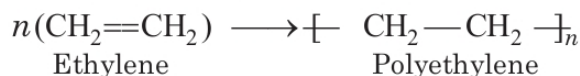


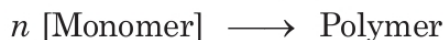
Polymers

The word **polymer** has a Greek origin, which means many units (parts). Polymer is defined as a chemical substance of a high molecular mass formed by the combination of a large number of simple molecules, called monomers, e.g.



Polymerisation

The process by which the monomers combine with each other and transform into polymers, is known as **polymerisation**.



Difference between Polymers and Macromolecules

Polymers are also called macromolecules due to their large size but converse is not always true. A macromolecule may or may not contain monomer units, e.g. chlorophyll ($\text{C}_{55}\text{H}_{72}\text{O}_5\text{N}_4\text{Mg}$) is a macromolecule but not a polymer since, there are no monomer units present. So, we can conclude that all polymers are macromolecules while all macromolecules are not polymers.

Classification of Polymers Based on Source of Origin

- (i) **Natural polymers** Those polymers which occur in nature, i.e. in plants or animals, are called natural polymers.

Natural polymer	Occurrence
Starch	Main reserve food of plants
Cellulose	Main structural material of plants
Proteins	Act as building blocks in animals.
Natural rubber	Occurs as latex (a colloidal dispersion of rubber in water) in the bark of many tropical trees, particularly from <i>Hevea Brasiliensis</i> .

- (ii) **Synthetic polymers** The polymers which are prepared in the laboratory are known as synthetic polymers or man-made polymers, e.g. polythene, synthetic rubber, PVC, nylon-6,6, teflon, orlon etc.
- (iii) **Semi-synthetic polymers** Polymers obtained by making some modification in natural polymers by artificial means, are known as semisynthetic polymers, e.g. cellulose acetate (rayon), vulcanised rubber etc.

Classification of Polymers Based on Structure

- (i) **Linear polymers** These are the polymers in which the monomer units are linked to one another to form long linear chains. These linear chains are closely packed in space. The close packing results in high densities, tensile strength and high melting and boiling points. e.g. high density polyethene, nylon and polyesters are linear polymers.



Linear chain polymer

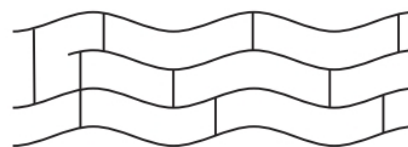
- (ii) **Branched chain polymers** In such polymers, the monomer units are linked to form long chains with some branched chains of different lengths attached to the main linear chain. As



Branched chain polymer

a result of branching, these polymers are not closely packed in space. Thus, they have low densities, low tensile strength as well as low melting and boiling points. Some common examples of such polymers are low density polyethene, starch, glycogen etc.

- (iii) **Cross-linked polymers or network polymers** These are formed from bi functional and tri functional monomers. In such polymers, the monomer units are



Cross linked polymer

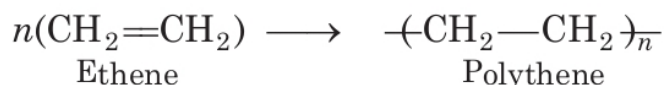
linked together to form three dimensional network. These are expected to be quite hard, rigid and brittle. Examples of cross linked polymers are bakelite, glyptal, melamine-formaldehyde polymer etc.

Classification of Polymers Based on Mode of Polymerisation

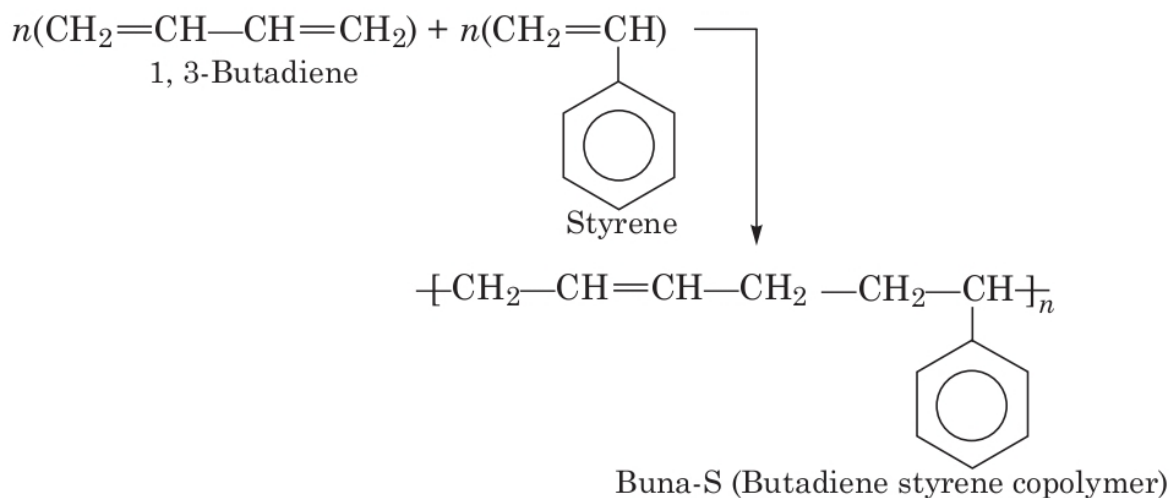
- (i) **Addition polymers** The polymers formed by the polymerisation of monomers containing double or triple bonds (unsaturated compounds) are called addition polymers. Addition polymers have the same empirical formula as their monomers.

Addition polymers can further be classified on the basis of the types of monomers into the following two classes:

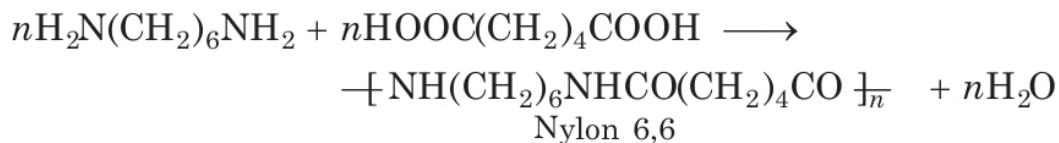
Homopolymers The polymers which are obtained by the polymerisation of a single type of monomer are called homopolymers.



Copolymers The polymers which are obtained by the polymerisation of two or more different types of monomers are called copolymers.



- (ii) **Condensation polymers** The polymers which are formed by the combination of monomers with the elimination of small molecules such as water, alcohol, hydrogen chloride etc., are known as condensation polymers, e.g. nylon 6,6 is formed by the condensation of hexamethylene diamine with adipic acid and water molecules are eliminated in the process.



