Chapter-15

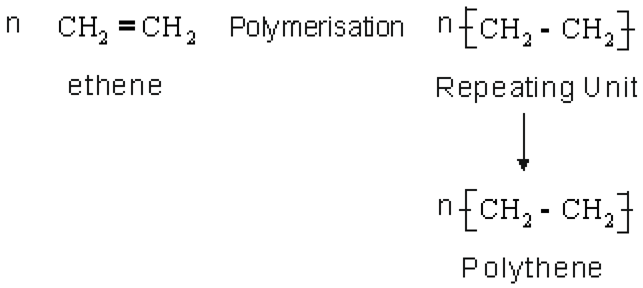
Polymer

LECTURE 01

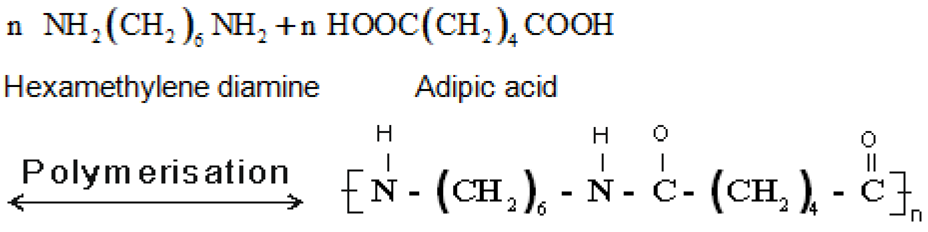
Polymerization the process by which many molecular join together to form a long chain compound (giant molecule) of high molecular mass is called polymerization. The long-chain compound is called polymer is the simple compound from which it is formed is called a monomer.

Examples :

01. Transformation of ethene to polythene :



$$n\ CH_2=CH_2 \xrightarrow{\text{Polymerisation}} n\{CH_2-CH_2\} \rightarrow n\{CH_2-CH_2\}$$



$$n\ NH_2(CH_2)_6NH_2 + n\ HOOC(CH_2)_4COOH \xleftrightarrow{\text{Polymerisation}} \left[\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{C}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n$$

Nylon-6,6

Classification of polymers:

Polymers can be classified in several ways.

- Classification based on source
- Classification is based on structure.
- Classification is based on the making of polymerization.
- Classification is based on molecular forces.
- Classification is based on a growth polymerization.

Classification based on the source.

Source :

- ❖ Natural polymers
- ❖ Semi-synthetic polymers
- ❖ Synthetic polymers

a) Natural Polymers: These polymers are found in plants and animals.

Example: Proteins, Cellulose, starch, rubber.

b) Semi-Synthetic polymers

Example: Cellulose derivatives as cellulose acetate (rayon), cell-lose nitrate.

c) Synthetic polymers (Man-made polymers)

Example: Plastic (Polythene), synthetic fibers (nylon6,6) synthetic rubbers (Buna-5)

Classification based on structures:

Structure :

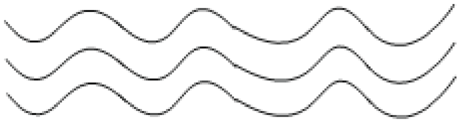
- ❖ Linear Polymers
- ❖ Branched-chain polymers
- ❖ Cross-linked or Network polymers

a) Linear polymers: These polymers consist of long and straight chains.

Examples: High-Density polythene (HDPE)

Polyvinyl chloride (PVC)

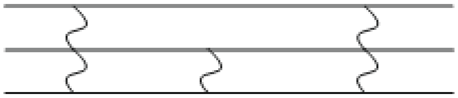
These are represented as:



b) Branched-chain polymers: These polymers contain linear chains having some branches.

Example: Low-density polythene (LDPE)

These are represented as :

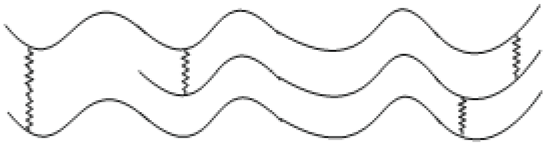


c) Cross-linked: Network Polymers.

These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains.

Examples: Bakelite, melamine

These are represented as:



Classification is based on the mode of polymerization.

Mode of Polymerisation :

- Addition polymers
- Condensation polymers

Addition polymers: These are formed by the repeated addition of monomer molecules containing double or triple bonds.

