

Synthetic & Natural Polymers

1. Introduction :

- [a] A polymer is a compound of high molecular mass formed by the combination of large number of small molecules and process is called polymerisation. The small molecules which constitute the repeating units in a polymer are called monomer units. These large molecule have relative molecular masses in the range $10^4 - 10^6$.



Where n is as high as 10^5 . The number of monomers units in a polymer is called the degree of polymerisation.

- [b] **Homopolymer** : The polymer formed from one kind of monomer is called homopolymer.

e.g. Polyethylene

- [c] **Copolymer or mixed polymer** : Polymer formed from more than one kind of monomer units is called copolymer.

e.g. Buna – S

2. Classification of Polymers :

Polymers are classification on the following ways :

2.1 Classification based upon origin or source :

These are of two types based on source

- [a] Natural polymers whose source is animal and plants are called natural polymers eg. starch, cellulose, protein etc.

- [b] Synthetic polymers : These are man made polymers synthesised in the laboratory from low molecular weight compounds.

e.g. Nylon, dacron, bakelite, synthetic rubber, polystyrene etc.

2.2 Classification based on structure :

These are of three types based on structure :

[a] Linear polymers

[b] Branched chain polymers

[c] Cross linked polymers

- [a] **Linear polymers** : In which monomer units are linked together to form long straight chains. The polymeric chains are stacked over one another to give a well packed structure. Such polymers have high densities, high tensile strength and high melting point.

eg. Polythene, Nylon and polyesters

- [b] **Branched chain polymers** : In this type of polymers, the monomeric units are linked to constitute long chains (called main chain). There are side chains of different lengths which constitute branches. Branched chain polymers are irregularly packed and they have lower tensile strength and lower melting points as compared to linear polymers.

eg. Amylopectin

- [c] **Cross linked polymers** : The monomeric units are linked together to constitute a three dimensional network, Cross linked polymers are hard, rigid and brittle because of their network structure.

eg. Bakelite, Formaldehyde, resin etc.

2.3 Classification based on synthesis :

These are of two types based on synthesis :

[a] **Condensation polymerisation** : In this the monomer (same or different) units link with each other by the elimination of a small molecule (e.g. water, methyl alcohol) as a by product. The polymer formed is known as condensation polymer. Nylon and terylene are the most common examples.





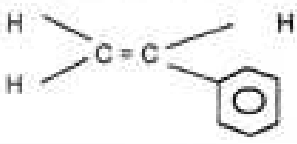
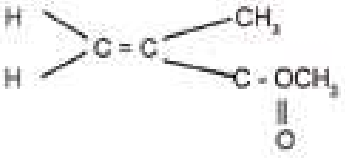
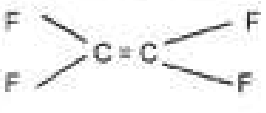
Since the condensation polymerisation proceeds by a stepwise intermolecular condensation, it is also known as step polymerisation and the polymer formed is known as step growth polymer.

[b] Addition polymerisation : This involves the self addition of several unsaturated molecules to one or two monomers without loss of any small molecule to form a single giant molecule. The polymer formed is known as addition polymer. Polythene is the most common example.

Differences between Addition and Condensation Polymers

S.N.	Addition Polymers	Condensation Polymers
1.	Formed by addition reaction	Formed by condensation process with elimination of small molecules like H ₂ O.
2.	Molecular mass is a whole number multiple of monomer.	Molecular mass is not whole number multiple of the monomer units.
3.	Generally involve one monomer unit.	Generally involve more than one monomer unit.
4.	Monomers are unsaturated molecules.	Monomer units must have two active functional groups.
5.	They are generally chain growth polymers.	They are generally step growth polymers.

