Chapter : Polymers

Top concepts

1. Polymers are high molecular mass substance consisting of large number of repeating structural units. As polymers are single, giant molecules i.e. big size molecules, they are also called macromolecules

2. Simple molecules which combine to form polymers are called monomers

3. Process of formation of polymers from respective monomers is called polymerization

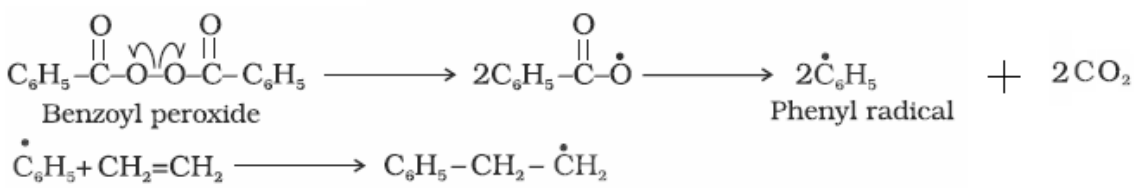
4. Classification of Polymers

No.	Classification based on	Types		Examples
1.	Source of availability	1. Natural polymers: Polymers obtained from nature,mostly plants and animals		Cellulose, starch, etc.
		2. Synthetic polymers: Polymers prepared in laboratory		Teflon, Nylon 6,6 , Synthetic rubber (Buna - S) etc.
		3. Semi synthetic polymers: Polymers derived from naturally occurring polymers by carrying out chemical modifications		Rayon (cellulose acetate), cellulose nitrate, etc.
2.	Structure of polymer	1. Linear polymers: Polymer consist of long and straight chains		High density polythene, polyvinyl chloride, etc.
		2.Branched chain polymers: Polymers contains linear chains having some branches		Low density polythene
		3.Cross linked or network polymers: Polymers in which monomer units are cross linked together to form a 3 dimensional network polymers		Bakelite, melamine, etc.
3.	Mode of polymerisation	1.Addition polymers :Polymers are formed by the repeated addition of monomers with double and triple bonds	1.Homopolymers: Polymers formed by the polymerisation of a single monomeric species	Polythene, Polystyrene
			2.Copolymers: Polymers formed by addition polymerisation of two different	Buna-S, Buna -N

		monomers	
		Condensation polymers: Polymers formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units with elimination of simple molecules	Nylon 6, 6, Nylon 6
4.	Molecular forces	1. Elastomers: Polymer chains are held together by weakest intermolecular forces. Polymers are rubber – like solids with elastic properties	Buna – S, Buna – N, Neoprene
		2. Fibre: Polymers have strong intermolecular force like hydrogen bonding. Fibres are the thread forming solids which possess high tensile strength and high modulus	Nylon 6, 6, Polyesters
		3. Thermoplastic polymers: Polymers are held by intermolecular forces which are in between those of elastomers and fibres. These polymers are capable of repeated softening on heating and hardening on cooling	Polythene, Polystyrene
		4. Thermosetting polymers: Polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and eventually undergoes a permanent	Bakelite, Urea-formaldelyde resins

5. Addition Polymerisation or Chain Growth Polymerisation: Most common mechanism for addition polymerisation reactions is free radical mechanism Steps involved are:

Step 1: Chain initiating step: Organic peroxides undergo homolytic fission to form free radicals which acts as initiator. Initiator adds to C-C double bond of an alkene molecule to form a new free radical



Step 2: Chain propagating step: Free radicals formed by homolytic cleavage adds to a double bond of monomer to form a larger free radical. Radical formed adds to another alkene molecule to form a larger free radical. This process continues until the radical is destroyed. These steps are called propagation steps.

$$C_6H_5-CH_2-\dot{C}H_2 + CH_2 = CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$\downarrow$$

$$C_6H_5\left(CH_2-CH_2\right)_n CH_2-\dot{C}H_2$$

Step 3: Chain terminating step: For termination of the long chain, free radicals combine in different ways to form polythene. One mode of termination of chain is shown as under:

$$\begin{matrix} C_6H_5\left(CH_2-CH_2\right)_n CH_2-\dot{C}H_2 \\ C_6H_5\left(CH_2-\overset{+}{C}H_2\right)_n CH_2-\dot{C}H_2 \end{matrix} \longrightarrow \underset{\text{Polythene}}{C_6H_5\left(CH_2-CH_2\right)_n CH_2-CH_2-CH_2-CH_2\left(CH_2-CH_2\right)_n C_6H_5}$$

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

6 .Important Addition Polymers:

No.	Name of polymer	Polymerisation Reaction & Uses
1	Low density polythene (LDP)	$\underset{\text{Ethene}}{nCH_2 = CH_2} \xrightarrow[\text{1000 to 2000 atm, Traces of } O_2]{350-570K} \underset{\text{Polythene}}{\left(CH_2-CH_2\right)_n}$ Uses: It is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes
2	High density polythene(HDP)	$\underset{\text{Ethene}}{nCH_2 = CH_2} \xrightarrow[\text{6 –7atm, Zieglar Natta catalyst}]{333-343\,K} \underset{\text{Polythene}}{\left(CH_2-CH_2\right)_n}$

		Uses: It is used for manufacturing buckets, dustbins, bottles, pipes, etc.
3	Polytetrafluoroethene (Teflon)	$n\,CF_2 = CF_2 \xrightarrow[\text{High pressure}]{\text{Catalyst}} \left[CF_2 - CF_2\right]_n$ Tetrafluoroethene → Teflon Uses: It is used in making oil seals and gaskets and also used for non – stick surface coated utensils
4	Polyacrylonitrile	$n\,CH_2 = CHCN \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerisation}} \left[CH_2 - \overset{\overset{\displaystyle CN}{\vert}}{CH}\right]_n$ Acrylonitrile → Polyacrylonitrile Uses: It is used as a substitute for wool in making commercial fibres as orlon or acrilan

7. Condensation Polymerisation or Step Growth polymerization:
Polymerisation generally involves a repetitive condensation reaction between two bi-functional monomers. In condensation reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on. Since, each step produces a distinct functionalised species and is independent of each other, this process is also called as step growth polymerisation.

8 .Important Condensation Polymers:
1. Polyamides: Polymers possess amide linkage (-CONH-) in chain. These polymers are popularly known as nylons.
Examples:

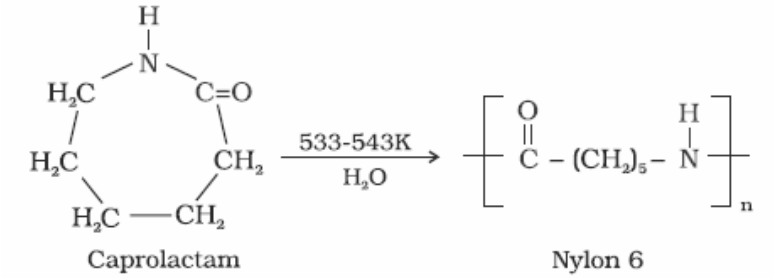
(a) Nylon 6, 6: It is prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.

$$n\,HOOC(CH_2)_4COOH + n\,H_2N(CH_2)_6NH_2 \xrightarrow[\text{High pressure}]{553K} \left[\overset{\overset{\displaystyle H}{\vert}}{N}-(CH_2)_6-\overset{\overset{\displaystyle H}{\vert}}{N}-\overset{\overset{\displaystyle O}{\Vert}}{C}(CH_2)_4-\overset{\overset{\displaystyle O}{\Vert}}{C}\right]_n$$

Nylon 6,6

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

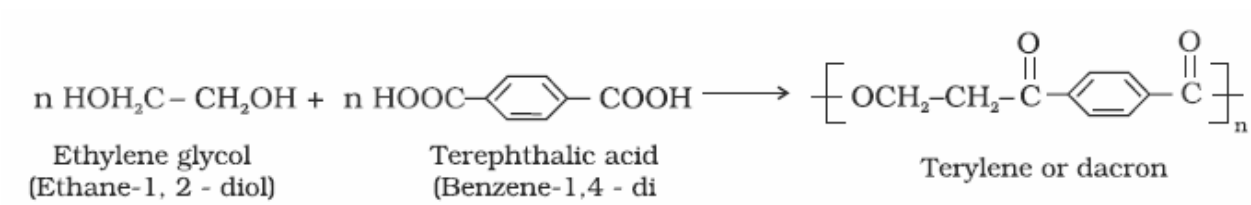
(b) Nylon 6: It is obtained by heating caprolactum with water at a high temperature



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

(2) Polyesters: These are the polycondensation products of dicarboxylic acids and diols
Example: Terylene or Dacron