These are of two types :

(i) Homopolymers

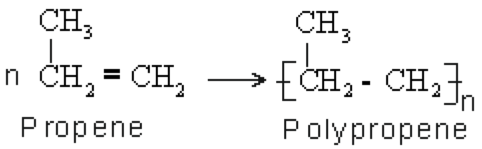
(ii) Copolymers

Homopolymers: These are the polymers formed by the polymerization of a single monomeric species.

Examples: Polythene, polypropylene

$$n\ CH_2 = CH_2 \longrightarrow \left[CH_2 - CH_2\right]_n$$

Ethene Polythene



$$n\ \overset{\overset{\displaystyle CH_3}{|}}{C}H_2 = CH_2 \longrightarrow \left[\overset{\overset{\displaystyle CH_3}{|}}{C}H_2 - CH_2\right]_n$$

Propene Polypropene

Copolymers: These are the polymers made by the addition of polymerization from two different monomers.

Classification is based on the mode of polymerization.

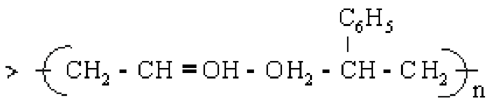
Mode of Polymerisation: (I) Addition polymers

(II) Condensation polymers

Addition polymers: These are formed by the repeated addition of monomer molecules containing double or triple bonds. These are the polymers made by the addition of polymerization from two different monomers.

$$n\ CH_2 = CH - CH = CH_2 + n\ C_6H_5 - CH = CH_2$$

Buta-1,3-diene styrene



$$> \left(CH_2 - CH = OH - OH_2 - \overset{\overset{\displaystyle C_6H_5}{|}}{CH} - CH_2 \right)_n$$

Butadiene-styrene copolymer(Buna-5)

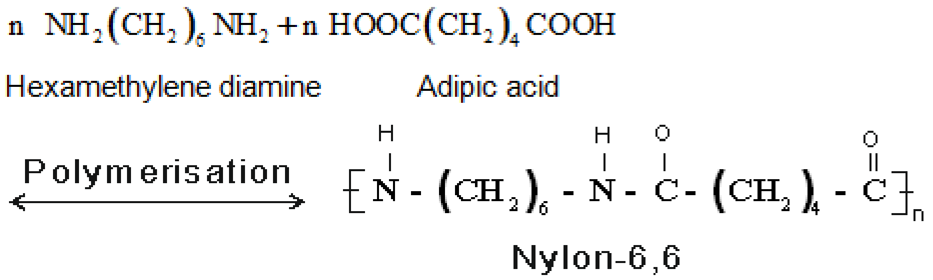
$$n\ CH_2 = CH - CH = CH_2 + n\ CH_2 = \overset{\overset{\displaystyle CN}{|}}{CH} \xrightarrow{\text{Copolymerisation}} \left(CH_2 - CH = CH - CH_2 - CH_2 - \overset{\overset{\displaystyle CN}{|}}{CH} \right)_n$$

Buta-1,3-diene Acrylonitile Buna-N

Condensation polymers:

These are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units with the elimination of small molecules such as water, alcohol & hydrogen chloride, etc.

Example: Terylene (Dacron), Nylon 6, 6, Nylon 6.



$$n\ NH_2(CH_2)_6NH_2 + n\ HOOC(CH_2)_4COOH \xrightarrow{\text{Polymerisation}} \left[\overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} \right]_n$$

Classification based on molecular forces :

Based on the magnitude of intermolecular forces, these polymers are classified into the following four subgroups.

Molecular forces : (I) Elastomers
(III) Fibers
(IV) Thermoplastic polymers
(V) Thermosetting polymers

Elastomers: These are rubber-like solids with elastic properties. The polymer chains are held together by the weakest intermolecular forces. Therefore, the polymers can be stretched. A few cross-links are introduced in between the chains of the polymers.

Example: Buna-S, Buna-N, Neoprene.

Fibers: These are the thread forming solids that possess high tensile strength and high modulus. The polymer chains are held together by strong intermolecular forces, as a result of which there is close packing of chains imparting crystalline nature.

Example: Polyamides (Nylon6,6), polyesters (terylene)

Thermoplastic polymers: These are linear or slightly branched long-chain molecules that soften on heating and harden on cooling. The intermolecular forces are intermediate between elastomers and fibers.

Example: Polythene, Polystyrene, Polyvinyls, etc.

Thermosetting polymers: These polymers are cross-linked which on heating undergo extensive cross-linking in a mould and again become infusible.

Example: Bakelite, urea-formaldehyde resins.

