



POLYMERS

Classification of polymers

- **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. are the usual examples of this sub category.

- **3. Synthetic polymers**

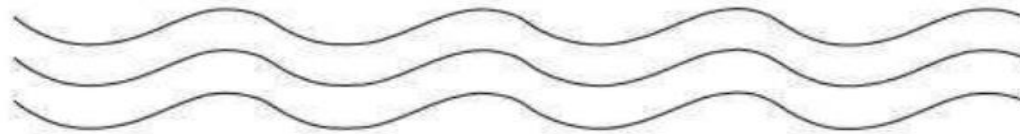
A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna – S) are examples of man-made polymers extensively used in daily life as well as in industry.

There are three different types based on the structure of the polymers.

Structural polymers

- **1. Linear polymers on Structure**

- These polymers consist of long and straight chains. The examples of Polymers are high density polythene, polyvinyl chloride, etc. These are represented as:



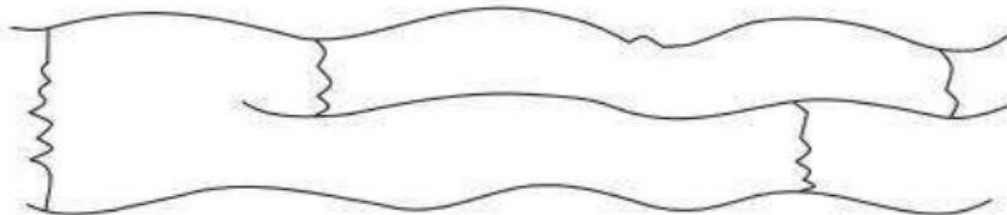
- **2. Branched chain polymers**

- These polymers contain linear chains having some branches, e.g., low density polythene. These are depicted as follows:



- **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, e.g. bakelite, melamine, etc. These polymers are depicted as follows:



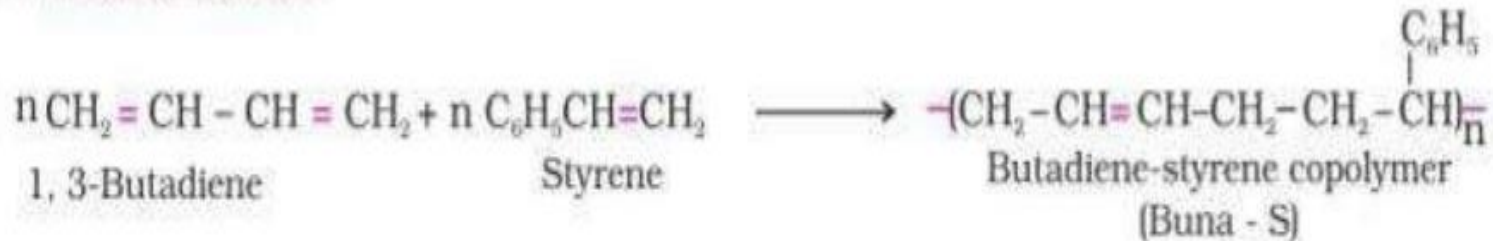
Addition polymers

- Addition polymers are formed from repeated units of monomer units possessing double and triple bonds.
- Polymers formed by addition of two different polymers are called co-polymers

Eg:-

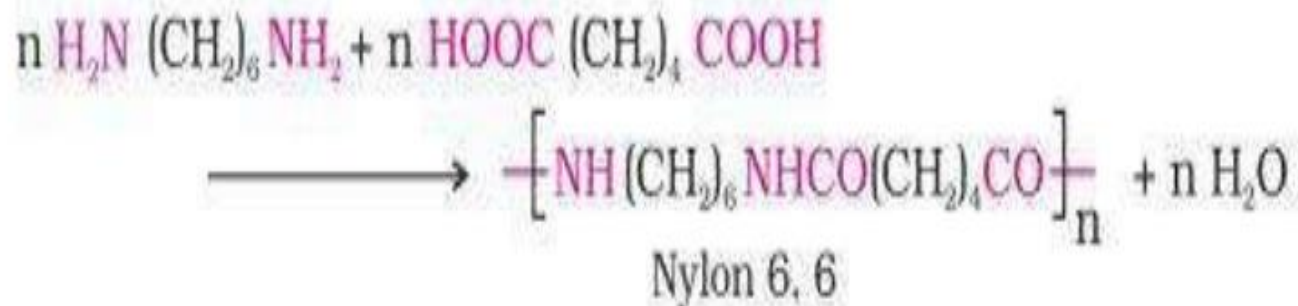


The polymers made by addition polymerisation from two different monomers are termed as copolymers
e.g., Buna-S, Buna-N, etc.



