Unit - 15 Polymers

Polymers – These are high molecular mass substances consisting of large no. of repeating structural units called MONOMERS. The process by which the simple molecules are converted into polymers is called **polymerization**.

$$nCH_2=CH_2 \rightarrow (-CH_2-CH_2-)_n$$

(monomer**)** **(**polymer**)**

Monomers – these are the simple molecules which combine to give polymer or high molecular mass substances.

Homopolymer – a polymer formed from only one type of monomers.

Co-polymer- a polymer formed from two or more different types of monomers.

Classification of polymer on several basis –

A. **Classification of Polymers on the Basis of Source.**

1**. Natural polymers—** The polymers obtained from nature are called natural polymers. For example, starch, cellulose, natural rubber, proteins etc.

2**. Synthetic polymer—**The polymer which are prepared in the laboratories are called synthetic polymers. For example, polyethylene, PVC, nylon, Teflon eyc.

3. **Semi synthetic polymer-** the polymers which are derived from naturally occurring polymers by chemical modifications are called semi synthetic polymers. E.g. nitrocellulose, cellulose acetate etc.

B. **Classification of Polymers on the Basis of Structure.**

1. **Linear polymers**—These are the polymers in which monomeric units are linked together to form linear chains. Example polyethylene, nylons, polyesters etc.

Properties – high density, high tensile strength, high melting point.

2. **Branched chain polymers**—These are the polymers in which monomers are joined to form long chain with side chains or branches of different lengths. Example glycogen, starch,low density polythene etc.

Properties – low density, low tensile strength, low melting point.

3.**Cross-linked polymers—**These are polymers in which monomer units are cross-linked together to form a three-dimensional network. Examples Bakelite, resin etc .

Properties – hard , rigid , brittle.

C. **Classification of Polymers on the Basis of Molecular Forces**

1. **Elastomers**—The polymers which have very weak intermolecular forces between the polymeric chains and posses elastic character like rubber are called elastomers.Example Buna –N, Buna –S, vulcanized rubber.

2. **Fibers**—These are the polymers which have strong intermolecular forces between the chains. These forces are either hydrogen bonds or dipole-dipole interaction. Example nylon-66, Dacron, silk etc.

3. **Thermoplastics**—These are the polymers which can be easily softened repeatedly when heated and hardened when cooled with little change in their properties. Examples polythene, polystyrene, Teflon etc.

4. **Thermosetting polymers**—These are the polymers which undergo permanent change on heating. Examples Bakelite, melamine formaldehyde etc .

D. **Classification of Polymers on the Basis of mode of Synthesis**

1.Addition polymers—A polymer formed by direct addition of repeated monomers without the elimination of by product molecules is called addition polymers. Example polythene or polypropylene, Teflon, natural rubber.

2.Condensation polymers—A polymers formed by the condensation of two or more monomers with the elimination of simple molecules like water, ammonia, alcohol etc. is called condensation polymers. Example nylon66, proteins, dacron.

E. **Classification of Polymers on the Basis of mechanism**

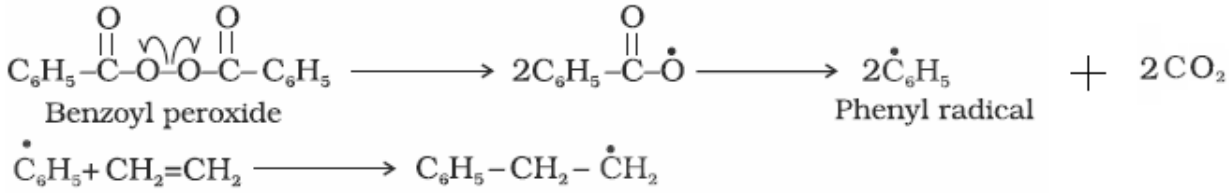
Chain growth polymerization & Step growth polymerization- The addition and condensation polymers are nowadays also referred as chain growth polymers and step growth polymers depending on the type of polymerisation mechanism they undergo during their formation.