Classification based on growth polymerization:

Growth polymerization: (I) Addition or chain-growth polymerization

(II) Condensation or step-growth polymerization

Addition or chain-growth polymerization:

In this type of polymerization, the molecules of the same monomer or different monomer add together on a large scale to form a polymer. The monomers used are unsaturated compounds. This mode of polymerization leading to an increase in chain length or chain growth can take place through the formation of either free radicals or ionic species. The common-mode is a free radical mechanism.

Free radical mechanism : 3 steps

(I) Chain initiating step

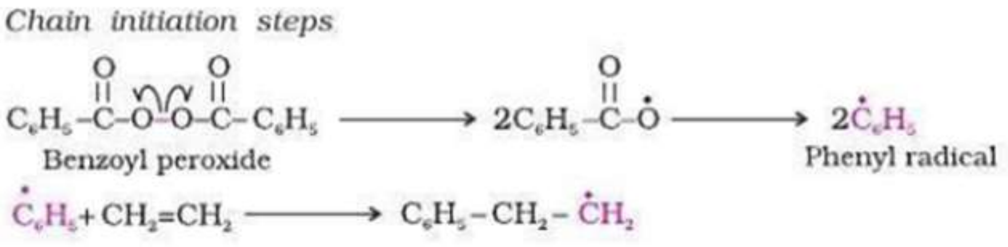
(II) Chain propagating step

(III) Chain terminating step

Consider the polymerization of ethene.

Chain initiating step:

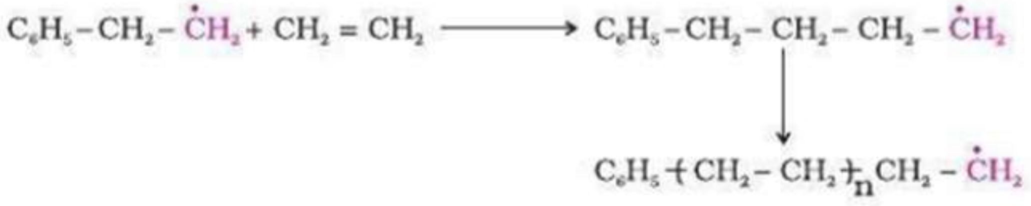
Free radical generating initiator (catalyst) like benzoyl peroxide is used to yield phenyl radicals. Which adds on the ethene double bond generating a new and large free radical?



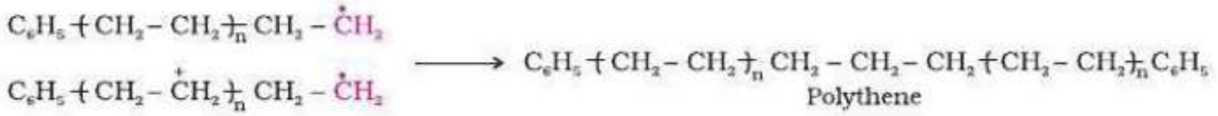
$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{O} \longrightarrow 2\dot{C}_6H_5$$

$$\dot{C}_6H_5 + CH_2=CH_2 \longrightarrow C_6H_5-CH_2-\dot{C}H_2$$

Chain propagating step



Chain terminating step :



Preparation of some important addition polymers :

(a) **Polythene :** (I) High-density polythene (HDPE)

(II) Low-density polythene(LDPE)

Preparation of LDPE

$$n(CH_2{=}CH_2) \xrightarrow[\substack{\text{1000 to 2000 atm}\\ \text{(Traces of oxygen}\\ \text{or a peroxide}\\ \text{initiator)}}]{\text{350 K-570 K}} -[CH_2-CH_2]_n- \atop \text{LDP}$$

LDPE is chemically inert, tough but flexible and a poor conductor of electricity. Therefore, it is used in the insulation of electricity.

Carrying wires and manufacture of squeeze bottles, toys, and flexible pipes.

HDPE Preparation

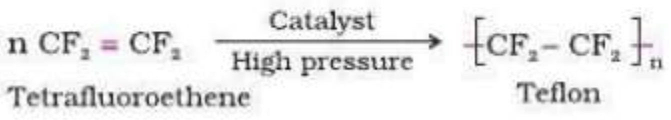
$$n(CH_2{=}CH_2) \xrightarrow[\substack{\text{6-7 atm}\\ \text{(Ziegler Natta}\\ \text{catalyst)}}]{\text{333-343 K}} (CH_2-CH_2)_n$$

It consists of linear molecules and has a high density due to close packing. It is more tough and hard, chemically inert.