Condensation polymers

- The condensation polymers are formed by repeated condensation reaction between two different bi-functional 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.

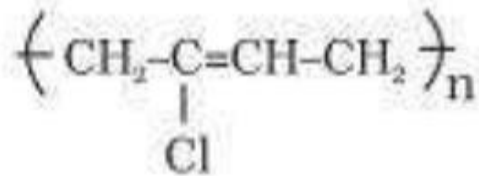


Classification of polymers based on molecular forces

- A large number of polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forces, e.g., van der Waals forces and hydrogen bonds, present in the polymer.
- These forces also bind the polymer chains. Under this category, the polymers are classified into the following four sub groups on the basis of magnitude of intermolecular forces present in them.

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.



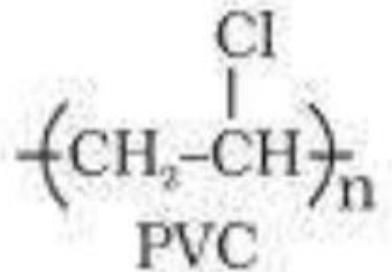
Neoprene

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.

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.



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, urea-formaldelyde resins, etc.



Classification based on growth polymers

- There are 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

- In this type of polymerisation, the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds, e.g., alkenes, alkadienes and their derivatives. 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.
- **Free radical mechanism:-**

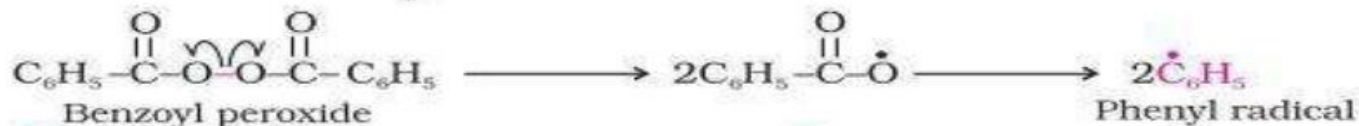
The polymerisation of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator.

The process starts with the addition of phenyl free radical formed by the peroxide to the ethene double bond thus generating a new and larger free radical.

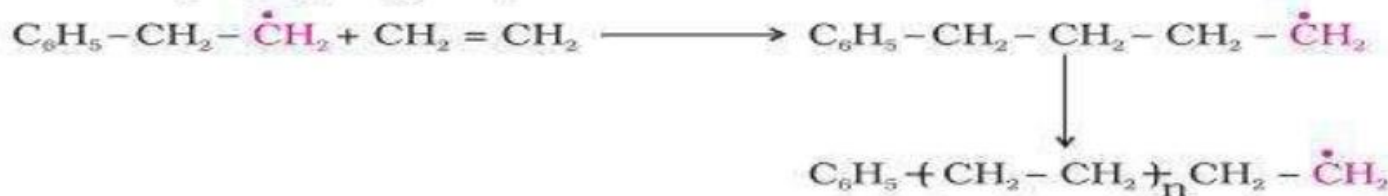
This step is called **chain initiating step**.

As this radical reacts with another molecule of ethene, another bigger sized radical is formed.

The repetition of this sequence with new and bigger radicals carries the reaction forward and the step is termed as chain propagating step. Ultimately, at some stage the product radical thus formed reacts with another radical to form the polymerised product.