These are generally copolymers. A condensation homopolymer is nylon-6.

Classification of Polymers Based on Molecular Forces

- (i) **Elastomers** These are rubber like solid polymers in which the polymer chains are held together by weakest intermolecular forces, e.g. natural rubber, buna-S, buna-N etc.

The weak binding forces permit the polymers 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 case of vulcanised rubber.

- (ii) **Fibres** Fibres belong to a class of polymers which are thread-like and can be woven into fabrics. These are widely used for making clothes, nets, ropes, gauzes, etc. Fibres possess high tensile strength because the chains possess strong intermolecular forces such as hydrogen bonding. The fibres are crystalline in nature and have sharp melting points. A few examples of this class are nylon-6,6, terylene and polyacrylonitrile (PAN).

- (iii) **Thermoplastics** These are linear polymers and have weak van der Waals' forces acting in the various chains. These forces are intermediate of the forces present in the elastomers and in the fibres. When heated, they melt and form a fluid which sets into a hard mass on cooling. Thus, they can be cast into different shapes by using suitable moulds, e.g. polyethene and polystyrene.

Plasticizers are high boiling esters or haloalkanes. These are added to plastics to make them soft like rubber.

- (iv) **Thermosetting plastics** These are normally semifluid substances with low molecular masses. When heated, they become hard and infusible due to the cross-linking between the polymer chains. As a result, they form three dimensional network. A few common thermosetting polymers are bakelite, melamine-formaldehyde resin and urea formaldehyde resin.

Types of Polymerisation Reactions

1. Chain Growth or Addition Polymerisation

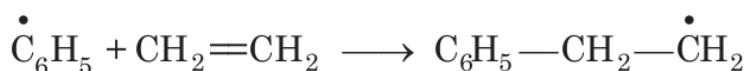
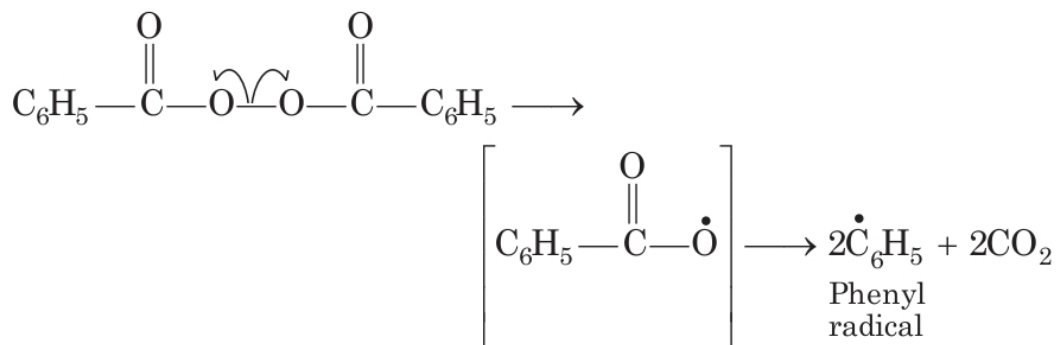
It involves formation of reactive intermediate such as free radical, a carbocation or a carbanion. For this polymerisation monomers used are unsaturated compounds like alkenes, alkadienes and their derivatives. Depending upon the nature of the reactive species involved, chain growth polymerisation occurs by the following mechanisms:

- (i) Free radical addition polymerisation
- (ii) Cationic polymerisation
- (iii) Anionic polymerisation

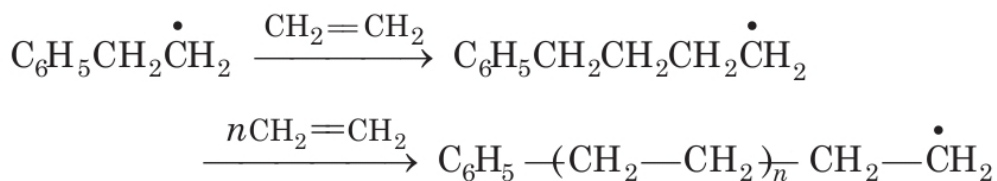
- (i) **Free radical addition polymerisation** The monomers used are generally monosubstituted alkenes. The most commonly used catalysts are benzoyl peroxide, hydrogen peroxide or *t*-butylperoxide etc.

Mechanism The reaction involves the following steps :

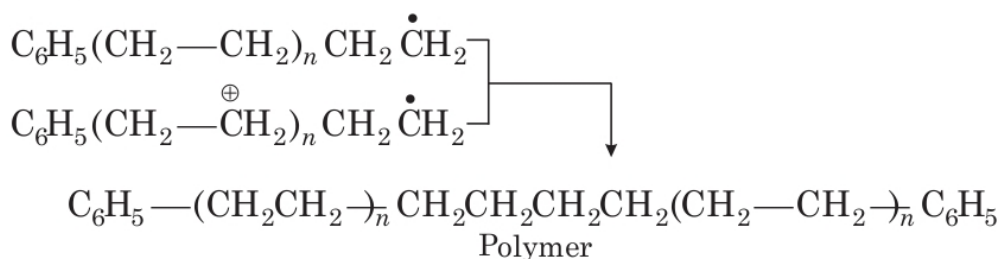
Step I Chain initiation step In this step, peroxide undergoes homolytic fission, e.g. benzoyl peroxide on heating produces phenyl free radical which work as initiator.



Step II Chain propagation step The new free radical adds to another molecules of monomer to form a larger free radical.

