15. POLYMERS

Polymers are very large molecules having high molar mass and are formed by the combination of a large number of simple molecules called monomers. The process of formation of polymers from respective monomers is called *polymerisation*.

The word 'polymer' is derived from two Greek words - poly (means many) and mer (means unit or part). Polymers are also called *macromolecules*.

E.g. polythene, polypropene, polystyrene, polyesters, polyamides, synthetic fibres, synthetic rubbers etc.

Classification of Polymers

The following are some of the common classifications of polymers:

I) **Classification Based on Source**: Based on this, polymers are classified into three:

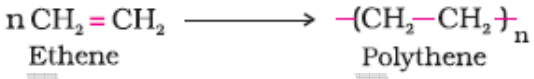
1. ***Natural polymers***: These polymers are found in nature. Examples are proteins, cellulose, starch, natural fibres and natural rubber.
2. ***Semi-synthetic polymers***: Cellulose derivatives such as cellulose acetate (rayon) and cellulose nitrate are the examples of this category.
3. ***Synthetic polymers***: These are man-made polymers. E.g. plastics like polythene, poly styrene, PVC etc. Synthetic fibres like nylon 6,6 and synthetic rubbers like Buna – S.

II) **Classification Based on Structure of Polymers**: Based on this polymers are divided into three:

1. ***Linear polymers***: They contain long and straight chains of polymers. E.g. 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. E.g. bakelite, melamine, etc.

III**)** **Classification Based on Mode of Polymerisation**: Based on this polymers are classified into two:

1. ***Addition polymers***: These are polymers formed by addition polymerisation reaction. Here the monomer molecules should possess double or triple bonds. Addition polymers are now known as chain growth polymers.
   E.g. polythene, polypropene, polystyrene, polyvinyl chloride etc.



2. ***Condensation polymers***: These are polymers formed by condensation polymerisation reaction. In this polymerisation reaction, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc take place. Here the monomers should be bifunctional or polyfunctional. Condensation polymers are now known as step growth polymers.
   E.g. Nylon- 6,6, Nylon- 6, terylene, glyptal etc.

IV**)** **Classification based on the type of monomers**: Based on this, polymers are of two types:

1. ***Homopolymers***: These are polymers containing only one type of monomer unit.
   E.g.: polythene, polystyrene. polypropene etc.
2. ***Copolymers***: These are polymers containing different types of monomer units.
   E.g.: Polyesters like glyptal, terylene etc. poly amides like Nylon-6, Nylon-6,6 etc.

V) **Classification based on the Molecular Forces**: Based on this, polymers are of 4 types:

1. ***Elastomers***: These are rubber – like solids with elastic properties. In these polymers, the polymer chains are held together by the weakest intermolecular forces (van der Waal's force). So they can be stretched. A few 'cross links' are formed in between the chains, which help the polymer to regain to its original position after the force is released. E.g. buna-S, buna-N, neoprene, etc.

2. ***Fibres***: Fibres are the thread forming solids which possess high tensile strength and high modulus. Here the different polymer chains are held together by strong intermolecular forces like hydrogen bonding. So they have close packed structure and are crystalline in nature. E.g. Nylon-6,6, Nylon-6, terylene etc.
3. ***Thermoplastic polymers***: These are the linear or slightly branched long chain molecules. They can be repeatedly softening on heating and hardening on cooling. On heating a physical change occurs. These polymers possess intermolecular forces of attraction in between that of elastomers and fibres. Some examples are polythene, polystyrene, polyvinyls, etc.
4. ***Thermosetting polymers***: These polymers are cross linked or heavily branched molecules. On heating, they undergo extensive cross links and become infusible. These cannot be reused. There occurs a chemical change on heating. Some common examples are bakelite, urea-formaldelyde resins, glyptal, terylene etc.

Types of Polymerisation Reactions

There are two types of polymerisation reactions - addition or chain growth polymerisation and condensation or step growth polymerisation.