Types of polymerization reactions –

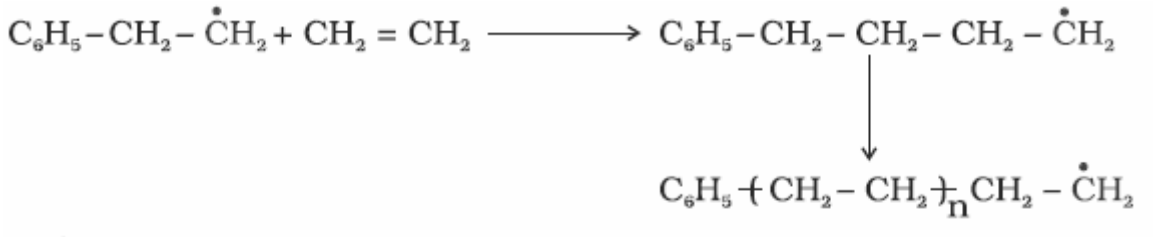
1.Addition polymerization or chain growth polymerization - This process involves a series of reaction each of which consumes a reactive particle and produced another similar particle resulting a chain reaction. So this is called chain growth polymerization.
the reactive particle may be free radical or ions to which monomers get added by a chain reaction.
It consists of three steps:

(i) chain initiation
(ii) chain propagation
(iii) chain termination

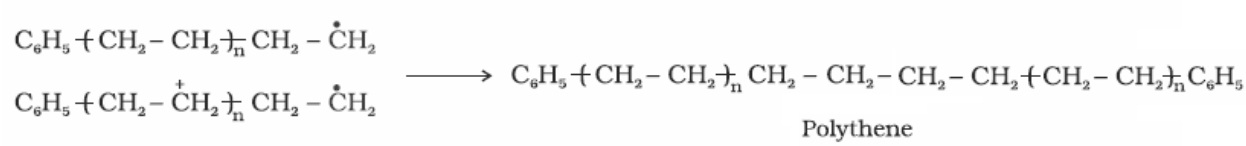
In the initiation step, the initiator (free radical, a cation, or anion) produces a reactive species. This species combines with a molecules of a monomer forming another reactive molecule.



In chain propagation this active molecule is added to another monomer forming another intermediate.



In chain termination step the reaction is terminated when the active end reacts with a species which do not formed reactive species.

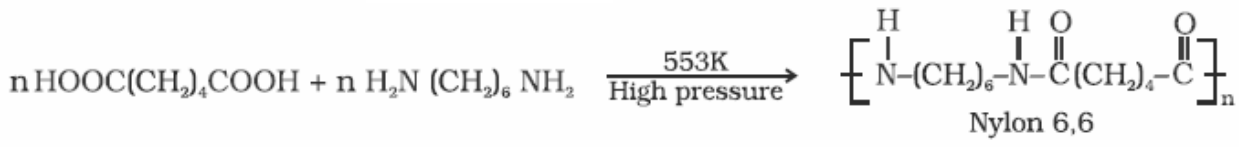


Addition polymerisation is called chain growth polymerisation because it occurs through stages leading to increase in chain length, and each stage produces reactive intermediates for use in the next stage of the growth of the chain.

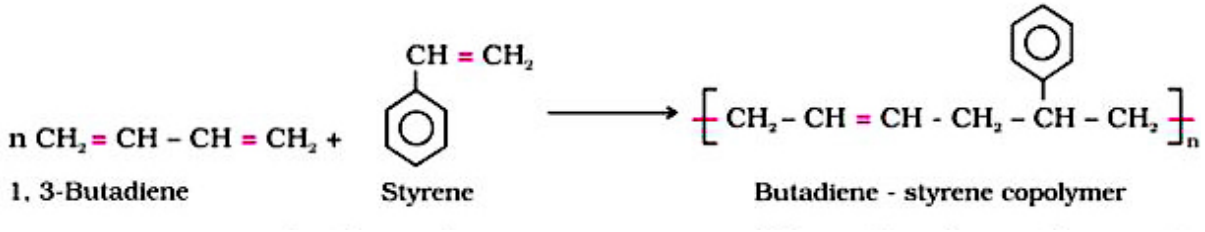
2.Condensation polymerization or step growth polymerization-

Condensation polymers are formed by this process. These are formed through a series of independent condensation reactions, In this type the monomers contain two functional groups. In this process, no Initiator is needed and each step is the same type of chemical reaction. The polymer is formed in a stepwise manner.