It is used for the manufacture of buckets, dust bins, bottles, pipes, etc.

(b) Polytetrafluoro ethane: (Teflon) :

Preparation: It is manufactured by heating tetrafluoro ethane with a free radical or persulphate catalyst at high pressures.



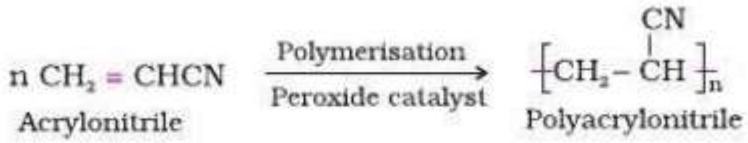
$$n\,CF_2=CF_2 \xrightarrow[\text{High pressure}]{\text{Catalyst}} \left[CF_2-CF_2\right]_n$$

It is chemically inert and resistant inert and resistant to corrosion.

It is used in making oil seals, gaskets, non-stick surface coated utensils.

(c)Polyacrylonitrile(PAN)

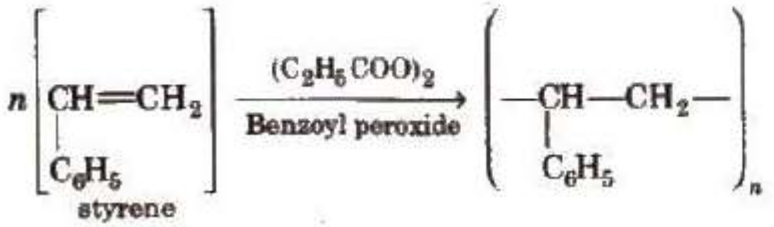
Preparation: It is prepared by the addition polymerization of acrylonitrile in the presence of a peroxide catalyst.



$$n\,CH_2=CHCN \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerisation}} \left[CH_2-\underset{}{\overset{CN}{CH}}\right]_n$$

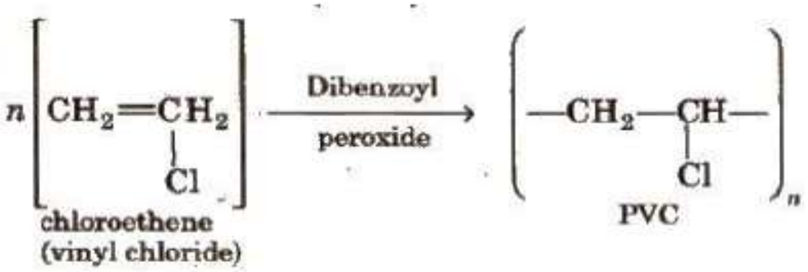
It is used as a substitute for wool in making commercial fibers. These have good resistance to stains, chemicals, insects, and fungi.

Polystyrene (Styrone): The monomers are styrene molecules. It is a thermoplastic. It is used for making toys, radio and TV cabinets



$$n\left[\underset{C_6H_5}{CH}=CH_2\right] \xrightarrow[\text{Benzoyl peroxide}]{(C_6H_5COO)_2} \left(-\underset{C_6H_5}{CH}-CH_2-\right)_n$$

Polyvinylchloride (PVC):



$$n\left[CH_2=\underset{Cl}{CH_2}\right] \xrightarrow[\text{peroxide}]{\text{Dibenzoyl}} \left(-CH_2-\underset{Cl}{CH}-\right)_n$$

LECTURE 02

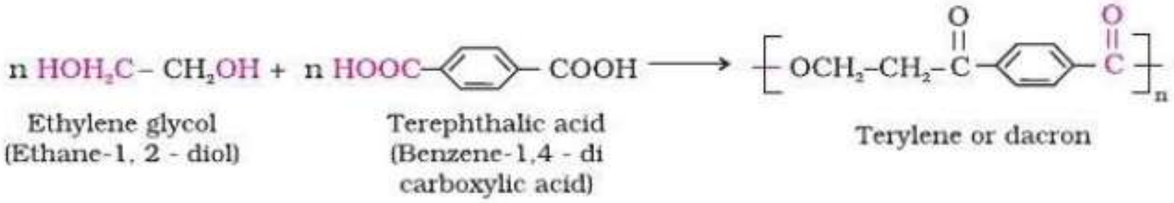
Condensation polymerization of step-growth.

Polymerization:

It involves a repetitive condensation reaction between two bifunctional monomers resulting in the removal of some simple molecules as water, alcohol, etc forming high molecular mass condensation polymers.