SOME COMMON ADDITION POLYMERS

Monomer	Name	Polymer	Uses
	Ethylene	Polythene	Bags, toys, etc.
	Propylene	Polypropylene	Beakers, milk cartons etc.
	Vinyl chloride	Poly vinyl chloride (PVC)	Rain coats, pipes, tiles etc.
	Acrylonitrile	Poly acrylonitrile (PAN), Orlon	Carpets etc.
	Styrene	Polystyrene	Thermocole, insulating material etc.
	Methyl methacrylate	Perspex or plexiglass	Transparent objects lenses etc.
	Tetra fluoro ethylene	Teflon (PTFE)	Chemical equipment (Non stick cookware)

- 2.4 Classification based on interparticle forces :** The mechanical properties of polymers such as tensile strength, toughness, elastically etc depend upon intermolecular forces like vander wall forces and hydrogen bonds existing in the macromolecules. In polymers there is a combined effect of these forces all along chains longer chain are more intense in the effect intermolecular forces. Polymers have been classified into four categories.
- [a] Elastomers :** These are the polymers having elastic character. The polymer chains in such type of polymers are held together by weakest intermolecular forces. These forces permit the polymer to be stretched under stress but they regain their former shape when the stress is relieved. The elasticity of such polymers can be further modified by introducing few cross links between the chains.
eg. Natural rubber, a gummy material has poor elasticity, but heating gummy rubber with sulphur produced a material which was no longer sticky but had modified elasticity. Such a material was called vulcanised rubber.
- [b] Fibers :** These are the polymers which have quite strong interparticle forces such as H-bonds.
eg. Nylon, dacron etc.
- [c] Thermoplastics :** These are the polymers which can be easily moulded into desired shapes by heating and subsequent cooling to room temperature. The intermolecular forces in thermoplastic polymers are intermediate to those of elastomers and fibers. Thermoplastic polymers soften on heating and becomes fluids but on cooling they become hard.
eg. Polyethene and polystyrene
- [d] Thermosetting polymers :** These are the polymers which become hard and infusible on heating. Heating results in excessive cross linking between the chains forming three dimensional network of bonds.
eg. Bakelite, malamine

3. Molecular weight of Polymers :

There are two types of average molecular weight in case of polymers.

[a] \bar{M}_n = Number average molecular weight.

[b] \bar{M}_w = Weight average molecular weight.

[a] Number average molecular weight (\bar{M}_n)

$$(\bar{M}_n) = \frac{\text{Oxidation}}{\text{ation}} \rightarrow$$

If :

n_1 molecules are there of mol. wt. M_1 .

n_2 molecules are there of mol. wt. M_2 .

n_3 molecules are there of mol. wt. M_3 . Then

$$\bar{M}_n = \frac{n_1M_1 + n_2M_2 + n_3M_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

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

[b] Weight average molecular weight \bar{M}_w

$$\bar{M}_w = \frac{w_1M_1 + w_2M_2 + w_3M_3 + \dots}{w_1 + w_2 + w_3 + \dots}$$

[Weight = no. of molecules \times molecular weight]

Where : w_1 = weight of the molecules of mol. wt. M_1

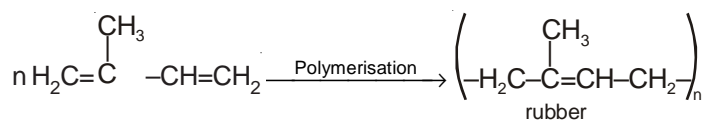
w_2 = weight of the molecules of mol. wt. M_2

w_3 = weight of the molecules of mo. wt. M_3

Note : It should be noted that $\bar{M}_w > \bar{M}_n$

4. Natural Rubber :

Preparation : When isoprene is heated with concentrated HCl, a rubber like material is obtained.