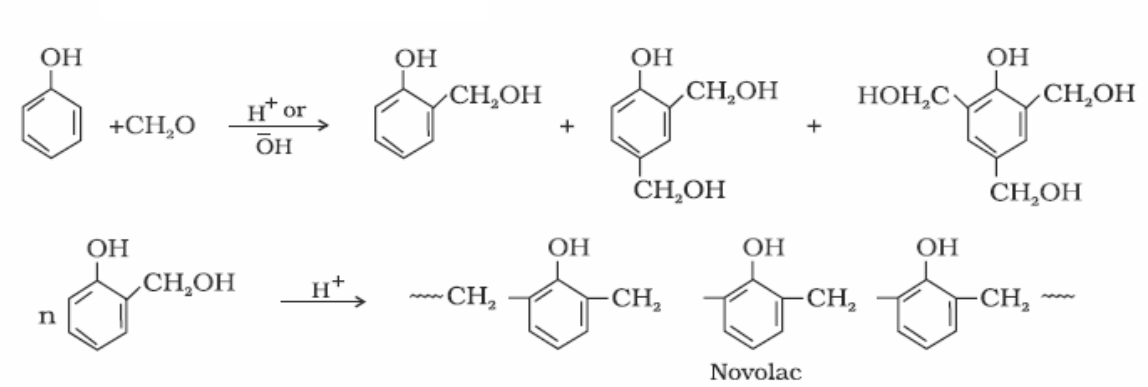
Terylene or Dacron: It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetate-antimony trioxide catalyst



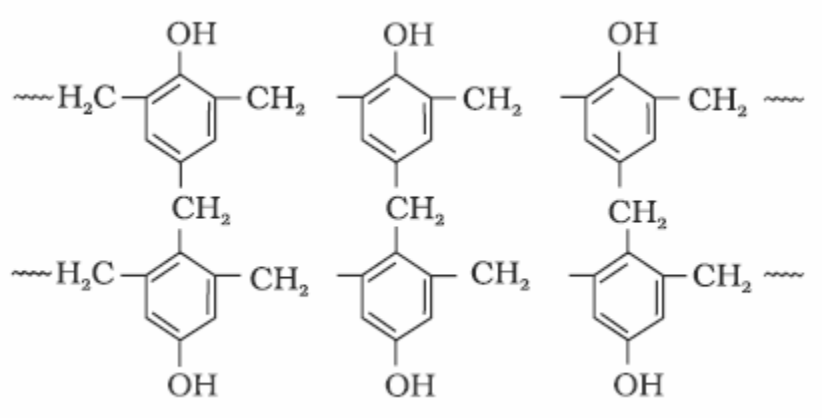
Uses: Dacron fibre (terylene) is crease resistant and is used in blending with cotton and wool fibres and also as glass reinforcing materials in safety helmets, etc.

3. Phenol - formaldehyde polymer (Bakelite and related polymers)

Bakelite: 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 could be a linear product – Novolac used in paints.