Since each step produces a distinct functionalized species and is independent of each other, this process is called step-growth polymerization.

Consider the formation of **Terylene or Dacron** by the polymerization of ethylene glycol is terephthalic acid.

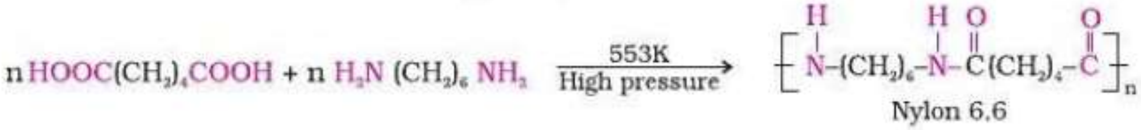


Some important condensation polymers:

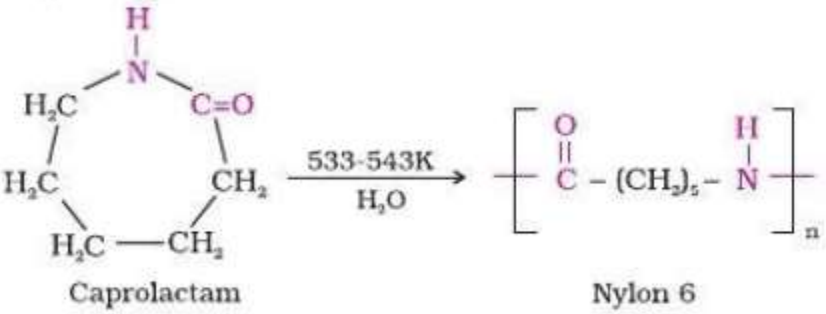
Polyamides: These polymers possess amide linkage. It consists of condensation polymerization of diamines with dicarboxylic acids.

Examples: Nylon 6,6 Nylon 6

Nylon 6,6: It is prepared by the condensation polymerization of hexamethylenediamine with adipic acid under high pressure and at high temperature.



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



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

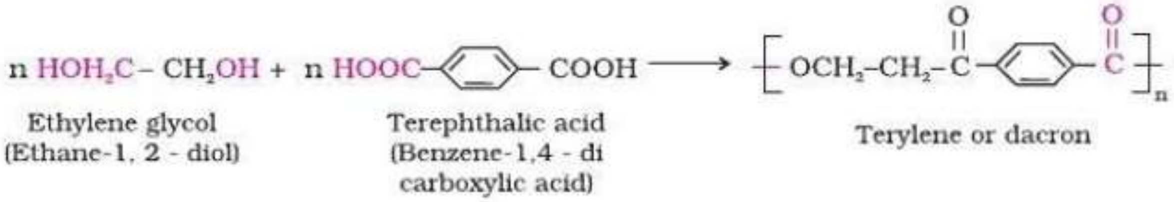
2. Polyesters :

These are the polycondensation products of dicarboxylic acids and diols.

Example: Terylene or Dacron.

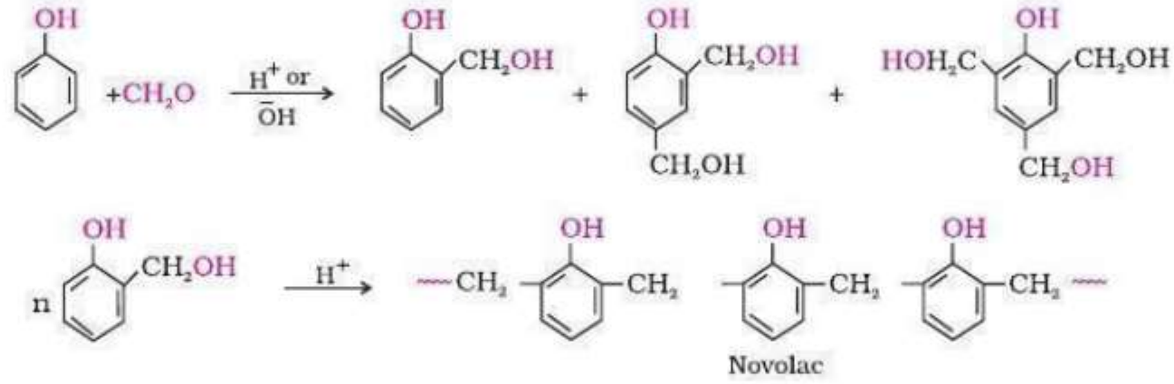
It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460K in the presence of a zinc acetate antimoney trioxide catalyst.