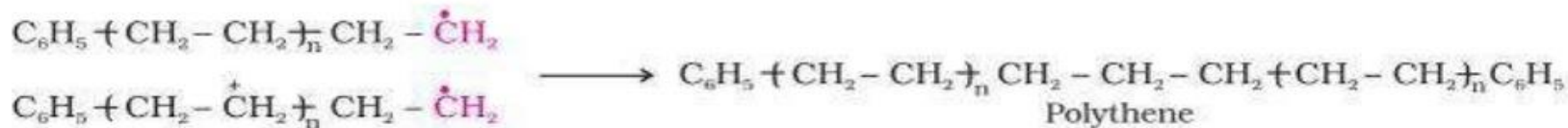


Chain propagating step



Chain terminating step

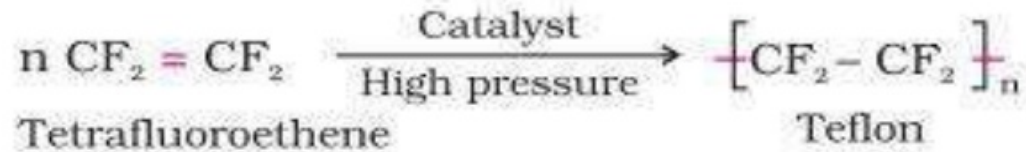
For termination of the long chain, these free radicals can combine in different ways to form polythene. One mode of termination of chain is shown as under:



Preparation of important addition polymers

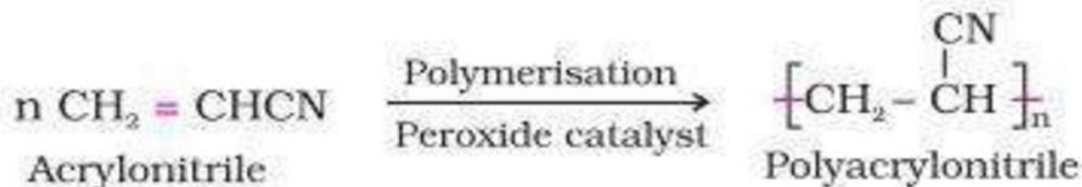
Polytetrafluoroethene (Teflon)

- 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.



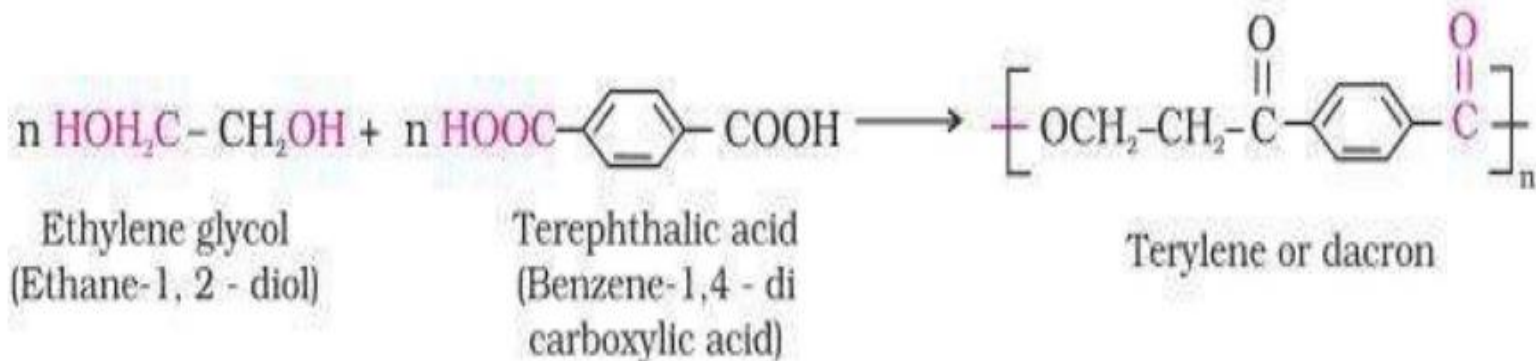
Polyacrylonitrile

- 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 orlon or acrilan.



Condensation polymerisation or step growth polymerisation

- This type of polymerisation generally involves a repetitive condensation reaction between two bi-functional monomers.
- These polycondensation reactions may result in the loss of some 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 on. Since, each step produces a distinct functionalised species and is independent of each other, this process is also called as step growth polymerisation.
- The formation of terylene or dacron by the interaction of ethylene glycol and terephthalic acid



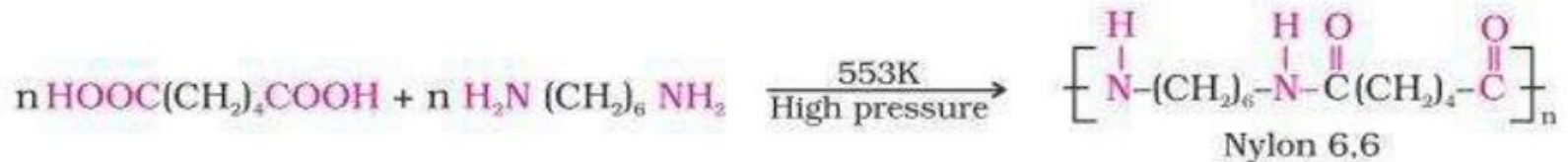
polyamides

These polymers possessing amide linkages are important examples of synthetic fibres and are termed as nylons.

