Chapter - 13 Polymers

* **Introduction:**
These are the most important products which surrounding us in every walk of life. Carbohydrates and proteins are the natural polymers and are important constituents of our food. Synthetic fibres and synthetic rubbers are all polymers. These are obtained by the polymerisation of certain substances.

* **Polymerization:-** It is defined as the process by which a large number of molecules (of small size) join to form a macro or a giant molecule of high molecular weight.

* **Polymers:-** Polymers are high molecular mass compounds whose structures are composed of a large no. of simple molecules.
Example: Polythene, PVC, Bakelite, Buna-S-rubber, Teflon etc.

* **Monomers:-** Monomer is the single repeating unit which on polymerization gives a polymer. For example, Ethene is the monomer unit of Polyethene polymer.

Ethene (Monomer) → Polyethene (Polymer)

* **Degree of Polymerisation:**
The no. of repeating units present in a polymer is called as the degree of polymerisation and it is denoted by the small letter (n).
If, $n > 10,000$, called high Polymer.
$n < 100 - 1500$, called low Polymer.

* **Homopolymer:** The polymer which is formed by the combination of one type of monomer or repeating units through covalent bonds in a regular fashion is called Homopolymer.
Example: Polythene, PVC, Polystyrene etc.

$\cdots\cdots M-M-M-M-M-\cdots\cdots$, where, M is the monomer unit.

* **Co-Polymer:**
A polymer which is formed from two or more different monomers through covalent bond is called Co-Polymer.

Example: Bakelite is a co-polymere of two monomeres: Phenol and formaldehy de

$\ldots\ldots M_1 - M_2 - M_1 - M_2 - M_1 - M_2 \ldots\ldots$, where M_1, M_2 are two types of monomeres.

* Types of Polymers :-

(A) Depending upon the sources, polymers may be classified into two types;

(i) Natural Polymers :- These are the polymers which occure in nature.

Ex :- Natural rubber, silk, Polysaccharides, starch, cellulose etc.

(ii) Synthetic Polymers :- These are the polymers which are manufactured in industries.

Ex :- Polythene, PVC, Bakelite, Teflon, Nylon, Buna-S etc.

(B) Depending upon the nature of Polymeric chain/structure, Polymers may be classified as:

(i) Linear Polymers :- These are the polymers in which the monomere units are linked to one another to form long linear chains.

Ex :- HDP, nylon and Polyesters etc.

(ii) Branched Chain Polymers :- In such Polymers, the monomere units are linked to form long chains with some branched chains of different lengths with source.

Ex :- LDP, starch, glycogen etc.

(iii) Cross-linked or network Polymers :- In such Polymers, the monomere units are linked together to form three-dimensional network like structure.

Ex :- Bakelite, glyptal, melamine-formaldehyde Polymer etc.

(C) Depending upon the mode of Polymerisation;

(i) Addition Polymers :- The Polymers formed by the polymerisation of monomeres containing double or tripple bonds (unsaturated compounds) without elimination of simple molecules are called addition Polymers.

Ex :- Polythene, PVC, Polystyrene etc.

(ii) Condensation Polymers :- The Polymers which are formed by the combination of monomeres with the elimination of small molecules such as water, alcohol, hydrogen chloride etc are known as condensation Polymers.

Ex :- Nylon-6,6, Bakelite etc.

Thermoplastic	Thermosetting
1. These are formed by addition Polymerisation.	These are formed by condensation Polymerisation.
2. These have usually linear structures.	These have 3-d cross-linked structures.
3. These soften and melt on heating and harden again on cooling.	These don't soften on heating but rather become hard. On prolonged heating, these started burening.
4. These can be remoulded, recast and reshaped.	These cannot be remoulded or reshaped.
5. These are less brittle and soluble in some organic solvents.	These are more brittle and insoluble in organic solvents.
6. Examples: Polythene, PVC, Nylon etc.	Examples: Bakelite, Terylene etc.