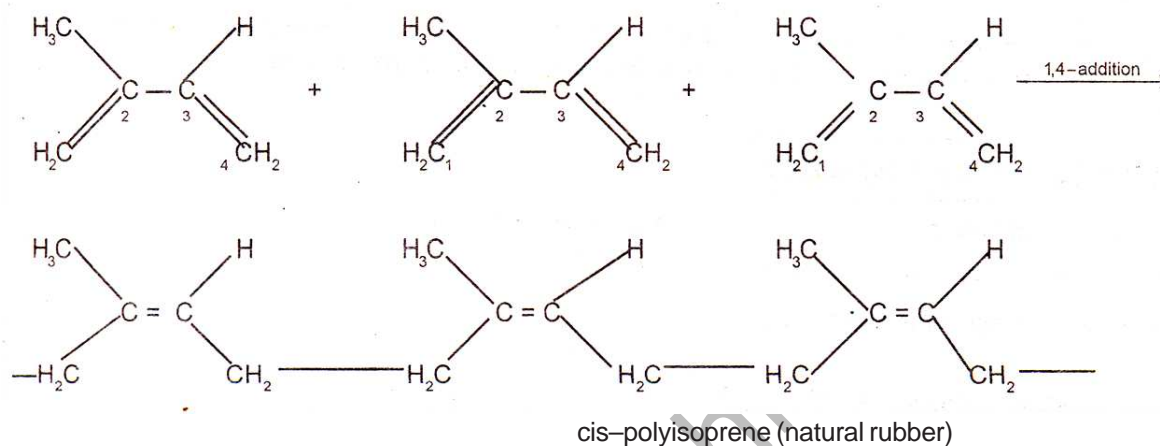


There are two kinds of natural rubber

[a] Natural rubber

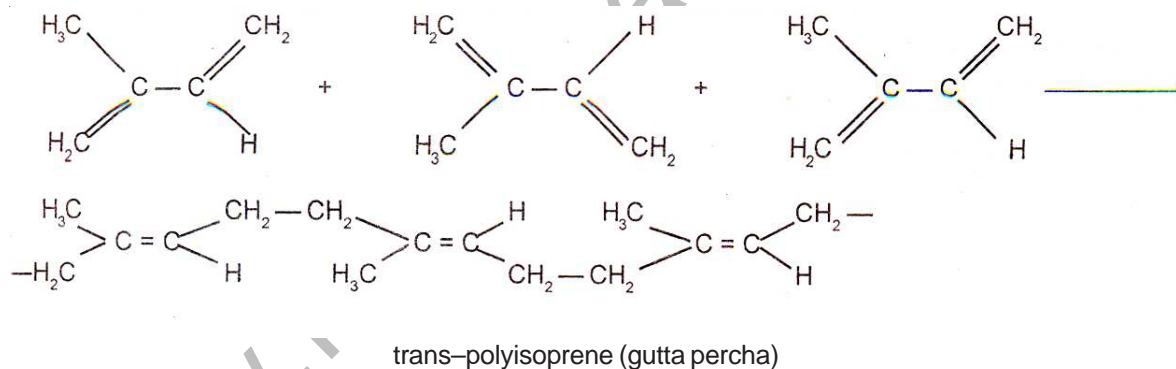
[b] Gutta percha

[a] Natural rubber



In the above structure all the $-\text{CH}_2-\text{CH}_2-$ groups are on the one side (cis form)

[b] Gutta percha

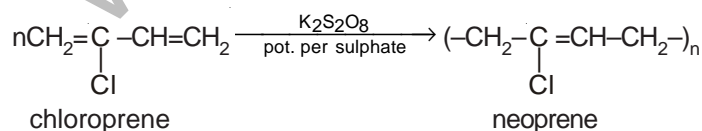


5. Some Important polymers :

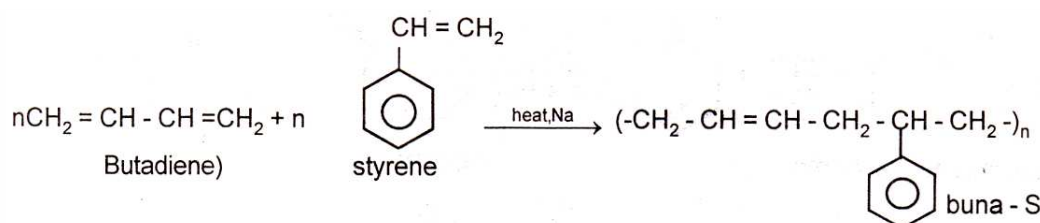
5.1 Addition polymers

[a] Polydienes :

[i] Neoprene



[ii] Buna S : It is copolymer of 1, 3 butadiene and styrene, It is obtained by the polymerisation of butadiene and styrene in the ratio of 3 : 1 in the presence of sodium.