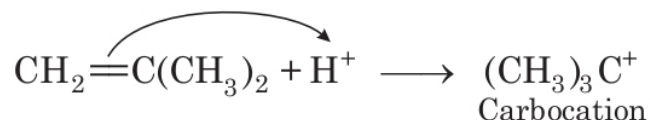
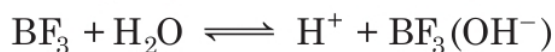
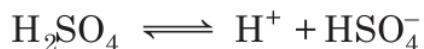


Step III Chain termination step There are three ways of chain termination: Coupling reaction, disproportionation reaction, chain transfer reaction. One mode of termination of chain is shown as under:

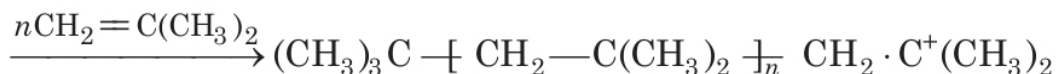
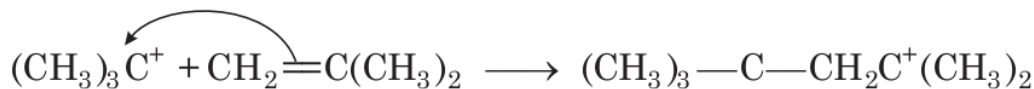


- (ii) **Cationic polymerisation** It involves formation of carbocation which are generated by Lewis acids (like BF_3 , AlCl_3 , SnCl_4 , etc.) and protonic acids such as H_2SO_4 , HF , etc. Higher the stability of carbocation intermediate, more is the reactivity of monomers towards cationic addition polymerisation. It involves the following steps:

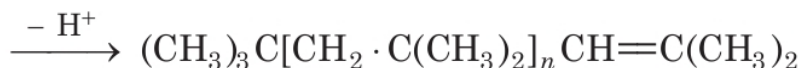
Step I. Initiation step



Step II. Propagation

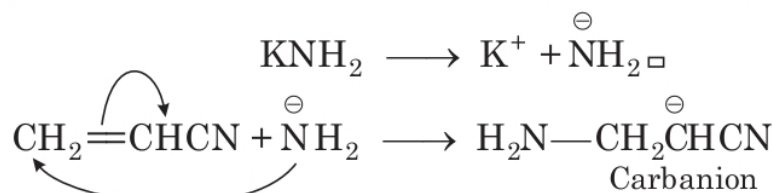


Step III. Termination

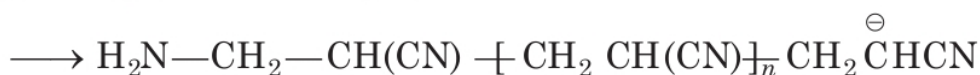


(iii) **Anionic polymerisation** It involves formation of a carbanion. Steps involved in this process are

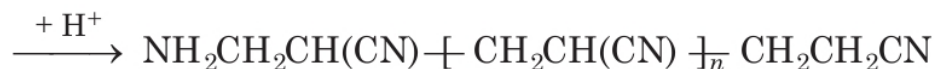
Step I Initiation Strong bases act as initiator.



Step II Propagation



Step III Termination



2. Step Growth on Condensation Polymerisation

Condensation polymerisation which occurs in a stepwise manner with elimination of some smaller molecules like H_2O , NH_3 , HCl , ROH , etc., is concerned with step growth polymerisation, e.g. adipic acid and hexamethylenediamine; phenol and formaldehyde etc., undergo step growth polymerisation.

Distinction Between Chain Growth Polymerisation and Step Growth Polymerisation

S.No.	Chain growth polymerisation	Step growth polymerisation
1.	It proceeds by a chain mechanism characterised by initiation, chain propagation and chain termination.	It proceeds by an equilibrium step mechanism. The step growth process is usually much slower than chain growth polymerisation.
2.	Only one repeating unit is added at a time.	Any two species present can react with elimination of some by product.
3.	Reaction mixture contain only monomers, polymers and the growing chain.	All the molecular species are present at every stage of polymerisation.

Molecular Mass of Polymers

The growth of the polymer chain depends upon the availability of the monomers in the reaction. Thus, the polymer sample contains chain of varying lengths and hence, its molecular mass is always expressed as an average molecular mass.

Number-Average Molecular Mass (\bar{M}_n)

If N_1 molecules have molecular mass M_1 each, N_2 molecules have molecular mass M_2 each, N_3 molecules have molecular mass M_3 each and so on,

then,

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

It is determined by osmotic pressure method.

Mass-Average Molecular Mass (\bar{M}_w)

Supposing, as before that N_1, N_2, N_3 etc., molecules have molecular mass M_1, M_2, M_3 etc., respectively,

then,

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

It is determined by light scattering and ultracentrifugation method.

Polydispersity Index

It is the ratio of the mass average molecular mass to the number average molecular mass

$$PDI = \frac{\bar{M}_w}{\bar{M}_n}$$

For natural polymers, PDI is usually equal to one which means that they are monodisperse. In other words, such polymers are more homogeneous. On the contrary, synthetic polymers generally have $PDI > 1$ which means that they are less homogeneous.

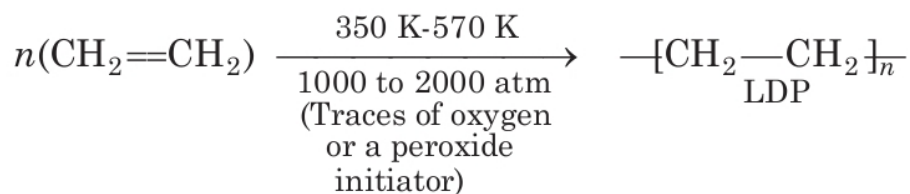
Polyolefins

These are obtained by the addition polymerisation of ethylene and its derivatives.

1. Polythene

Polymer of ethylene or ethene.

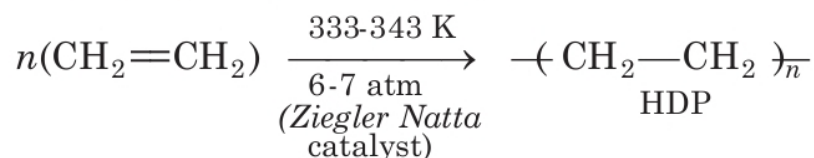
(i) Low density polythene (LDP)



It is tough, flexible, transparent, chemically inert as well as poor conductor of electricity. It has moderate tensile strength but good tearing strength.

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

(ii) High density polyethylene (HDP)

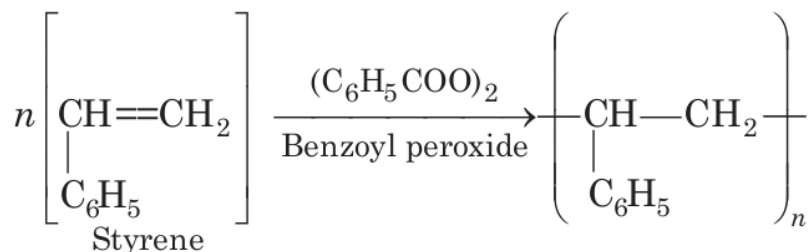


It has high density due to close packing. It is also chemically inert and poor conductor of electricity. It is tougher and harder than LDP.