It is used in blending with cotton and wool fibers and glass reinforming materials in safety helmets, etc.



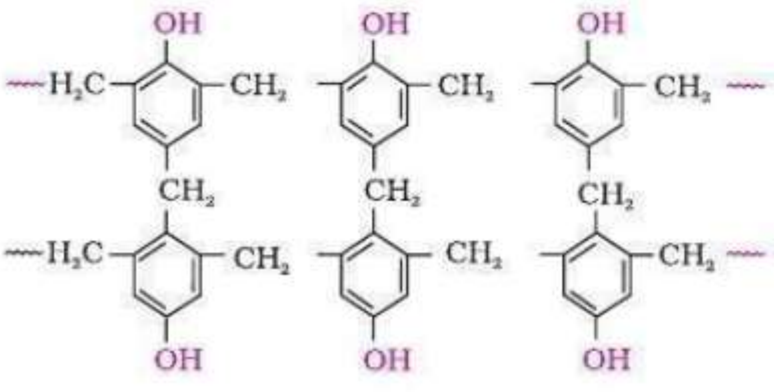
3. Phenol formaldehyde polymer. (Bakelite and related polymers)

These are synthetic polymers obtained by the condensation reaction of phenol with formaldehyde in the presence of acid is base, as a catalyst.



Novolac on heating with Novolac undergoes cross-linkage to form an infusible solid mass called bakelites.

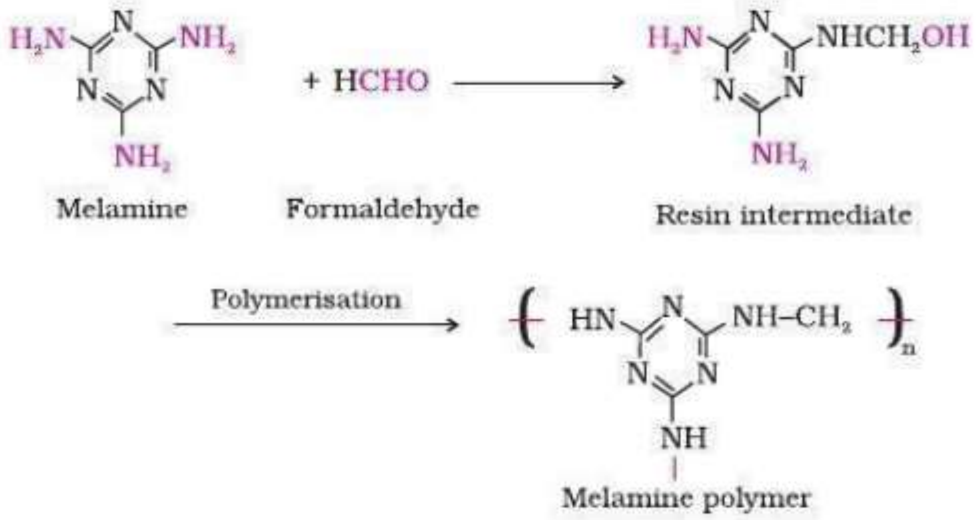
Bakelite is used for making combs, electrical switches, and handles of various utensils.



Bakelite

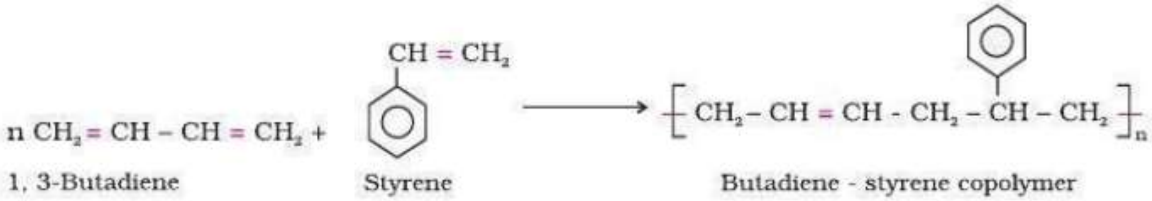
4. Melamine formaldehyde polymer:

It is formed by the condensation polymerization of melamine and formaldehyde.



Copolymerization: In this type of polymerization, a mixture of more than one monomeric species polymerizes to form a copolymer which can be made both by chain-growth polymerization and step-growth polymerization.

Consider the polymerization of a mixture of 1,3-butadiene and styrene.



Their polymer is quite tough and is a good substitute natural rubber. It is used for the manufacture of auto tyres, floor tiles, footwear components, cable insulation, etc.