The general method of preparation consists of the condensation polymerisation of diamines with dicarboxylic acids and also of amino acids and their lactams.

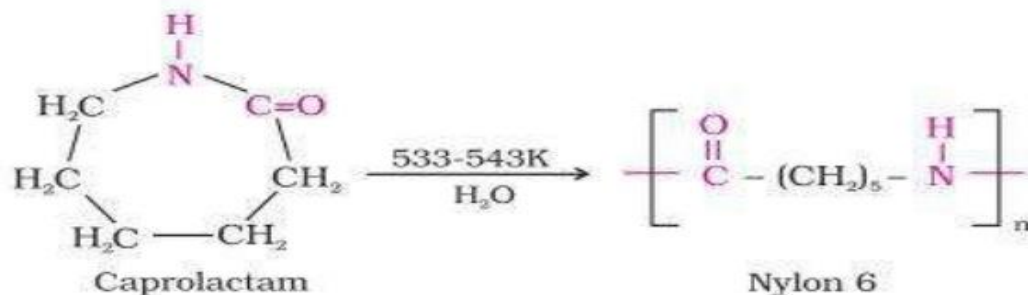
Preparation of nylons

- **(i) Nylon 6,6:** It is prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.



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

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

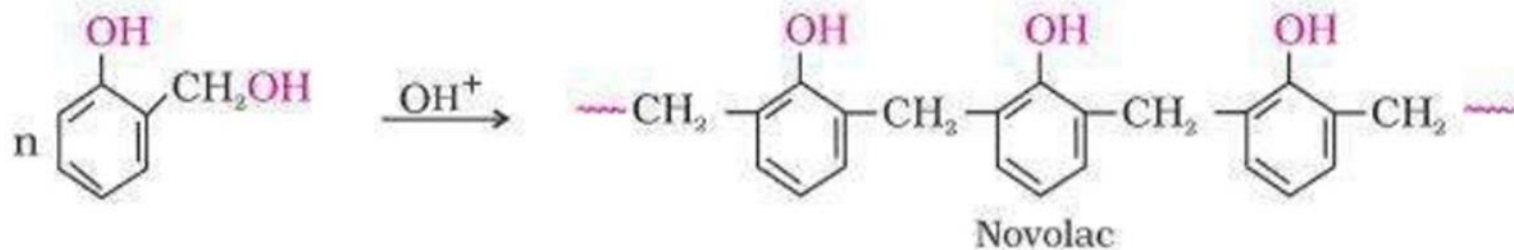
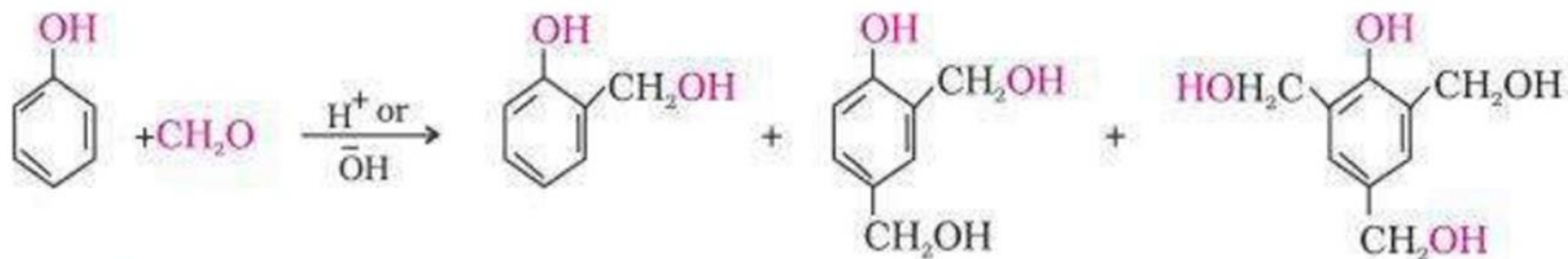


Nylon 6 is used for the manufacture of tyre cords, fabrics and ropes.