e.g, Nylon 6,6

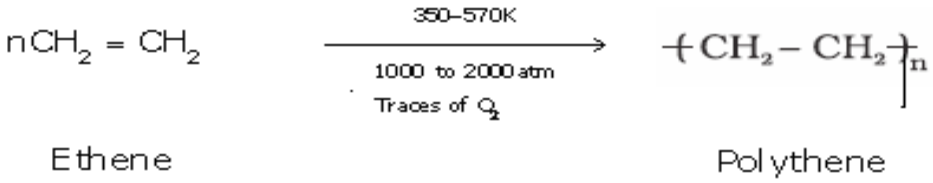


Copolymerisation : Copolymerisation is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise and form a copolymer.



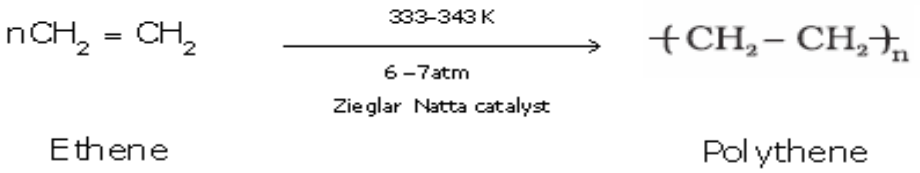
Some important addition polymers:

Low density polythene(LDP) –



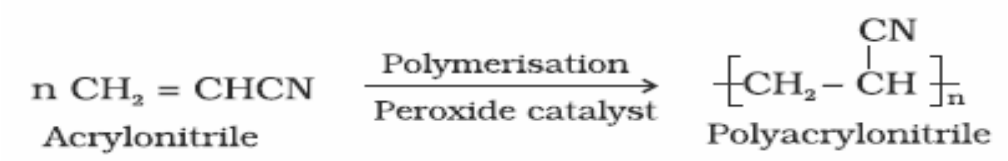
Uses: It is used in the insulation of electricity-carrying wires and the manufacture of squeeze bottles, toys and flexible pipes

High density polythene (HDP) :



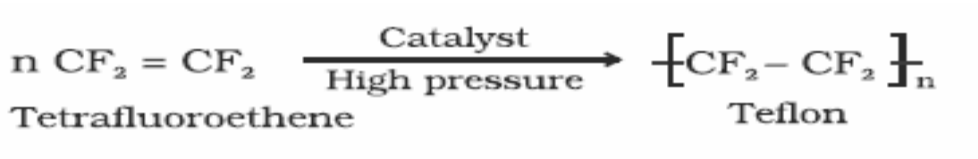
Uses: It is used for manufacturing buckets, dustbins, bottles, pipes etc

Polyacrylonitrile–



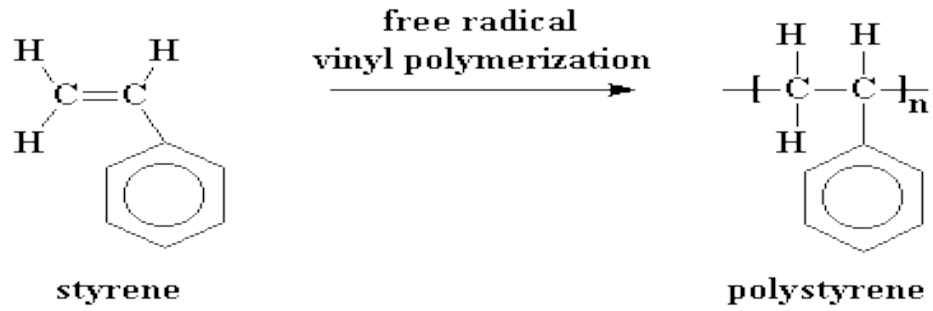
Uses: It is used as a substitute for wool in making commercial fibres as orlon or acrilyn.

Polytetrafluoro ethane (teflon)-



Uses: It is used in making oil seals and gaskets and also used for non-sticky surface-coated utensils.