I) <u>Addition Polymerisation or Chain Growth Polymerisation</u>

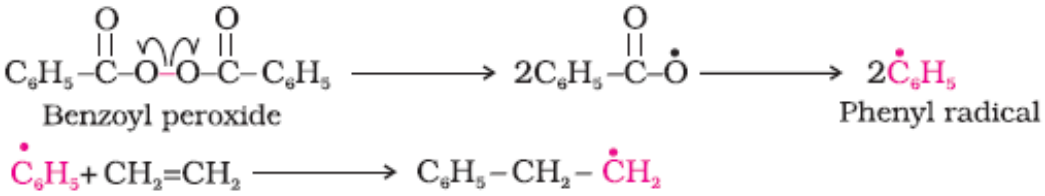
Here the monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds like alkenes, alkadienes and their derivatives. This type of polymerisation leads to an increase in chain length or chain growth. So it is also called chain growth polymerisation.

This type of polymerisation mainly takes place through *free radical mechanism*. In this mechanism, the reaction takes place in presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide etc.

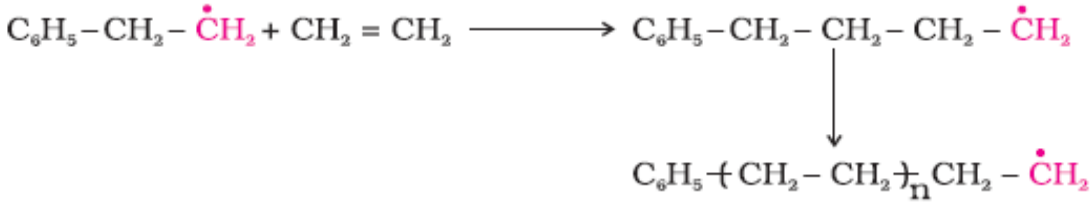
For example the polymerisation of ethene to polythene is carried out by heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator.

The process consists of three steps:

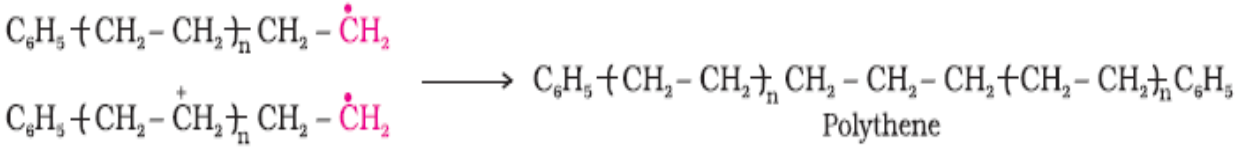
1. *Initiation step*: In this step, a phenyl free radical is formed by the homolysis of the benzoyl peroxide. It is then added to the ethene double bond thus generating a new and larger free radical.



2. *Propagation step*: The free radical formed in the above step, reacts with another molecule of ethene to form another bigger sized radical.



3. *Termination step*: Here two free radicals combine together to form the polymerised product. This step is called the chain terminating step.



Preparation of some important addition polymers

1. **Polythene**: There are two types of polythene – Low density polythene and high density polythene

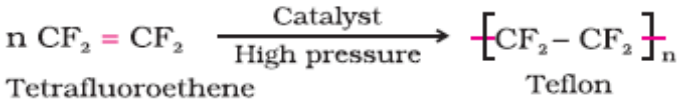
i) ***Low density polythene (LDP):*** It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 to 570 K in the presence of an organic peroxide (catalyst).

It is chemically inert, tough, flexible and a poor conductor of electricity. Hence, it is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes.

ii) ***High density polythene (HDP)***: It is formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres.

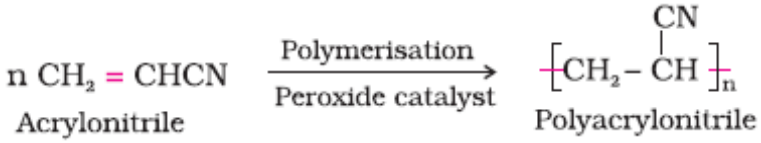
It consists of linear molecules and has a high density due to close packing. It is also chemically inert and more tough and hard. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

2. **Teflon**: It 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 (non-sticky pans).

3. **Polyacrylonitrile (PAN)**: It is prepared by the addition polymerisation of acrylonitrile in presence of a peroxide catalyst. It is used as a substitute for wool in making commercial fibres as orlon or acrilan.