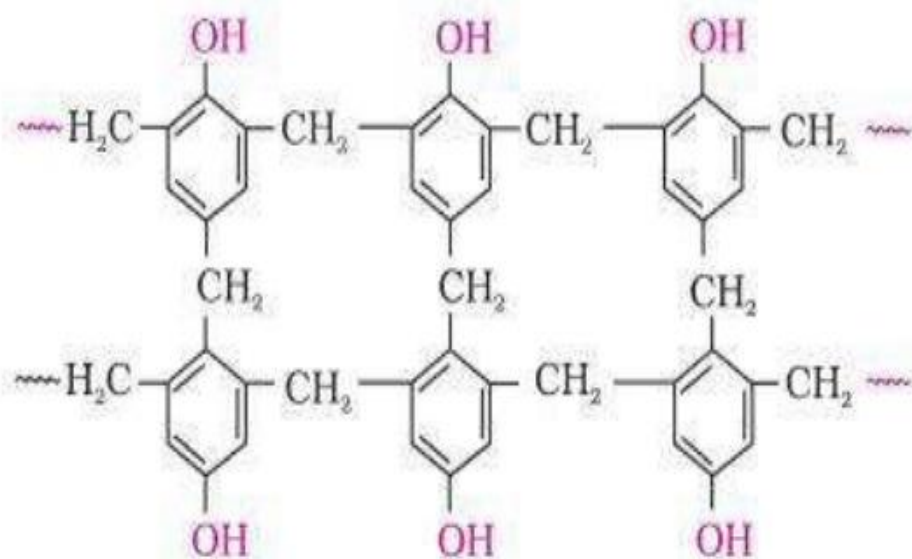
Preparation of polyesters

- These are the polycondensation products of dicarboxylic acids and diols.
- Dacron or terylene is the best known example of polyesters. It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetate antimony trioxide catalyst as per the reaction given earlier.
- 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.

- Phenol – formaldehyde polymers are the oldest synthetic polymers.
- These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst.
- The reaction starts with the initial formation of o-and/or p-hydroxymethylphenol derivatives, which further react with phenol to form compounds having rings joined to each other through –CH₂ groups. The initial product could be a linear product – Novolac used in paints.



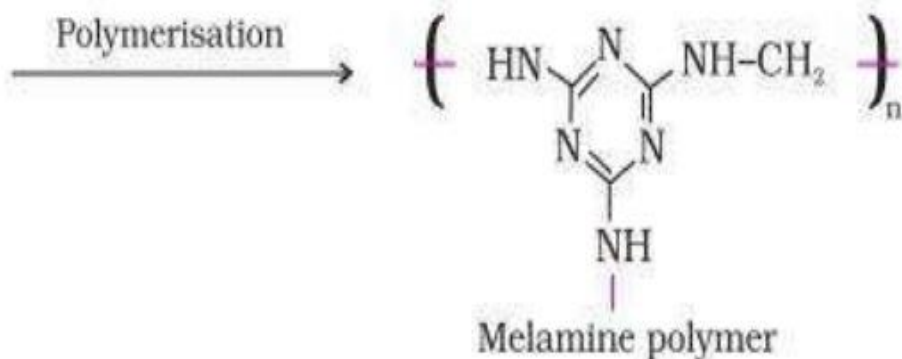
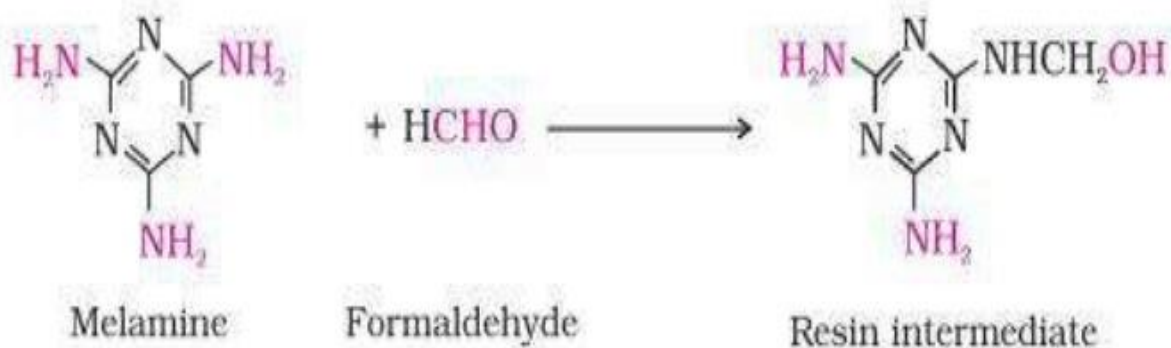
- Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called bakelite. It is used for making combs, phonograph records, electrical switches and handles of various utensils.