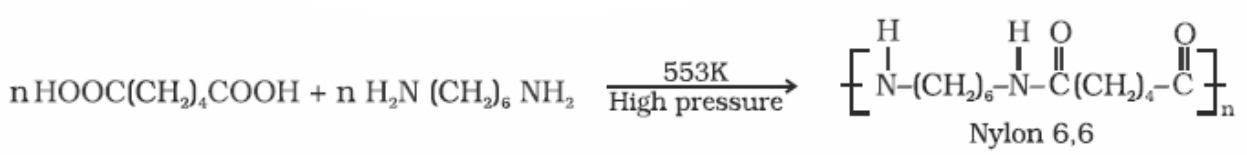
Polystyrene :



Uses : it is used in packaging things, shower units. Also known as thermocole.

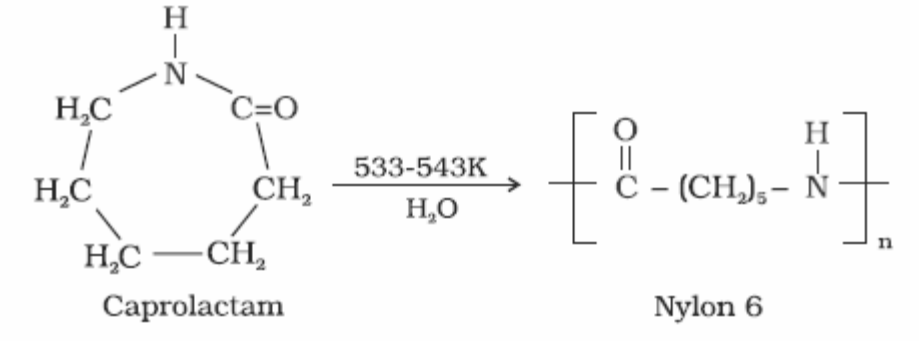
Some important condensation polymers:

Nylon 6, 6: It is prepared by condensation polymerisation of hexa methylene di amine with adipic acid under high pressure and at high temperature.



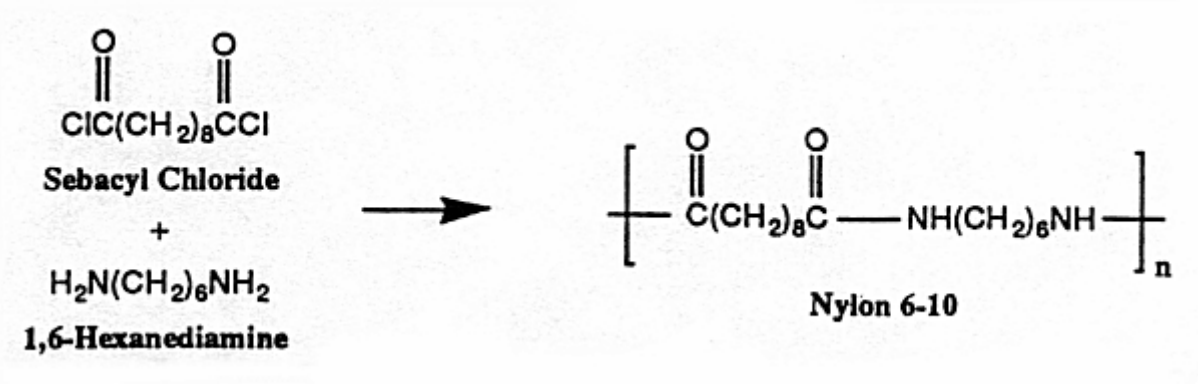
Uses: Nylon 6, 6 is used in making sheets, bristles for brushes and in the textile industry.

