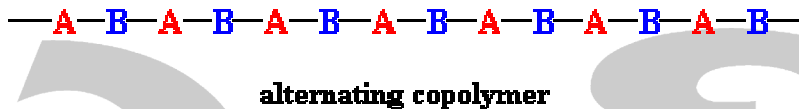
VERY SHORT ANSWER QUESTIONS

1. What is homopolymer and copolymer?

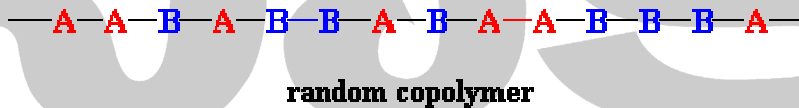
Ans: Homopolymer: A polymer resulting from the polymerization of a single monomer; a polymer consisting substantially of a single type of repeating unit.

Copolymer: When a polymer is made by linking only one type of small molecule, or monomer, together, it is called a homopolymer. When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer. Let's imagine now two monomers, which we'll call *A* and *B*. *A* and *B* can be made into a copolymer in many different ways.

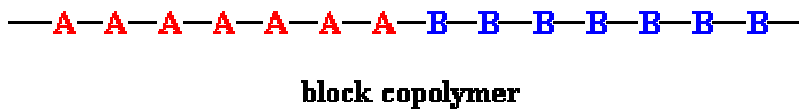
When the two monomers are arranged in an alternating fashion, the polymer is called, of course, an alternating copolymer:



In a random copolymer, the two monomers may follow in any order:



In a block copolymer, all of one type of monomer are grouped together, and all of the other are grouped together. A block copolymer can be thought of as two homopolymers joined together at the ends:

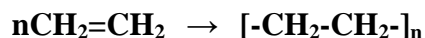


2. What is a polymer?

Ans: Polymers are defined as high molecular mass **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 and are linked to each other by covalent bonds

3. What is polymerisation?

Ans: This process of formation of polymers from respective monomers is called **polymerisation**. The transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon 6, 6 are examples of two different types of polymerization reactions.



4. What are natural polymers?

Ans: Natural polymers: These polymers are found in plants and animals.

Examples are proteins, cellulose, starch, resins and rubber.

5. What are semi-synthetic polymers?

Ans: Semi-synthetic polymers: Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the usual examples of this sub category.

6. What are synthetic polymers?

Ans: Synthetic polymers: Polymers made by man in laboratory.

A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna - S) are examples of manmade polymers extensively used in daily life as well as in industry.

7. What are elastomers?

Ans: 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 ‘crosslinks’ 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.

8. What are fibres?

Ans: 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.

9. What are thermoplastics?

Ans: 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 fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

10. What are thermosetting polymers?

- **Ans: Thermosetting Polymers:** These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite,

నాస్తి