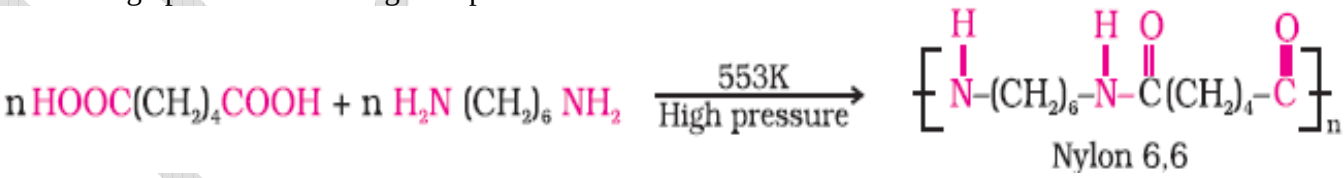
II) <u>Condensation Polymerisation or Step Growth polymerisation</u>

This type of polymerisation involves a repetitive condensation reaction between two bi-functional monomers. It results in the loss of some simple molecules like 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. Since, each step produces a different functionalised species and is independent of each other; this process is also called as *step growth polymerisation*. Some examples of condensation polymers are:

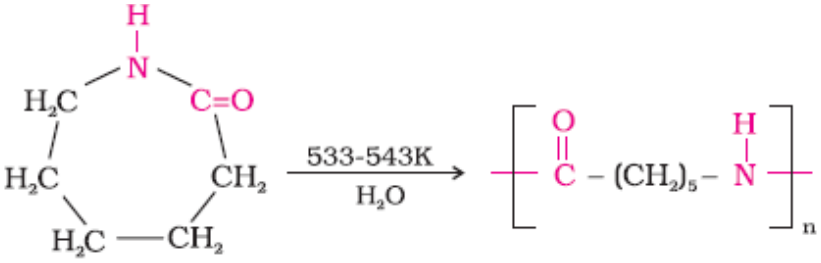
1. **<u>Polyamides</u>**: These polymers possess amide linkages. They are also known as nylons.

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



It is used in making sheets, bristles for brushes and in textile industry.

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



Caprolactam Nylon 6

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

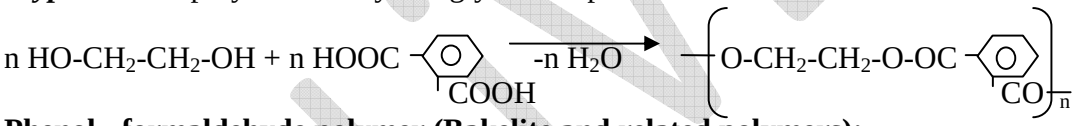
2. <u>Polyesters</u>: These are the polycondensation products of dicarboxylic acids and diols. Some e.g. are:

a) ***Terylene (Dacron):*** 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.

Ethylene glycol (Ethane-1, 2 - diol) Terephthalic acid (Benzene-1,4 - di carboxylic acid) Terylene or dacron

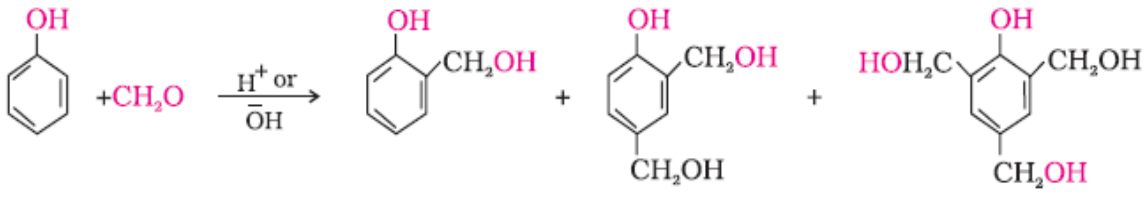
Dacron fibre (terylene) is used in blending with cotton and wool fibres and also as glass reinforcing materials in safety helmets, etc.

b) ***Glyptal***: It is a polymer of ethylene glycol and phthalic acid.