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



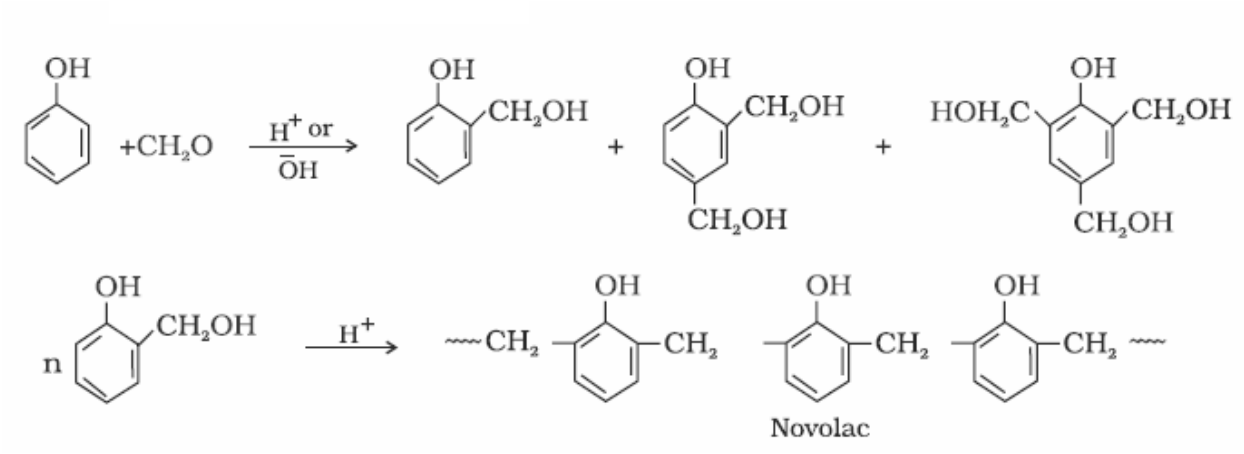
Uses: Nylon 6 is used for the manufacture of tyre cords, fabrics and ropes.

Nylon 6,10 : It is prepared by condensation polymerisation of hexa methylene di amine with sebacyl chloride.

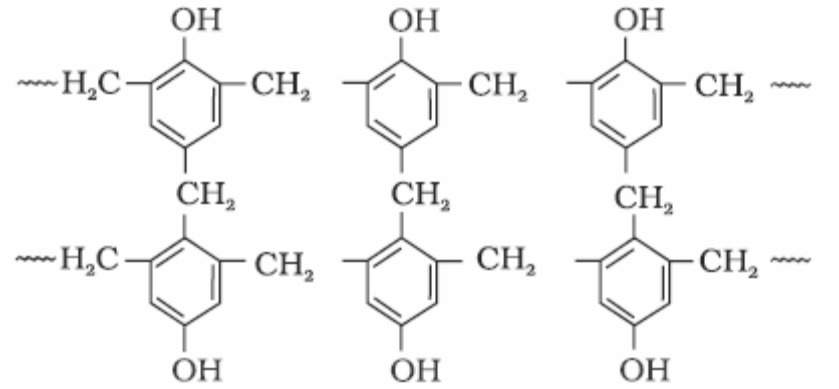


Bakelite :(phenol formaldehyde resin)

These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst. The initial product is a linear product—Novolac, which is used in paints.



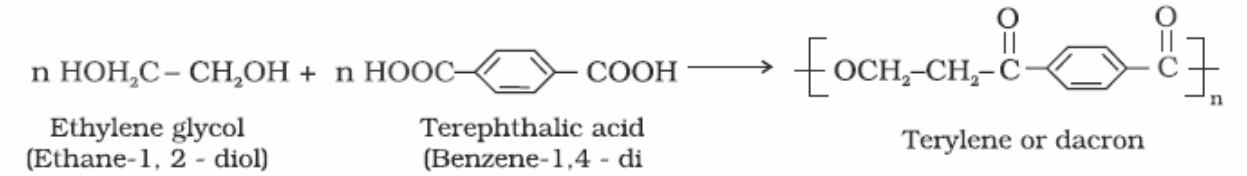
Novolac is a linear polymer which on heating with formaldehyde forms Bakelite.



Uses: It is used for making combs, phonograph records, electrical switches and handles of various utensils.

Terylene or Dacron (a polyster) –

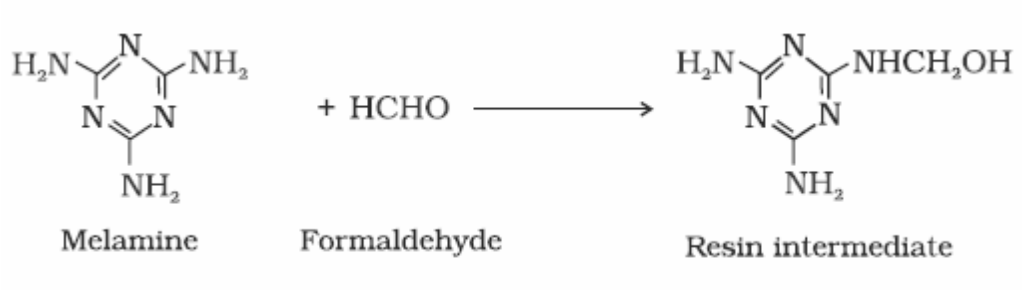
It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetate–antimony trioxide catalyst.