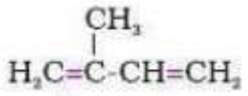
Rubber: It is of two types.

(a) Natural Rubber

(b) Synthetic Rubber

(a) **Natural Rubber:** It is manufactured from rubber later which is a colloidal dispersion of rubber in water. This ladder is obtained from the bark of the rubber tree.

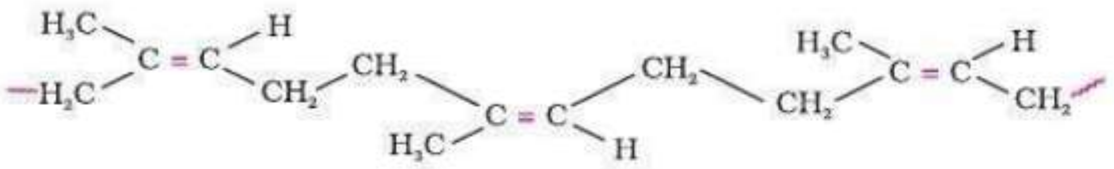
It is a linear polymer of isoprene. (2-Methyl buta-1,3-diene)



$$H_2C=\overset{CH_3}{\overset{|}{C}}-CH=CH_2$$

Isoprene

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



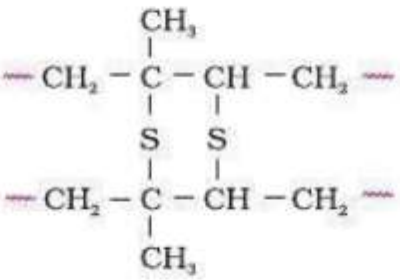
Natural rubber

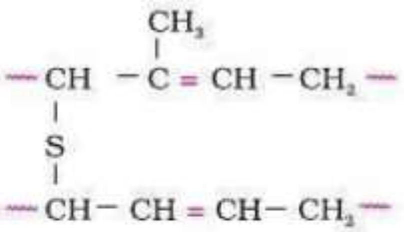
Vulcanization of Rubber: Natural rubber becomes soft at high temperature (>335K) and brittle at low temperature (<283k). It has high water absorption capacity, solute in non-polar solvents, and not resistant to oxidizing agents. To improve upon these physical properties, the vulcanisation process is carried out.

It is the process of heating the row rubber with sulphur at about 373 K to 415 K.

On vulcanization, sulphur forms cross-link at the reactive sites of double bonds as a result of which the rubber gets stiffened. In the manufacture of tyre rubber, 5% of sulphur is used as a cross-linking agent.

Structures of vulcanized rubber:



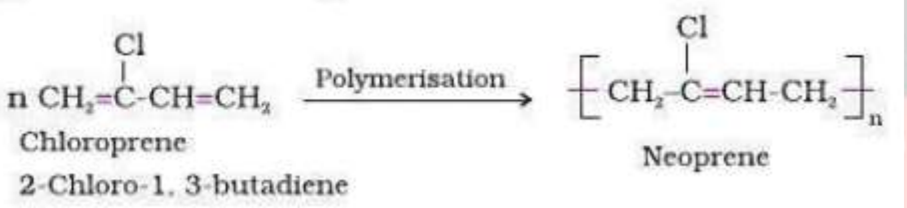


(b) **Synthetic Rubber:** These are capable of stretching twice their length and return to their original shape and size when the external stretching force is released. These can be both homopolymers and copolymers.

Preparation:

Neoprene: (Polychloroprene)

It is formed by the free radical polymerization of chloroprene.



$$n\,CH_2{=}\overset{\overset{\large Cl}{|}}{C}{-}CH{=}CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2{-}\overset{\overset{\large Cl}{|}}{C}{=}CH{-}CH_2\right]_n$$

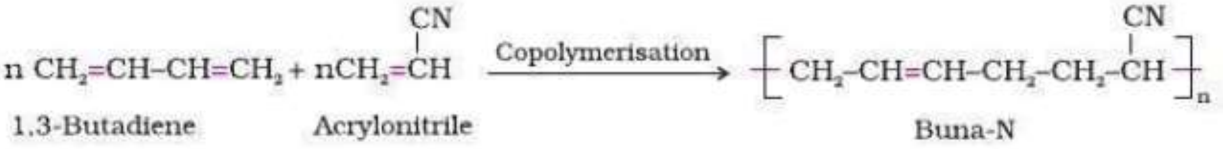
Chloroprene

2-Chloro-1, 3-butadiene

Neoprene

It is used for the manufacture of conveyor belts, gaskets, and hoses.