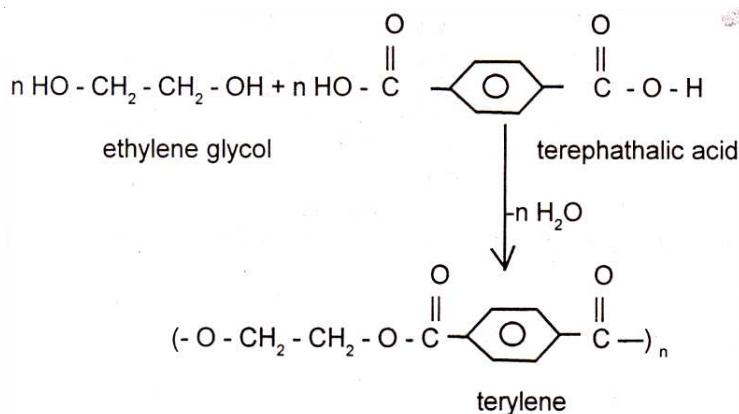
Uses : Buna – S is also vulcanised and used in making tyres for the vehicles. It is also used as rubber soles and in making water proof shoes.

5.2 Condensation polymers :

[a] Polyesters : These are the polymers having ester linkage ($-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$)

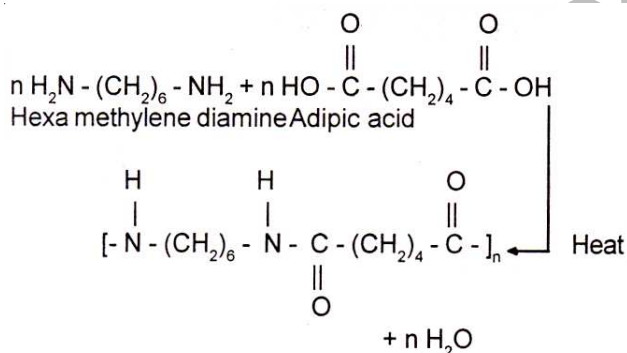
Examples :

[a] Terylene :



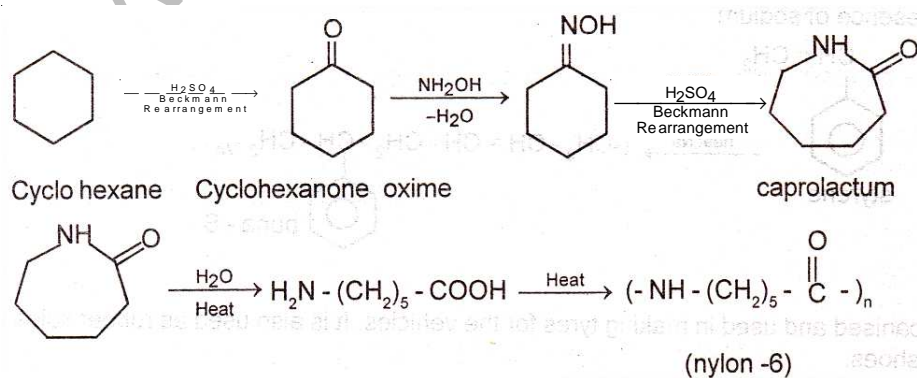
[b] Polyamides : Such polymers have amide linkage ($-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-$) in the chain