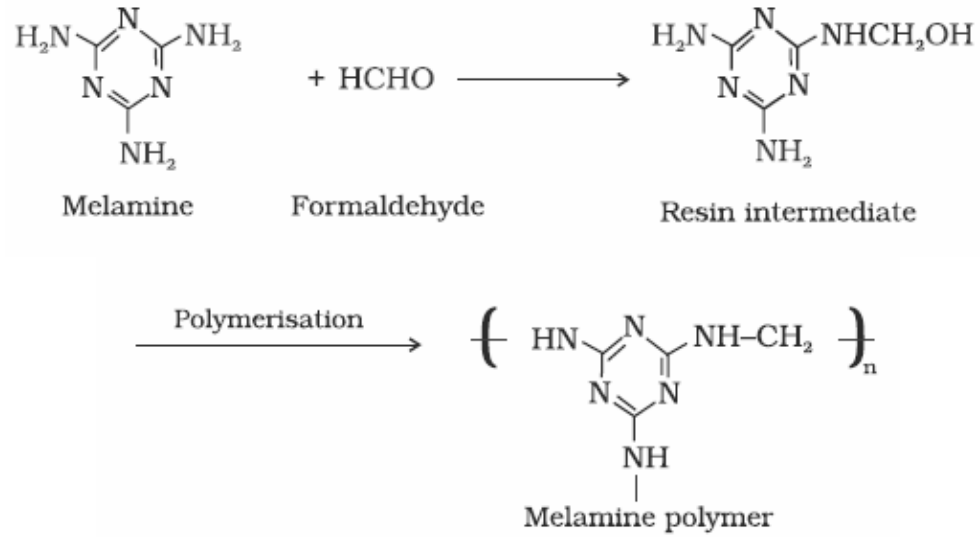


Novolac on heating with formaldehyde forms Bakelite



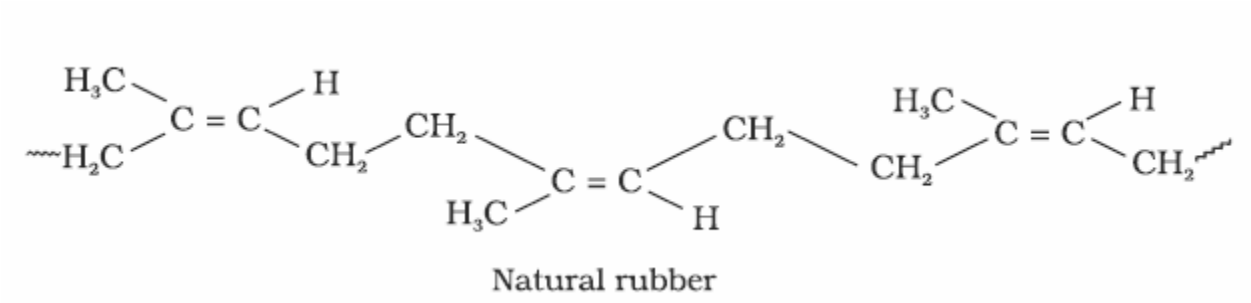
Uses: It is used for making combs, phonograph records, electrical switches and handles of various utensils

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



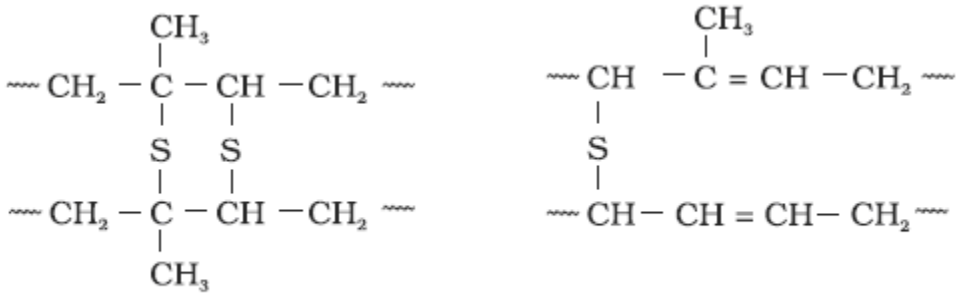
Uses: It is used in the manufacture of unbreakable crockery

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



Natural rubber

Vulcanisation of rubber*:* Process of heating a mixture of raw rubber with sulphur and an appropriate additive in a temperature range between 373 K to 415 K to improve upon physical properties like elasticity, strength etc.

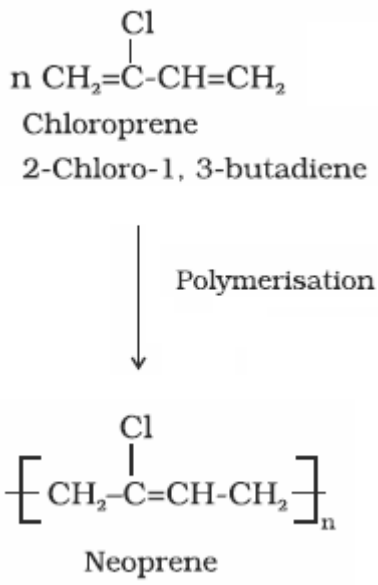
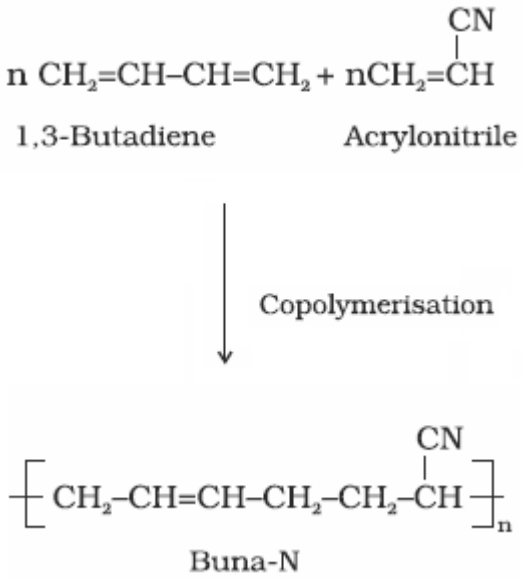