* **Polythene:**

$$n(CH_2=CH_2) \xrightarrow{\text{Polymerisation}} \{CH_2-CH_2\}_n$$

⇒ Low density Polythene (LDPE) is obtained by using free-radical initiators.
⇒ High density Polythene (HDPE) is obtained by using ionic catalysts.

(i) **Low density Polythene (LDPE):**

$$n(CH_2=CH_2) \xrightarrow[\text{1000 to 2000 atm}]{\text{350K - 570K}} \{CH_2-CH_2\}_n$$

Ethene (Traces of oxygen or a peroxide initiator) LDPE

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

Uses: It is used
⇒ in the insulation of electrical wires, cables.
⇒ manufacture of bottles, toys and flexible pipes.

(ii) **High density Polythene (HDPE):**

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

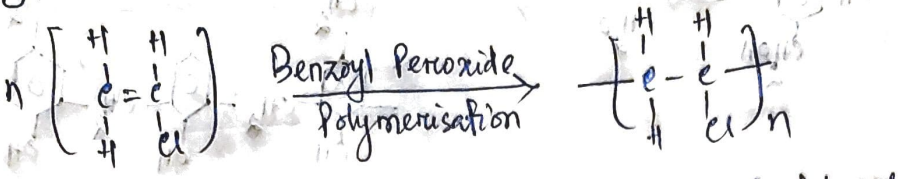
Ethene (Ziegler Natta catalyst) HDPE

It has high density due to close packing. It is also chemically inert, tougher and harder.

Uses: It is used
⇒ in making containers
⇒ house wares
⇒ bottles
⇒ toys,
⇒ electric insulation etc.

* PVC (Poly Vinyl Chloride) :

When vinyl-chloride undergo polymerisation in presence of a small quantity of benzoyl peroxide, poly-vinyl-chloride is formed.



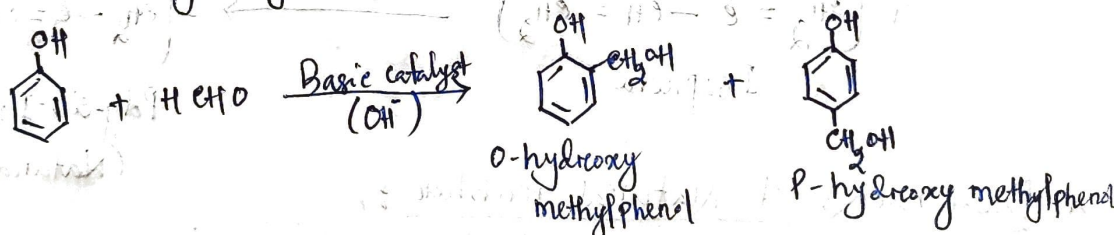
Vinyl chloride — Polyvinyl chloride

Uses : It is used for making :

- Sheets for tank lining.
- Safety helmets.
- Refrigerator components.
- Tyres, cycle and motorcycle mudguards.
- Raincoat Packing.
- Tablecloths.
- Electrical insulators.
- Chemical containers etc.

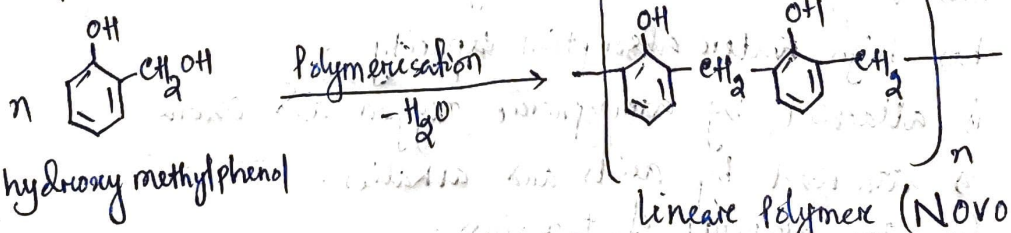
* Bakelite (Phenol-formaldehyde Resin) :

It is a co-polymer of Phenol and formaldehyde. When Phenol and formaldehyde are reacted together two isomeric compounds O-hydroxy methylphenol and P-hydroxymethylphenol are obtained.