Buna-N: It is obtained by the copolymerization of 1,3-butadiene and acrylonitrile in the presence of a peroxide catalyst.



$$n\,CH_2{=}CH{-}CH{=}CH_2 + n\,CH_2{=}\overset{\overset{\large CN}{|}}{CH} \xrightarrow{\text{Copolymerisation}} \left[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{\large CN}{|}}{CH}\right]_n$$

1,3-Butadiene

Acrylonitrile

Buna-N

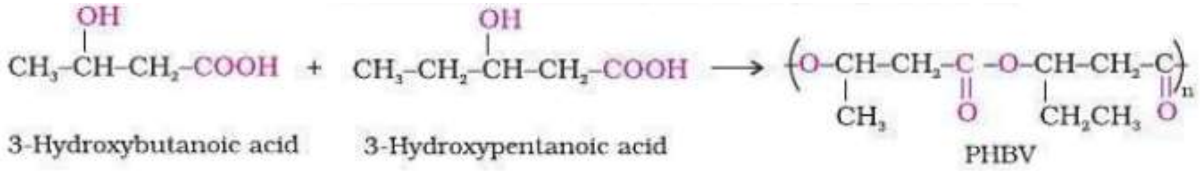
It is resistant to the action of petrol, lubricating oil, and organic solutions.

It is used in making oil seals, tank lining, etc.

Biodegradable polymers:

Examples: Poly b-hydroxybutyrate-co-p-hydroxy valerate (PHBV), Nylon2-nylon6.

PHBV: It is obtained by the copolymerization of 3-hydroxy butanoic acid and 3-hydroxy pentaoxide acid.



$$CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-COOH + CH_3-CH_2-\overset{OH}{\overset{|}{C}}H-CH_2-COOH \longrightarrow \left(O-\underset{CH_3}{\underset{|}{C}}H-CH_2-\underset{O}{\underset{\|}{C}}-O-\underset{CH_2CH_3}{\underset{|}{C}}H-CH_2-\underset{O}{\underset{\|}{C}} \right)_n$$

It is used in special packaging, orthopedic devices, and in the controlled release of drugs.

Nylong-2-nylon 6: It is a copolymer of glycine and aminocaproic acid.

Answer the following questions:

Q.1

Is $-\!\!\!\!\left[CH_2-CH(C_6H_5) \right]\!\!\!\!-_n$ a homopolymer or a copolymer?

Q.2

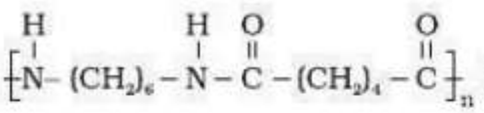
What are polymers ?

How are polymers classified on the basis of structure?

Q.3

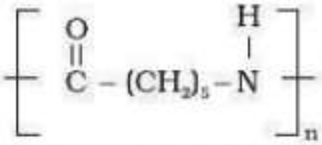
Write the names of monomers of the following polymers:

(i)



$$\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_n$$

(ii)



$$\left[\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}} \right]_n$$

(iii) $\left[CF_2-CF_2 \right]_n$

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

Q.4

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

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

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

(ii) Nylon 6, Neoprene, Polyvinyl chloride.

5. Explain the terms polymer and monomer.

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

7. Distinguish between the terms homopolymer and copolymer and give an example of each.

8. Determine the groups where the polymers are graded according to molecular forces?

9. Explain the term copolymerization and give two examples.

10. Write the free radical mechanism for the polymerization of ethene.

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

12. Write the name and structure of one of the common initiators used in free radical addition polymerization.

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

14. Discuss the main purpose of the vulcanisation of rubber.

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

16. Write the names and structures of the monomers of the following polymers: (i) Buna-S (ii) Buna-N (iii) Dacron (iv) Neoprene

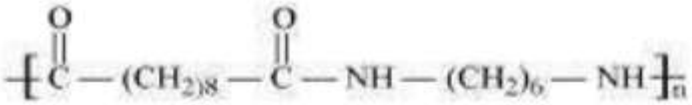
17. How is dacron obtained from ethylene glycol and terephthalic acid?

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

19. Write the monomers used for getting the following polymers. (i) Polyvinyl chloride (ii) Teflon (iii) Bakelite

20. Identify the monomer in the following polymeric structures.

(i)



$$\left[\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-NH \right]_n$$

(ii)