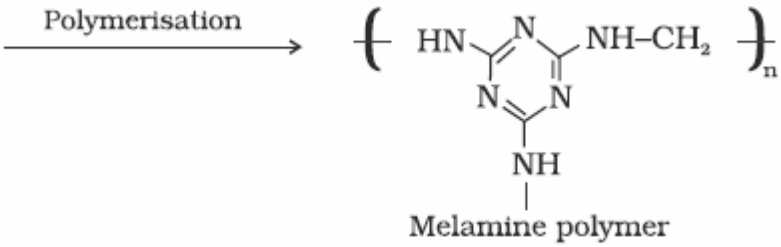


Uses: it is used in blending with cotton and wool fibres. It is also used as glass-reinforcing material in safety helmets.

Melmac (melamine- formaldehyde resin)-

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

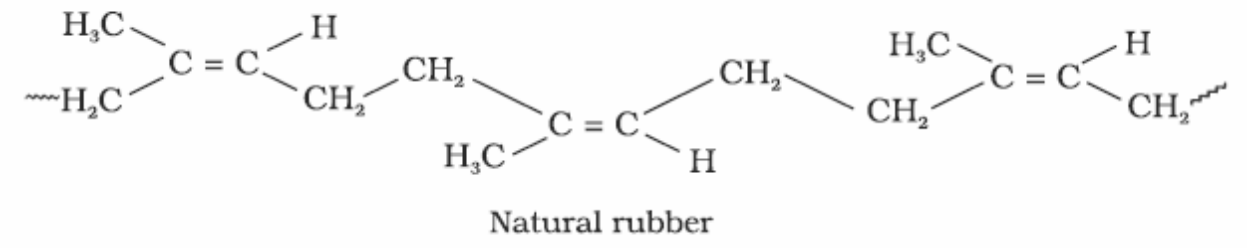




Uses: It is used in the manufacture of unbreakable crockery .it is often used in kitchen utensils and plates.

Rubber :

Natural rubber: Natural rubber is a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called *cis*-1, 4-polyisoprene.

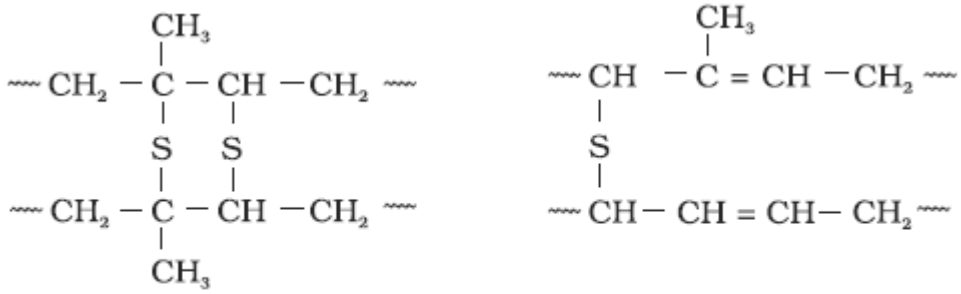


Note: Gutta purcha is trans isomer of natural rubber.

Vulcanisation of rubber :

natural rubber is soft and stiky and therefore, in order to give strength and elasticity natural rubber is vulcanized.

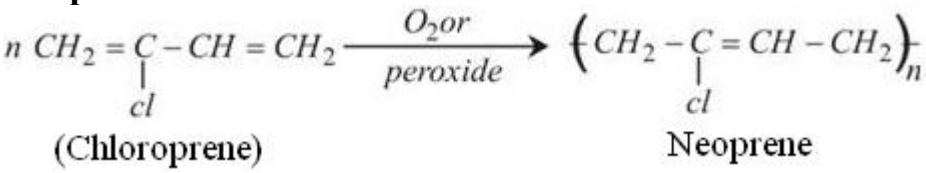
It is a process of heating a mixture of raw rubber with sulphur or some compounds of sulphur and an appropriate additive in a temperature ranging between 373 K and 415 K to improve its physical properties such as elasticity, strength etc.