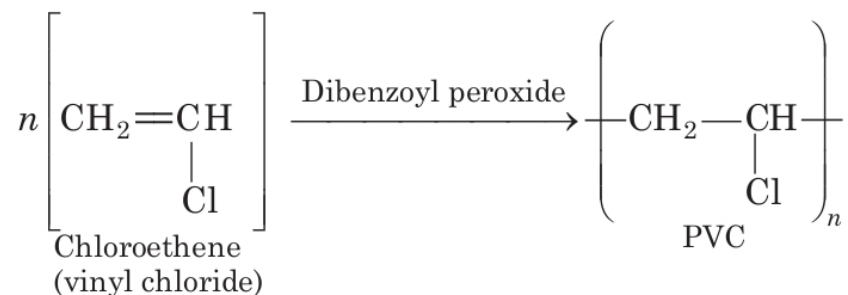
It is used for making containers, house wares, bottles, toys, electric insulation etc.

2. Polystyrene (Styrene)

The monomers are styrene molecules. It is thermoplastic. It is used for making toys, radio and TV cabinets.



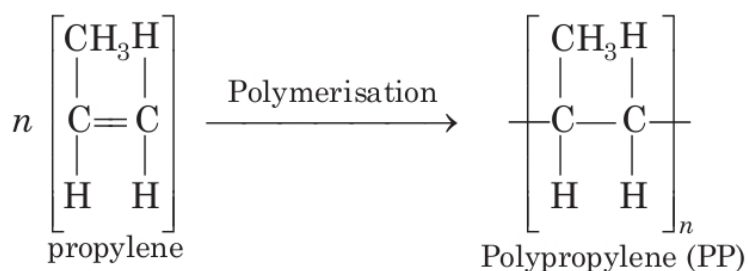
3. Polyvinylchloride (PVC)



It is used for making rain coats, toys, electrical insulation. It is hard and resistant to heat and chemicals.

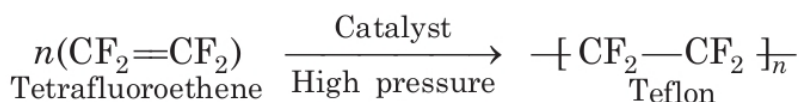
4. Polypropylene (PP)

It is obtained by polymerising propylene in the presence of *Ziegler-Natta* catalyst.



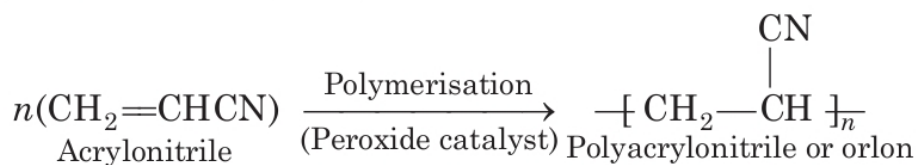
It is used for manufacturing of ropes, toys, pipes, fibres, etc.

5. Polytetrafluoroethene (Teflon)



It is chemically inert and resistant to attack by corrosive reagent. It is used in making oil seals, gaskets and also for non-stick surface coated utensils.

6. Polyacrylonitrile (PAN)



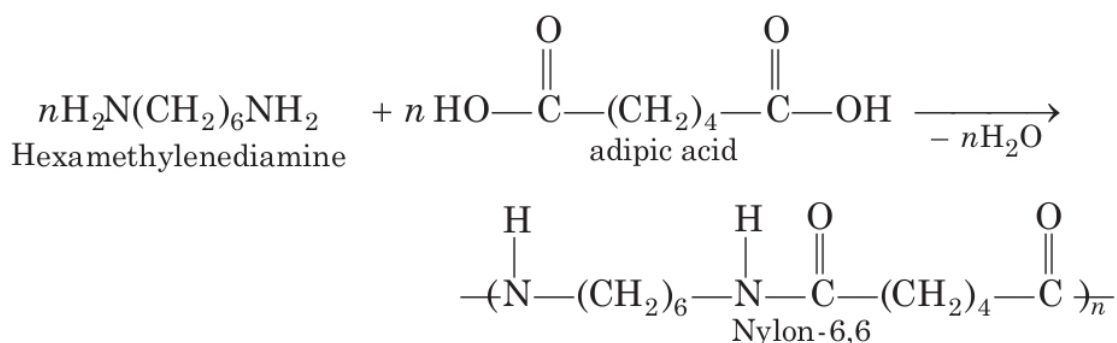
It is used as a substitute for wool in making of commercial fibres known as orlon or acrilan.

Polyamides

The polymers which contain an amide linkage in chain are known as polyamide, e.g. nylon-6,6.

1. Nylon-6,6

It is obtained by the condensation of adipic acid and hexamethylenediamine with the elimination of water molecule.



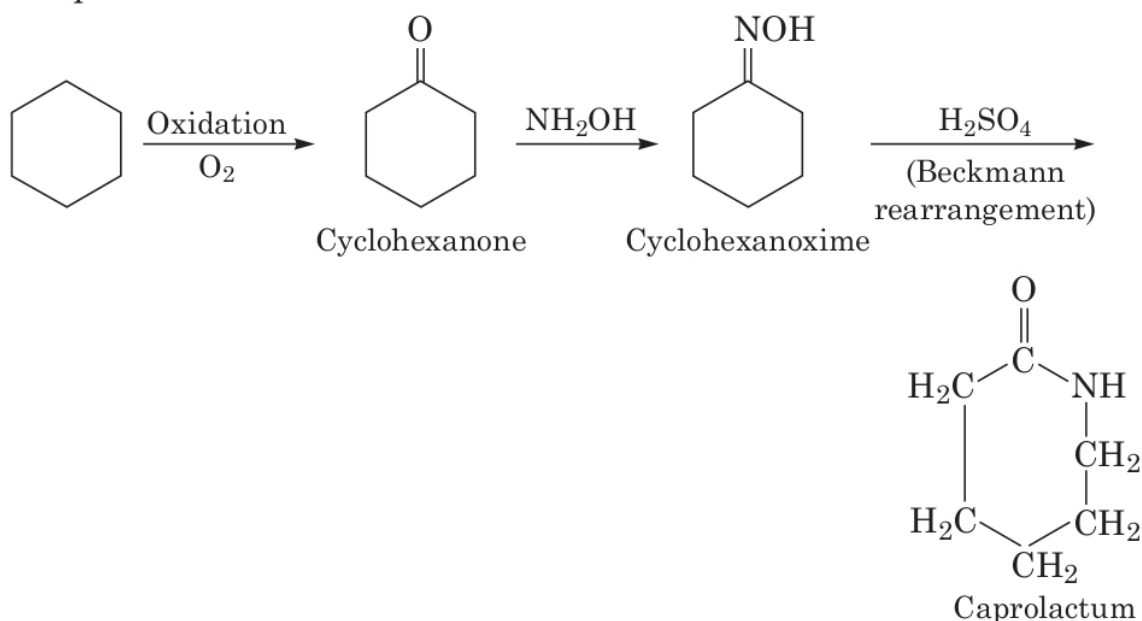
The polyamides are identified by numbers. These numbers refer to the number of carbon atoms in diamine and in the dibasic acid. As in the above case, the carbon atoms are 6 in each case, therefore the product is described as nylon-6,6.