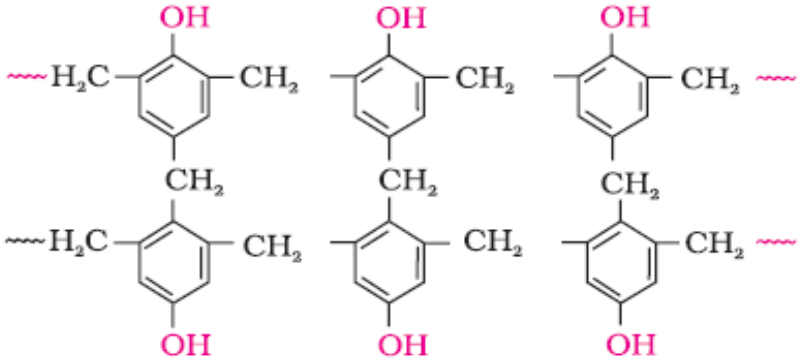
3. <u>Phenol - formaldehyde polymer (Bakelite and related polymers):</u>

These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst. Initially o-and p-hydroxymethylphenol derivatives are formed, which further react with phenol to form a linear product called *Novolac*. It is used in paints.



Novolac

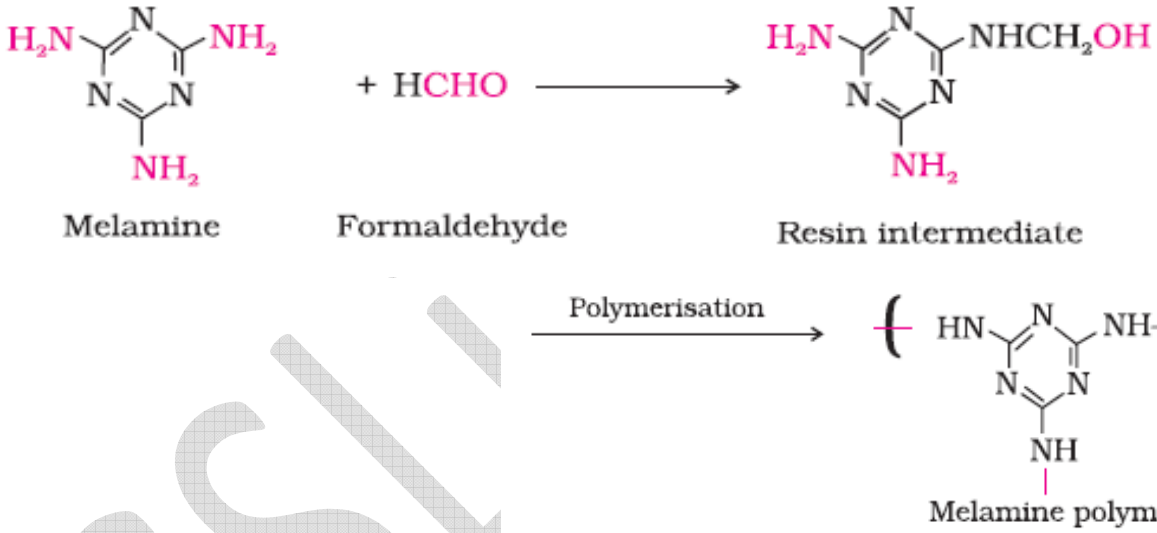
Novolac on heating with formaldehyde undergoes cross linking to form infusible solid mass called *bakelite.*



Bakelite

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

4. **Melamine – formaldehyde polymer:** It is formed by the condensation polymerisation of melamine and formaldehyde. It is used in the manufacture of unbreakable crockery.



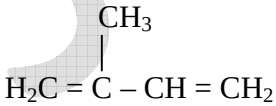
Melamine Formaldehyde Resin intermediate

Melamine polymer

RUBBER

1. **Natural rubber**:

It is a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as cis-1, 4 - polyisoprene.

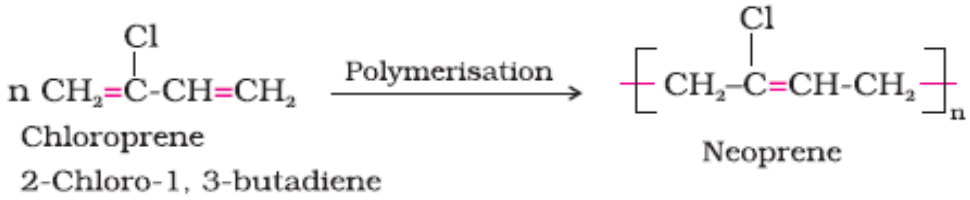


The various cis-polyisoprene chains are held together by weak van der Waals forces and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.