Bakelite

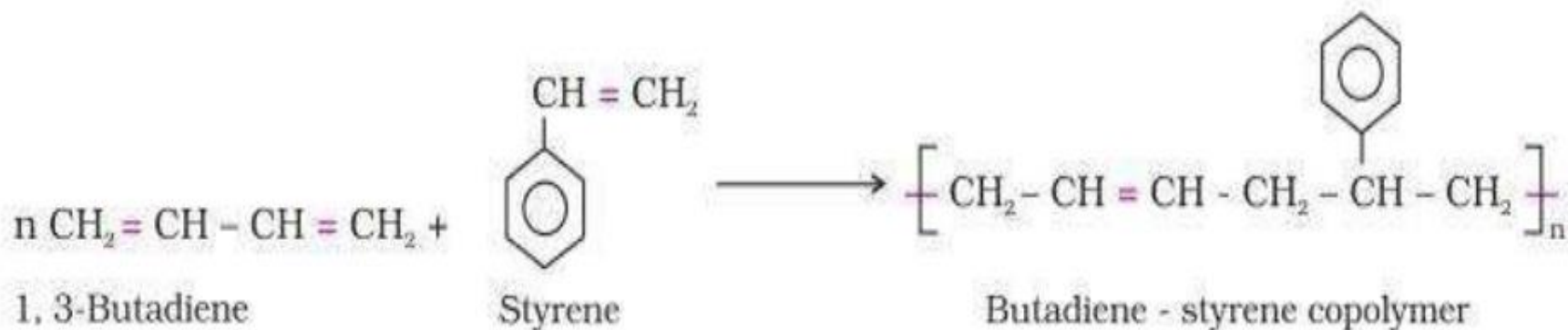
- Melamine -**formaldehyde polymer**

Melamine formaldehyde polymer is formed by the condensation polymerisation of melamine and formaldehyde.



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. It contains multiple units of each monomer used in the same polymeric chain. For example, a mixture of 1, 3 – butadiene and styrene can form a copolymer.



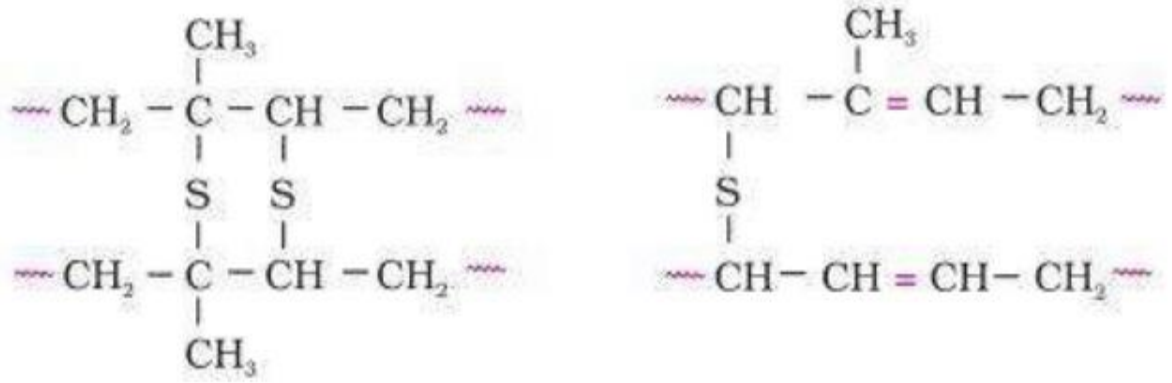
Rubber

1. Natural rubber

- Rubber is a natural polymer and possesses elastic properties. It is also termed as elastomer and has a variety of uses. It is manufactured from rubber latex which is a colloidal dispersion of rubber in water.
- Natural rubber may be considered as a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as cis – 1, 4 – polyisoprene.