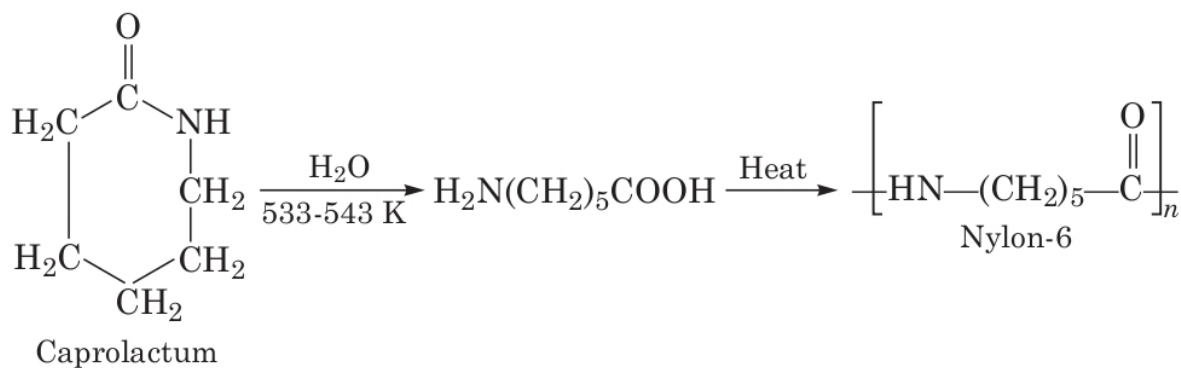
Properties and Uses

Nylon-6,6 is a linear polymer and has very high tensile strength. It shows good resistance to abrasion. Nylon-6,6 is usually fabricated into sheets. It is used in bristles for brushes and in textile.