O-hydroxy methylphenol — P-hydroxy methylphenol

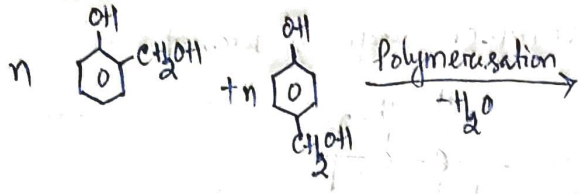
The O-hydroxy methylphenol undergoes polymerisation to form a linear polymer compound called "NOVOLAC".

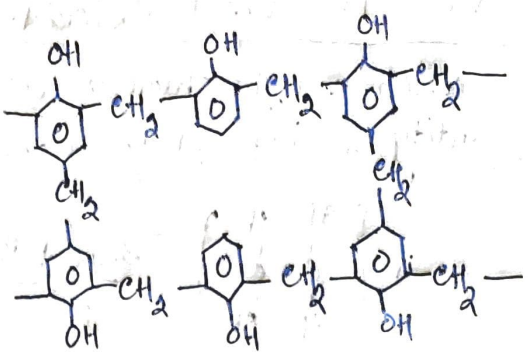


O-hydroxy methylphenol — Linear polymer (NOVOLAC)

During the process of polymerisation, a little quantity of hexamethylene tetraamine $[(CH_2)_6N_4]$ is added which converts "NOVOLAC" into a hard resinous mass called Bakelite.

Cross linking is also possible in the two isomeric benzyl alcohols to give cross-linked polymer.





Cross-linked Polymer - bakelite.

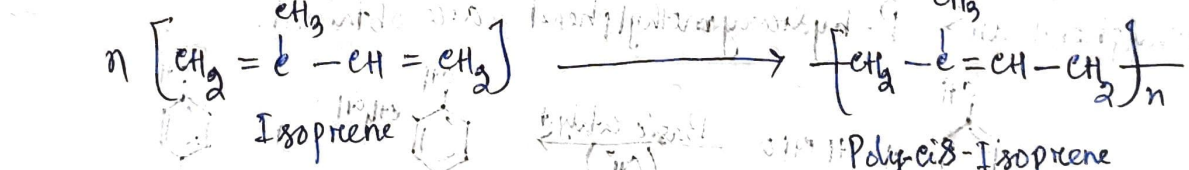
Uses: It is used in the manufacture of:

(i) Electrical insulators like plug, switch etc.
(ii) Cabinets for Radio and TV.
(iii) Telephone parts
(iv) Paints, varnishes.
(v) Hydrogen exchange resin for softening of hard water.

* Rubber:

Rubber is a naturally occuring polymer. It is obtained as latex from rubber trees. It is highly elastic. It can be easily deformed but regains its original shape after the stress is relieved.

Natural rubber consists of "isoprene" as the monomer units, which is in the form of the polymer poly cis-isoprene. Thus, natural rubber is nothing but the polymer poly cis-isoprene.



Isoprene

Poly-cis-Isoprene
(Natural rubber)

* Drawbacks of Natural rubber:

Natural rubber or raw rubber has the following drawbacks:

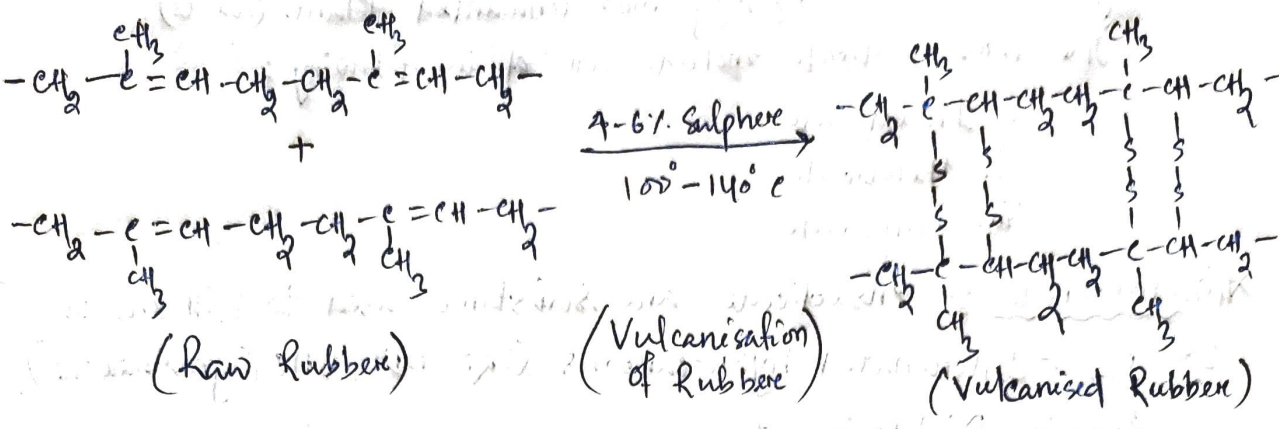
(i) It has very low thermal stability.
(ii) It has very low tensile strength.
(iii) It has high water absorption capacity.
(iv) It is attacked by atmospheric oxygen and ozone.
(v) It is attacked by acids and alkalies.
(vi) It has the property of tackiness.

* Vulcanisation of rubber:

Natural rubber is a thermoplastic. There are no cross links between the polymer chains. It becomes soft and sticky when heated. It is not hard and tough. The properties of natural rubber can be modified and improved by the process of vulcanisation. To improve the properties of natural rubber, it is heated with sulphur or sulphur

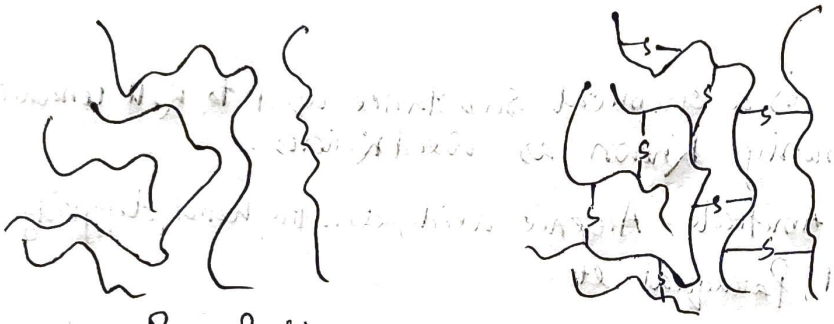
containing compounds at a temperature of 100°-140°C.

The chemical process in which natural rubber is heated upto 140°C with 4 to 6% sulphur or sulphur containing compounds with a view to overcome the drawbacks of natural rubber are called vulcanisation.



(Raw Rubber) (Vulcanisation of Rubber) (Vulcanised Rubber)

During vulcanisation, sulphur cross-links are formed in between the layers of polyisoprene at the carbon atoms containing double bond.



Raw Rubber Vulcanised Rubber

The formation of cross links makes rubber hard, tough with greater tensile strength. Although natural rubber is thermoplastic substance, yet on vulcanisation, it is set into a given shape which is retained.

* Advantages of Vulcanisation:

After vulcanisation, almost all the drawbacks of raw rubber are eliminated. Vulcanised rubber:

(i) has higher thermal stability.
(ii) has comparatively lower tensile strength.
(iii) has low water absorption capacity.
(iv) is not attacked by atmospheric oxygen and ozone.
(v) is resistant to acids and alkalies.