- Vulcanisation of rubber:** Natural rubber becomes soft at high temperature (>335 K) and brittle at low temperatures (On vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened. The probable structures of vulcanised rubber molecules are depicted below:



Preparation of synthetic rubbers

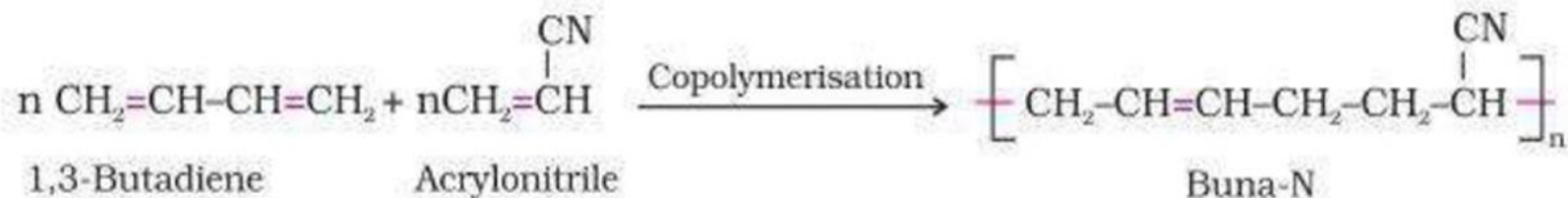
• 1. Neoprene

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



2. Buna – N

.Buna –N is obtained by the copolymerisation of 1, 3 – butadiene and acrylonitrile in the presence of a peroxide catalyst.



Biodegradable polymers

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

- It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3 – hydroxypentanoic acid. PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.

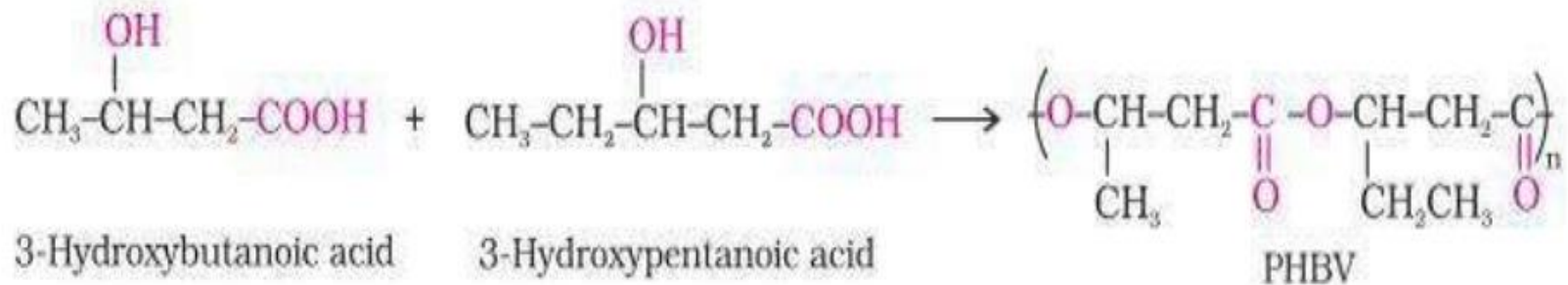


Table 15.1: Some Other Commercially Important Polymers

Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$\left(\text{CH}_2 - \overset{\text{CH}_3}{\underset{ }{\text{CH}}} \right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	$\left(\text{CH}_2 - \overset{\text{C}_6\text{H}_5}{\underset{ }{\text{CH}}} \right)_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride	$\left(\text{CH}_2 - \overset{\text{Cl}}{\underset{ }{\text{CH}}} \right)_n$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyde Resin	(a) Urea (b) Formaldehyde	$\left(\text{NH-CO-NH-CH}_2 \right)_n$	For making unbreakable cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid	$\left(\text{OCH}_2 - \text{CH}_2\text{OOC} \begin{array}{c} \diagup \\ \text{C}_6\text{H}_4 \\ \diagdown \end{array} \text{CO} \right)_n$	Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde	$\left(\begin{array}{c} \text{O-H} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{CH}_2 \end{array} - \begin{array}{c} \text{O-H} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{CH}_2 \end{array} \right)_n$	For making combs, electrical switches, handles of utensils and computer discs.