2. Nylon-6

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

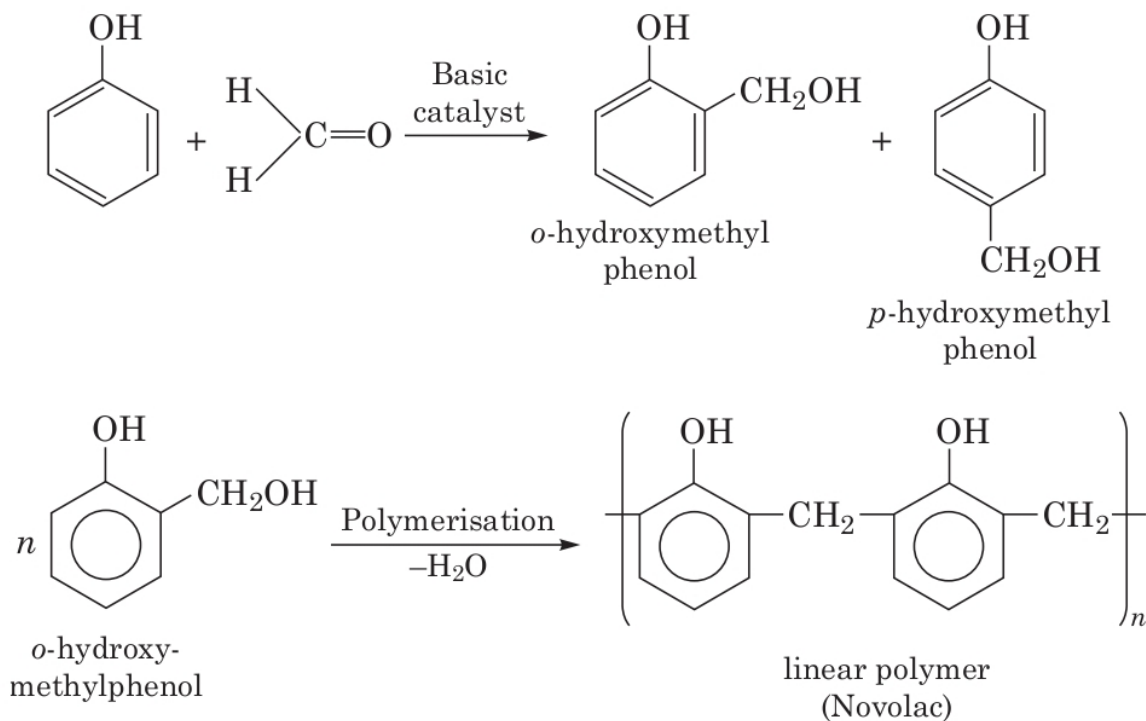


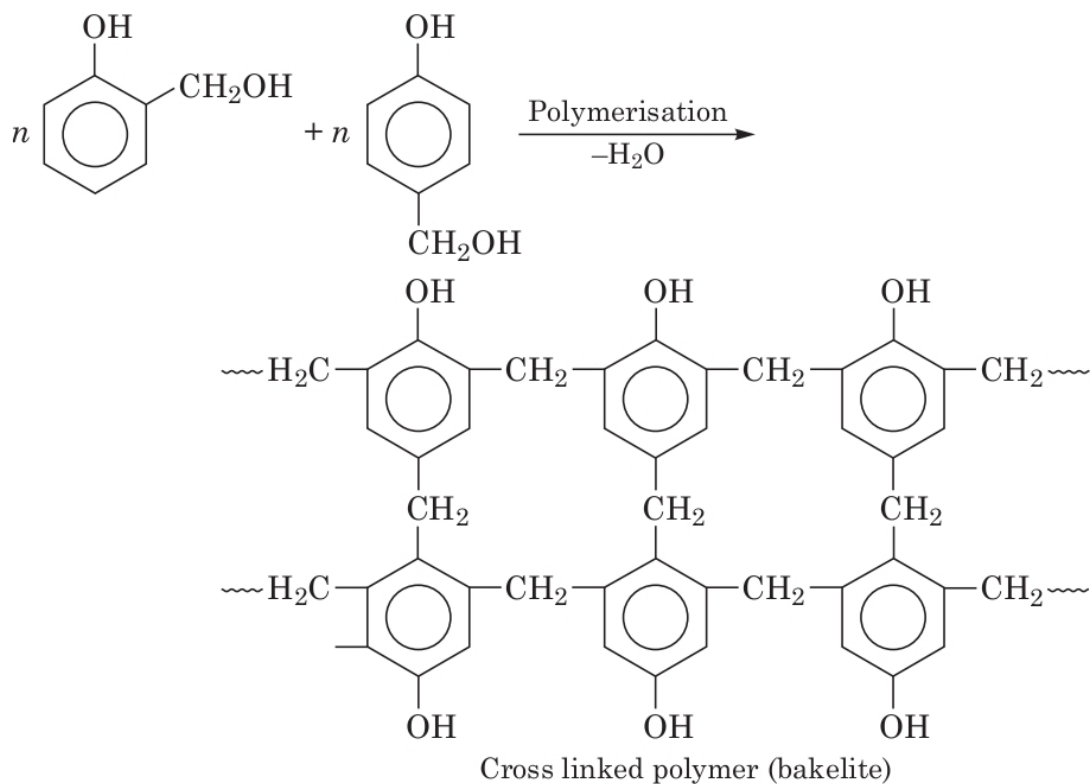


Resins

1. Phenol-Formaldehyde Polymer (Bakelite and Related Polymers)

These polymers are obtained by the condensation reaction of phenol with formaldehyde in the presence of either acid or a base catalyst. The reaction involves the formation of methylene bridge at *ortho*, *para* or both *ortho* and *para* positions. A linear or cross linked material is obtained depending upon the condition of reaction.



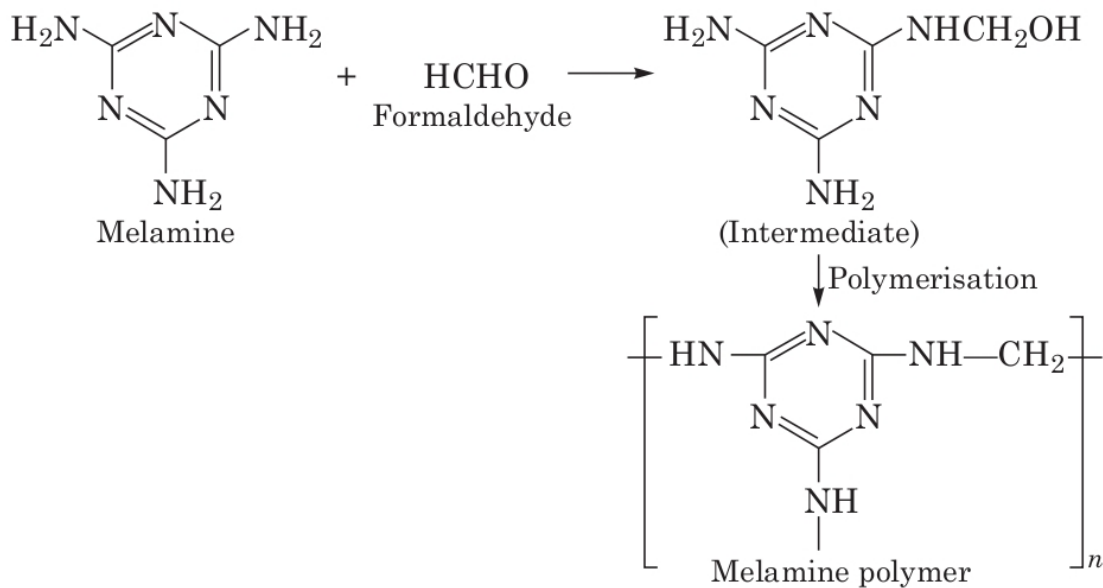


Uses

Bakelite is used for making combs, phonograph records, electrical switches etc. Soft bakelites with low degree of polymerisation are used as binding glue for laminated wooden plants, in varnishes and lacquers.

2. Melamine-Formaldehyde Resin

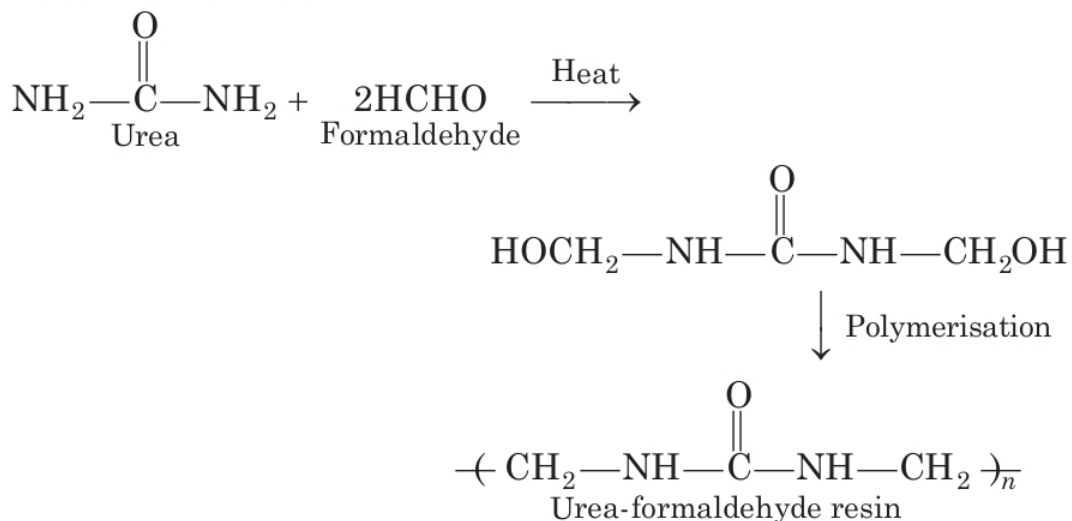
It is a copolymer formed by the polymerisation of melamine (which is a heterocyclic triamine) and formaldehyde as follows :



Properties and Uses

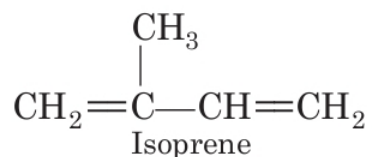
It is very hard and tough. It has assumed great importance these days particularly in making of crockery. They do not break even when dropped from a height.