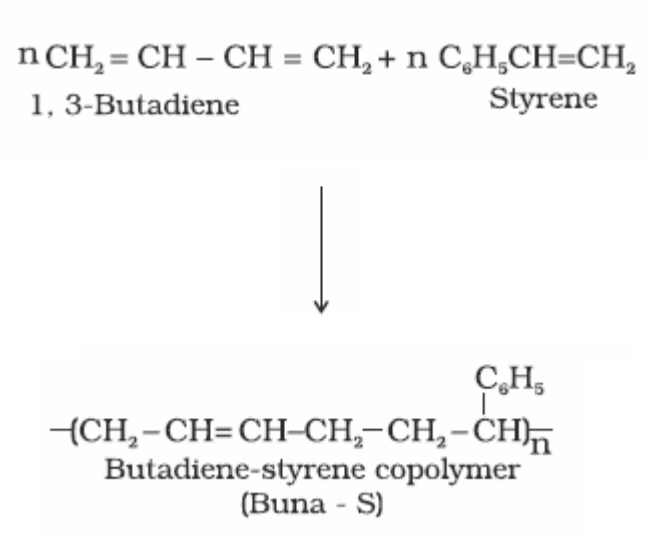
Sulphur cross links in vulcanised rubber

(ii) 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:

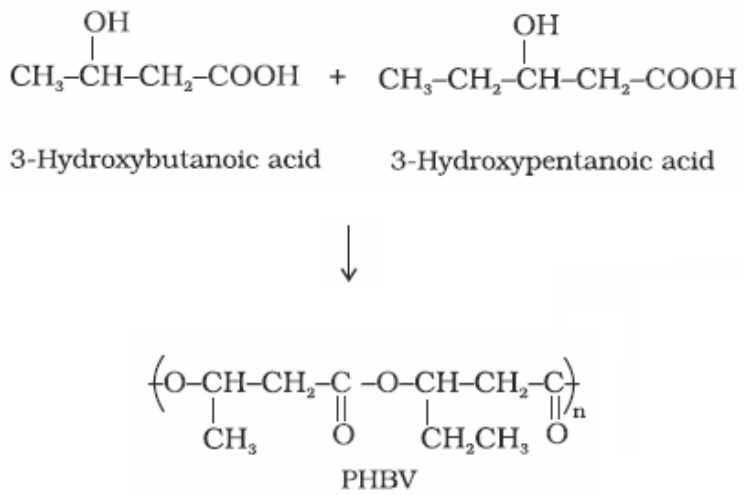
No.	Name of polymer	Polymerisation Reaction and uses
1	Neoprene or polychloropre ne	

		 Uses: It is used for manufacturing conveyor belts, gaskets and hoses
2	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
3	Buna – S	

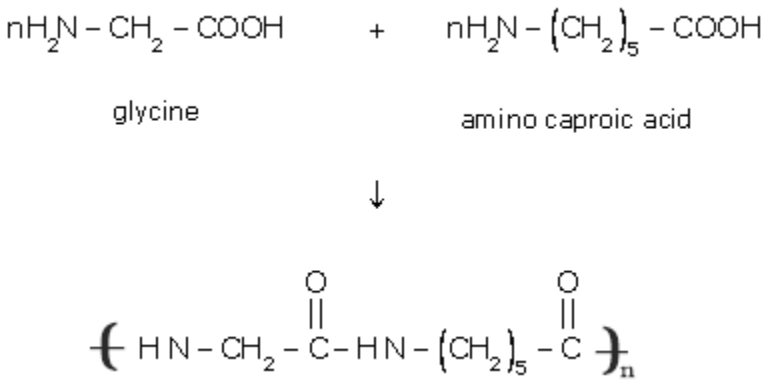
10. Biodegradable Polymers: Polymers which are degraded by microorganisms within a suitable period so that biodegradable polymers and their degraded products do not cause any serious affects on environment

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

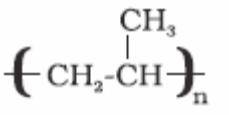
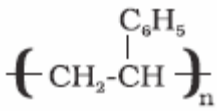
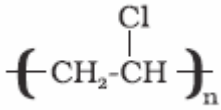
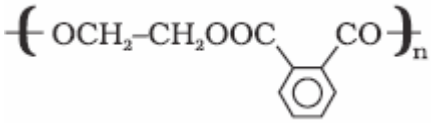


Uses: PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs

2. Nylon 2–nylon 6: It is an alternating polyamide copolymer of glycine ($H_2N–CH_2–COOH$) and amino caproic acid ($H_2N\ (CH_2)_5\ COOH$)



11. Some commercially important polymers along with their structures and uses

Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene		Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene		As insulator, wrapping material, manufacture of toys, radio and television cabinets
Polyvinyl chloride (PVC)	Vinyl chloride		Manufacture of rain coats, hand bags, vinyl flooring, water pipes
Glyptal	(a) Ethylene glycol Manufacture of (b) Phthalic acid		Manufacture of paints and lacquers