Sulphur cross links in vulcanised rubber

Synthetic rubber: Synthetic rubbers are either homopolymers of 1, 3-butadiene derivatives or copolymers of 1, 3-butadiene or its derivatives with another unsaturated monomer.
Examples of synthetic rubber –

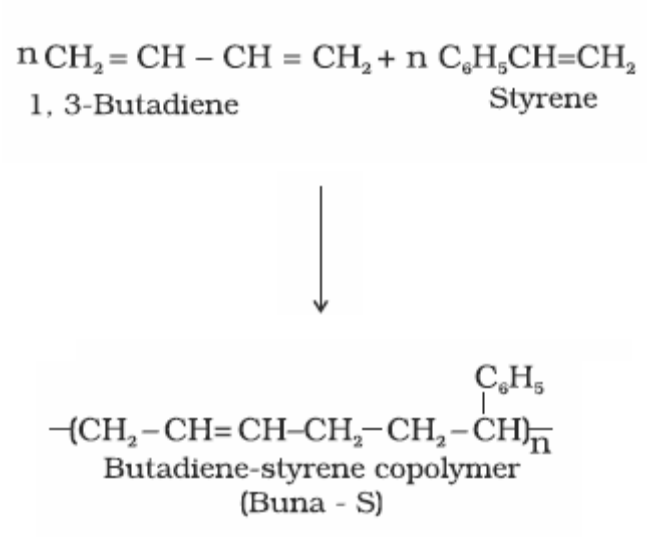
Neoprene –



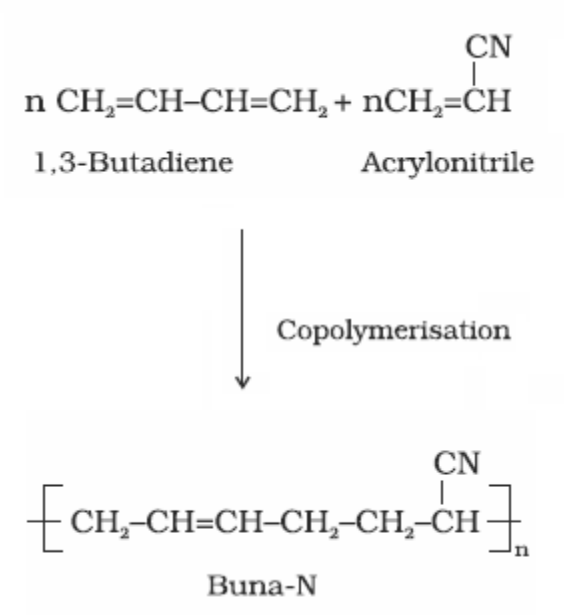
(Chloroprene) Neoprene

Uses : It is used for manufacturing conveyor belts, gaskets and hoses.

Buna -S – (Styrene Butadiene Rubber (SBR))
It is obtained by the polymerization of buta-1,3-diene and styrene in the ratio of 3:1 in the presence of sodium.



Buna -N –



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

Molecular mass of polymers :

A synthetic polymer contains a number of species of varying chain lengths. Since each species has a different molecular mass and a given sample of a polymer contains a such species, therefore, the polymer as a whole has an average molecular mass.

Types of average molecular mass-

(i) Number average molecular mass (Mn)-

If N_1, N_2, N_3.... are the number of macromolecules with molecular masses M_1, M_2, M_3... respectively then the number average molecular mass of the polymer is given by

$$Mn = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N_1 + N_2 + N_3....} = \frac{\sum NiMi}{\sum Ni}$$

Where Ni is the number of macromolecules of ith type with molecular mass Mi.