3. Urea-Formaldehyde Resin

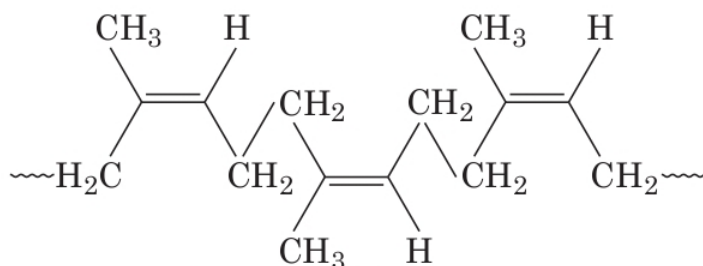


4. Natural Rubber

Natural rubber is a coiled linear 1,4-polymer of isoprene.



In the polymer chain of natural rubber, the residual double bonds are located between C₂ and C₃ of the isoprene unit. All these double bonds have *cis* configuration, and thus natural rubber is *cis*-1,4-polyisoprene.



In the natural rubber, there is no polar substituent. The only intermolecular forces are van der Waals' forces. The *cis*-configuration gives the polymeric chain of natural rubber a coiled structure. As a result, it can be stretched by the application of a force. When the force is removed, the chain returns back to its original coiled shape.

Natural rubber is soft and sticky. It can be used only in the temperature range 10°C–50°C. At higher temperature, it becomes soft and at low temperature, it becomes brittle. It has high water absorption capacity. It is attacked by oxidising agents and organic solvents. As such, it cannot be used very extensively for commercial purposes.

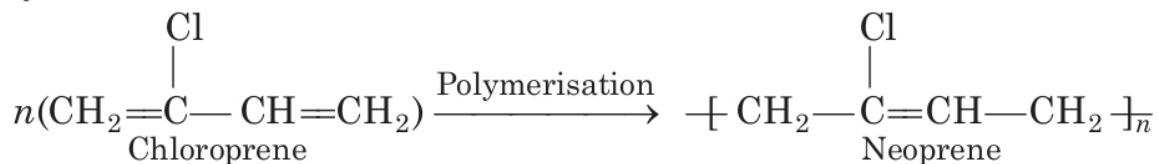
Vulcanisation of Rubber

The properties of natural rubber can be modified by introducing —S—S— polysulphide crosslinks in its structure. This process of introducing —S—S— crosslinks in the structure of natural rubber by heating with sulphur at 110°C is called **vulcanisation of rubber**.

Vulcanisation is carried out by adding sulphur (3-5%) and zinc oxide to the rubber, and then heating the object at about 110°C for about 20–30 minutes. **Zinc oxide accelerates the rate of vulcanisation**. Vulcanisation introduces polysulphide (—S—S—) bonds between the adjacent chains. These crosslinks tend to limit the motion of chains relative to each other.

5. Neoprene

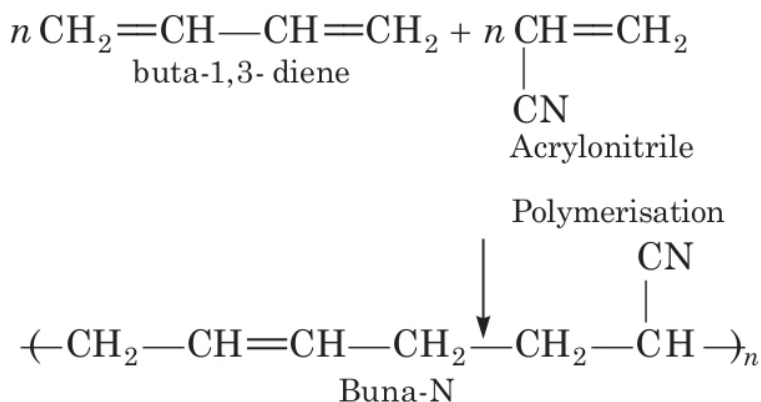
Polymer formed by polymerisation of chloroprene is called neoprene or synthetic rubber.



It is used for the manufacturing conveyers belts, gasket and hoses.

6. Buna-N

It is a copolymer of buta-1,3-diene and acrylonitrile. It is formed as follows



Properties and Uses

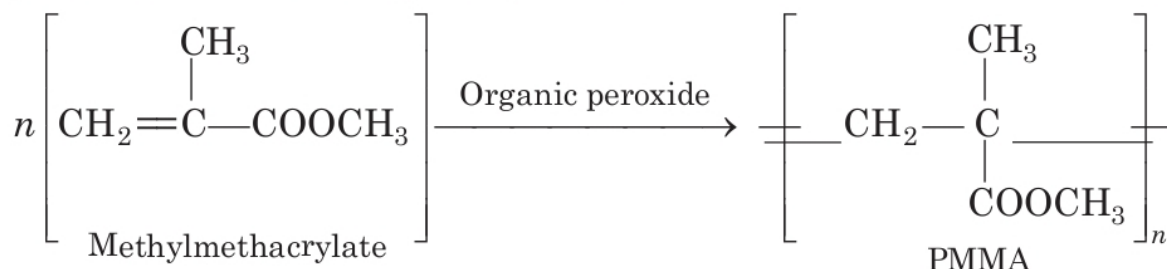
It act as insulator in nature and is used for making conveyor belts and printing rollers.

Polyesters

The polymers which contain an ester linkage are known as polyester, e.g. dacron.

1. Polymethylmethacrylate (PMMA)

It is prepared by the polymerisation of methylmethacrylate in the presence of suitable organic peroxide.



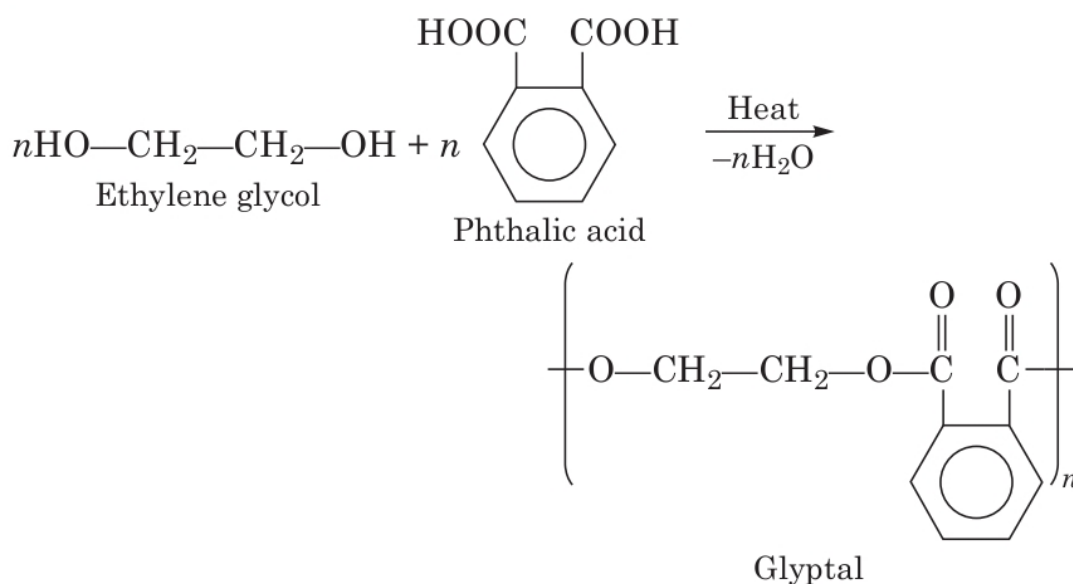
The polymer is known by several commercial names such as lucite, acrylite, plexiglass and perspex.