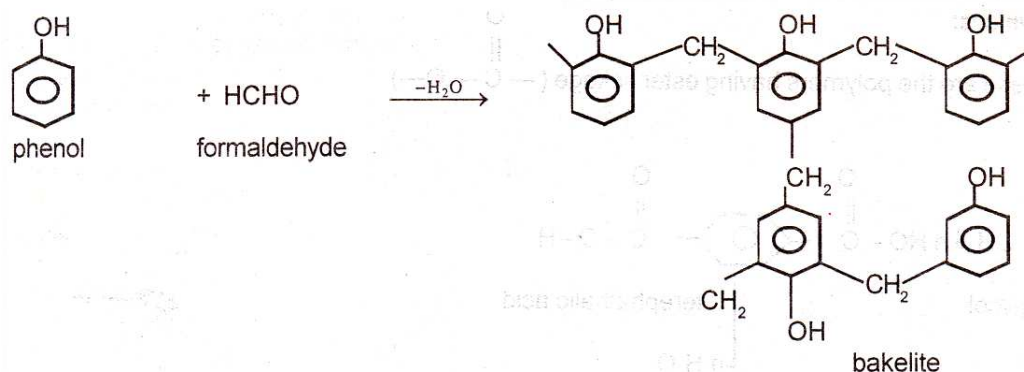
[i] Nylon – 66



Uses : Nylon 66 have high tensile strength so it is used in the manufacture of carpets, textile fibres and bristles for brushes. It is used in making elastic hosiery.

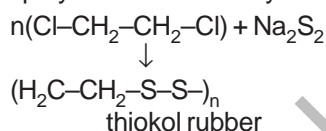
[ii] Nylon – 6



[c] Phenol – Formaldehyde resins (Bakelite)

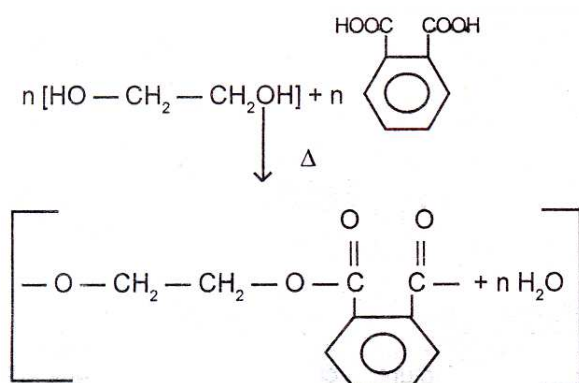
Because bakelite is hard and is a good electrical insulator, it is extensively used on making electrical switches, fuse holders, etc.

[d] Thiokol – It is prepared by the polymerisation of ethylene chloride with sodium polysulphide.



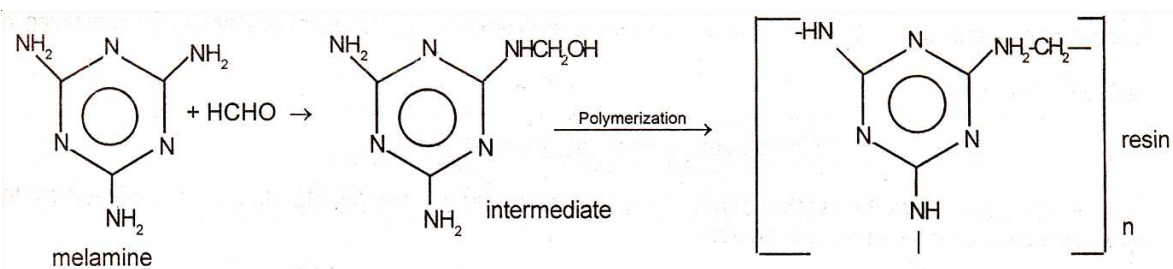
Uses : It is used for making gaskets, seals, pulleys etc.

[e] Glyptal or (alkyl resin) : The most simple glyptal (polyethylene phthalate) formed from the polycondensation of glycol and phthalic acid.



Uses : It is used in the manufacture of paints and lacquers.

[f] Melamine formaldehyde resin : Melamine formaldehyde resin is formed by the co-polymerisation of melamine and formaldehyde.



Uses : It is used for making non breakable plastic crockery i.e. cup plates etc.

[g] In vucanisation rubber is cured by heating (3 hrs) it with sulphur (3–10%) at a temperature of 125–140°C. Rubber hydrocarbon combines with the sulphur atoms to form the sulphur bridges. The resulting products is tough, non–elastic and resistance to heat. It becomes non abrasive and not affected by chemicals.