(ii) Weight average molecular mass(Mw)-

If m1, m2, m3.... are the masses of macromolecules with molecular masses M1, M2, M3..... respectively, then the weight average molecular mass of the polymer is given by

$$Mw = \frac{m1M1 + m2M2 + m3M3 + ...}{m1 + m2 + m3} = \frac{\sum miMi}{\sum mi}$$

But mi = NiMi where Ni is the number of macromolecules of ith type with molecular mass Mi.

$$Mw = \frac{\sum NiMi \times Mi}{\sum NiMi} = \frac{\sum NiMi_2}{\sum NiMi}$$

Poly Dispersed Index (PDI)—the ratio of weight average molecular mass and number average molecular mass is called poly dispersed index (PDI).

$$PDI = \frac{Mw}{Mn}.$$

PDI is used to determine the homogeneity of a polymer. On the basis of PDI, polymer have been classified in two categories.

(i) Monodisperse polymers- Polymers whose molecules have same or narrow range of molecular masses are called monodispersed polymers.

(ii) Polydispersed polymers – polymers whose molecules have a wide range of molecular masses are called polydisperse polymers.

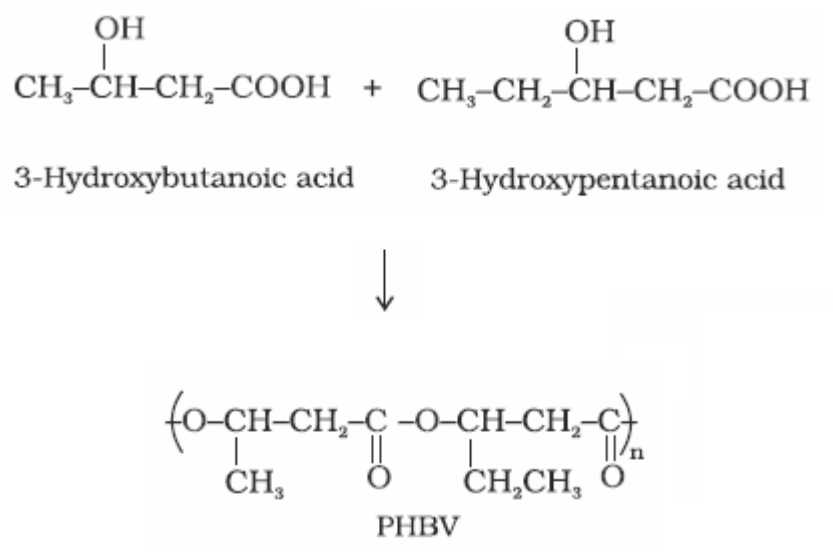
Biodegradable Polymers :

Polymers which are degraded by microorganisms within a suitable period so that biodegradable polymers and their degraded products do not cause any serious effects on the environment.

e.g.

Poly- β -hydroxybutyrate-co- β -hydroxyl-valerate (PHBV):

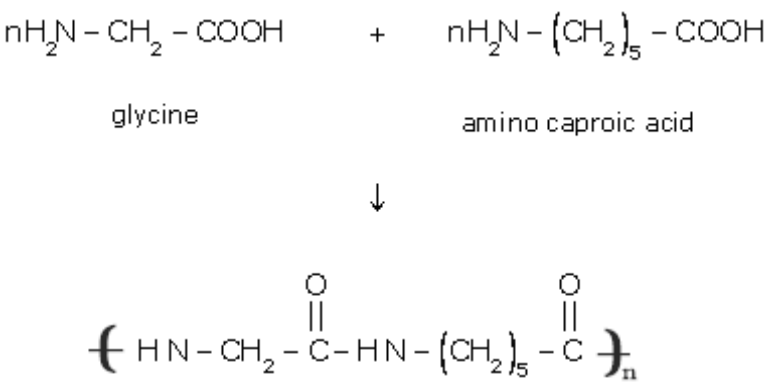
It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



Uses: PHBV is used in speciality packaging, orthopedic devices and in controlled release of drugs.

Nylon 2–nylon 6:

It is an alternating polyamide copolymer of glycine (H2N–CH2–COOH) and amino caproic acid (H2N (CH2)5 COOH).


nH2N – CH2 – COOH
+
nH2N – (CH2)5 – COOH
glycine
amino caproic acid
HN – CH2 – C – HN – (CH2)5 – C
n