Vulcanisation of rubber

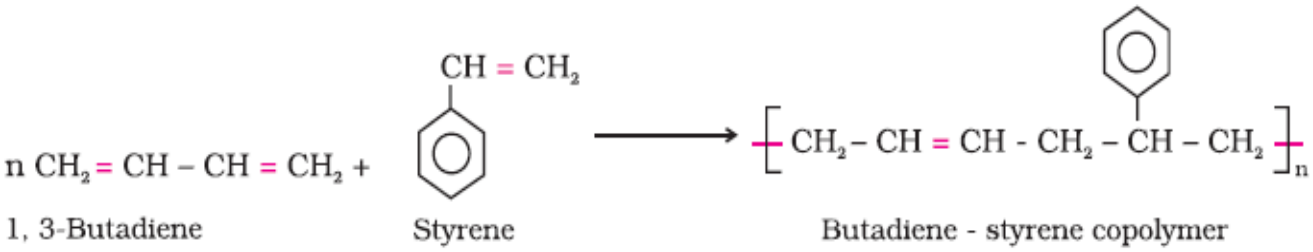
To improve the physical properties of natural rubber, it is heated with sulphur and an appropriate additive at a temperature of 373 to 415 K. This process is called vulcanisation. On vulcanisation, sulphur forms cross links between the different poly isoprene units and thus the rubber gets stiffened.

2. **Synthetic rubbers**: These are either homopolymers of 1, 3 - butadiene derivatives or copolymers of 1, 3 - butadiene or its derivatives with another unsaturated monomer. Some examples are:
   a) ***Neoprene (polychloroprene):*** It is formed by the polymerisation of chloroprene.



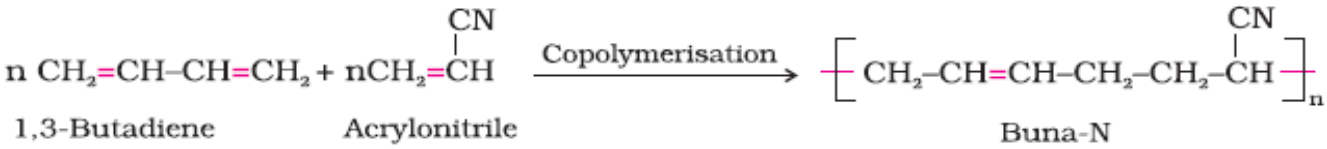
It is used for manufacturing conveyor belts, gaskets and hoses.

b) ***Buna - S:*** It is formed by the co-polymerisation of 1,3-butadiene with styrene.



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

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



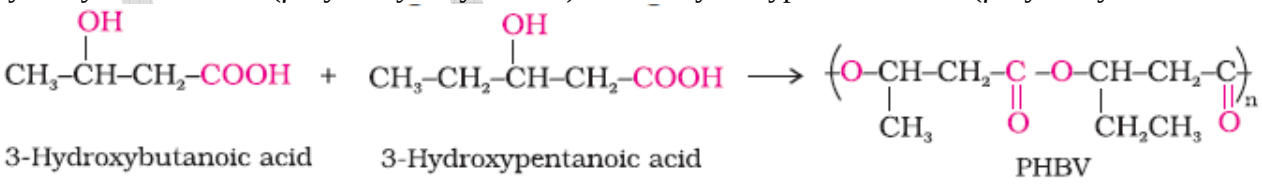
It is used in making oil seals, tank lining, etc.

Biodegradable Polymers

These are polymers which can be decomposed by micro organisms. They contain functional groups similar to the functional groups present in biopolymers like starch, cellulose etc.

Aliphatic polyesters are one of the important classes of biodegradable polymers. Some important examples are:

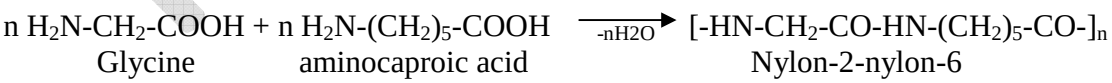
1. ***Poly β-hydroxybutyrate – co-β-hydroxy valerate (PHBV):*** It is obtained by the copolymerisation of 3-hydroxybutanoic acid (β-hydroxy butyric acid) and 3 - hydroxypentanoic acid (β-hydroxy valeric acid)



It is used in speciality packaging, orthopaedic devices and in controlled release of drugs.

2. ***Nylon 2–nylon 6:***

It is a copolymer of glycine ($H_2N–CH_2–COOH$) and amino caproic acid [$H_2N-(CH_2)_5-COOH$]



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