Properties and Uses

It is a hard and transparent polymer and is quite resistant to the effect of light, heat and ageing. It is used, in the manufacture of unbreakable lights, protective coatings, dentures, and in making windows for aircrafts.

2. Glyptal

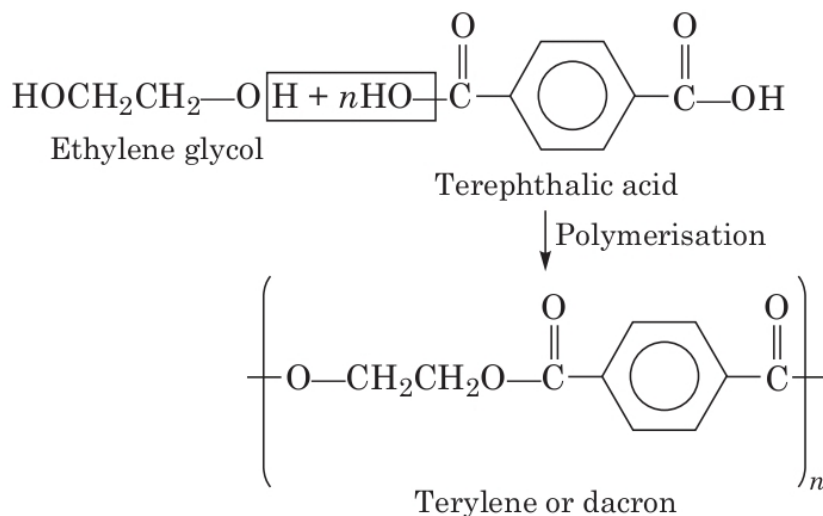
It is a polyester having crosslinks. It is a thermosetting plastic. It is obtained by condensation of ethylene glycol or glycerol and phthalic acid.



When its solution in a suitable solvent is evaporated, it leaves a tough but non-flexible film. It is, therefore, used in the manufacture of paints and lacquers.

3. Terylene (Dacron)

It is a condensation product of ethylene glycol and terephthalic acid. Polymerisation is carried out at 420 to 460 K in the presence of catalyst mixture of zinc acetate and antimony trioxide.



Properties and Uses

Terylene is highly resistant to the action of chemical and biological agents. Its fibres are quite strong and durable. It can also be blended with wool or cotton to obtain fabrics of desired composition.

Terylene is used in the manufacture of a variety of clothes such as terycot, terywool and terysilk as a result of blending with other yarns. It is also used for preparing magnetic recording tapes, conveyer belts, aprons for industrial workers etc.

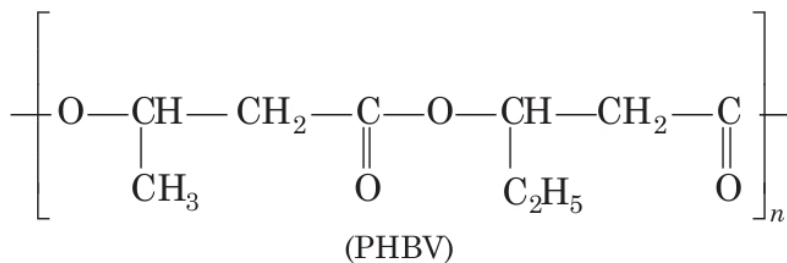
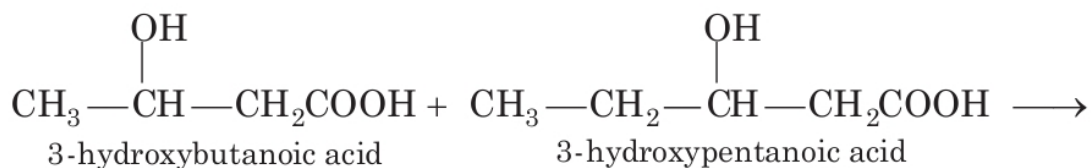
Biopolymers and Biodegradable Polymers

Synthetic polymers are mostly non-biodegradable i.e. it is very difficult to dispose off the polymeric waste, e.g. polythene bags.

Nature has provided us a variety of polymers which can be produced by the biological systems in plants and animals. These are called **biopolymers**, e.g. polysaccharides, proteins, nucleic acids, etc. In the biological system, these polymers decompose or hydrolyse in the presence of different enzymes. This means that they are biodegradable. Aliphatic polyesters are the common examples of biodegradable polymers.

1. PHBV (poly-β-hydroxybutyrate-co-β-hydroxyvalerate)

It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



2. Nylon-2-Nylon-6

It is an alternating polyamide copolymer of glycine

($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$) and amino caproic acid [$\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$]

and is biodegradable.

Few More Important Polymers

1. Saran is a copolymer of vinylidene chloride and other monomers and is used for wrapping food materials.
2. ABS rubber is a copolymer of acrylonitrile, buta-1,3-diene and styrene.
3. Bubble gum contains styrene butadiene (Buna-S) rubber.
4. Epoxy resins are used in making adhesives such as araldite, etc. These are the copolymer of epichlorohydrin and bisphenol-A.
5. Thikol is another variety of synthetic rubber which is a copolymer of ethylene chloride and sodium tetrasulphide (Na_2S_4).
6. Dynel is a copolymer of vinyl chloride and acrylonitrile and is used for making human hair wigs.
7. Silk is a thread like natural polymer which is obtained from cocoons of silk worms. It is a natural polyamide fibre.
8. Thermocol is a foamed plastic obtained by blowing air through molten polystyrene or polyurethane.
9. Superglue is a polymer of methyl α -cyanoacrylate and is obtained by anionic polymerisation of the monomer.