15. POLYMERS

Polymers (*poly*[G]= many + *mer*[G] =units) are **macromolecules**, made by linking together repeating units of small molecules called **monomers**. The process of linking respective monomers is called ***polymerisation***.

CLASSIFICATION

Based on	Polymer	Definition	Examples
Source	1. ***Natural***	Polymers found in nature, *i.e.*, in plants and animals.	Proteins, Starch, rubber
	2. ***Synthetic***	Polymers prepared in the laboratories.	Polythene, PVC, nylon 6,6 (fibre), Buna – S (rubber)
	3. ***Semi-synthetic***	Polymers obtained by chemically treating a natural polymer	Cellulose acetate (rayon), Vulcanized rubber
Structure	1. ***Linear***	Polymers contain long and straight chains of monomers	High Density Polythene (HDP), PVC
	2. ***Branched chain***	Polymers contain linear chains having some branches.	Low Density Polythene(LDP)
	3. ***Cross linked / Network polymers***	Polymers in which the monomers are cross-linked together between various linear polymer chains	Bakelite, Melamine
Type of monomers	1. ***Homopolymers***	Polymers those made of single type of monomer unit.	Polythene, Polystyrene, Polypropene
	2. ***Copolymers***	Polymers those made of different types of monomer units.	Buna-S, Buna-N
Mode of Polymerisation	1. ***Addition***	Polymers formed by repeated **addition** of same or different monomers having multiple bonds.	Polythene Teflon, Polyacrylonitrile **(**PAN)
	2. ***Condensation***	Polymers formed by the repeated **condensation** between monomer units with the elimination of small molecules such as water, alcohol, HCl etc.	Nylon, Bakelite, Terylene
Molecular Forces	1. ***Elastomers***	Polymers possessing an **elastic character**. In elastomers, the polymer chains are held together by the **weakest intermolecular forces** (van der Waal's force). So they can be stretched.	Buna-S, Buna-N, Neoprene
	2. ***Fibres***	Long, **thread-like** polymers. Here the different polymer chains are held together by **strong intermolecular forces** like H-bonding which gives high tensile strength.	Nylon-6,6, Nylon-6, Terylene
	3. ***Thermoplastic***	Polymers having **intermolecular forces of attraction in between that of elastomers and fibres.** These are the linear or slightly branched long chain polymers capable of repeatedly softening on heating and hardening on cooling (physical change).	Polythene, Polystyrene, PVC
	4. ***Thermosetting***	Polymers having **cross-linked or heavily branched molecules**. On heating they undergo extensive cross links and become infusible (chemical change, so they cannot be reused).	Bakelite, Urea-formaldelyde resins

METHODS OF POLYMERISATION

There are two types of polymerisation reactions- **addition** and **condensation**.

I) Addition Polymerisation or Chain Growth Polymerisation

This type of polymerisation proceeds through repetitive addition reaction between unsaturated monomers.
The process consists of 3 steps:

Step 1. Chain Initiation: Providing some reactive species like free radicals. These free radical then attack an unsaturated monomer and form a new and larger free radical.

$$R^{\bullet} + C=C \longrightarrow RC-C^{\bullet}$$

free radical   *unsaturated monomer*   *(or M)*

Step 2. Chain Propagation: The free radical formed goes on successively adding monomers and thus, grows the chain.

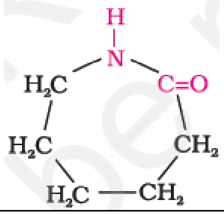
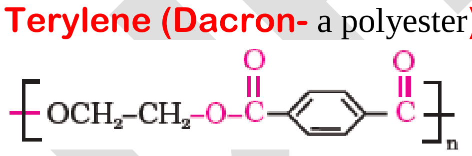
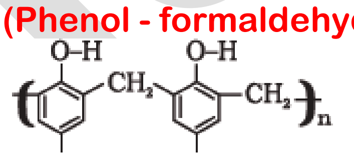
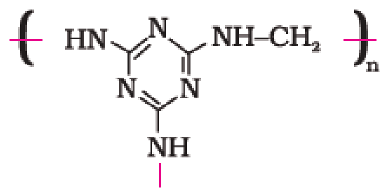
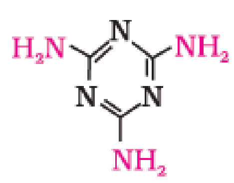
$$MM^{\bullet} + M \longrightarrow MMM^{\bullet}$$

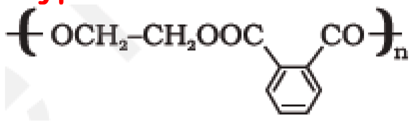
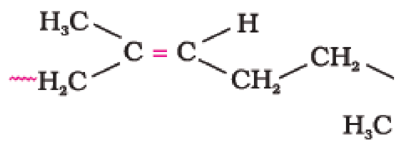
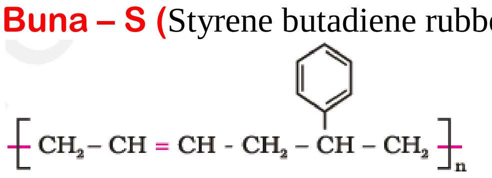
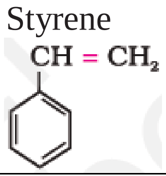
Step 3. Chain Termination: Finally, two free radicals combine together to form the polymerised product.

$$MMMMMM^{\bullet} + {}^{\bullet}MMMMMM \longrightarrow MMMMMMMMMMMM$$

II) Condensation Polymerisation or Step Growth polymerisation

This type of polymerisation proceeds through repetitive condensation reaction between two **bi-functional monomers**, results in the loss of some simple molecules like H_2O, CH_3OH etc., and lead to the formation of high molecular mass polymers.
Since it progress in step by step manner, it is also called as **step growth polymerisation**.

No.	Polymer	Monomer	Formation	Physical Properties	Uses
IMPORTANT ADDITION POLYMERS					
1	**Polythene** $-[CH_2-CH_2]_n-$	Ethene $CH_2 = CH_2$	***Low density polythene (LDP):*** Polymerisation of ethene under 2000 atm. at 350-570 K in the presence of a catalyst. ✓ *Density*- **0.92g/cm^3**	Inert, tough, transparent, flexible and a poor conductor of electricity.	As insulator of electric wires, making of squeeze bottles, flexible pipes.
			High density polythene (HDP): Polymerisation of ethene in a hydrocarbon solvent in the presence of **Ziegler-Natta** catalyst at 333-343 K and under 6-7atm. ✓ *Density*- **0.97g/cm^3**	Has a high density due to close packing. It is chemically inert and more tough and hard.	In making of buckets, dustbins, bottles, pipes, etc.
2	**Teflon (Polytetrafluoroethene)** $-[CF_2-CF_2]_n-$	Tetrafluoroethene $CF_2 = CF_2$	Heating **tetrafluoroethene** with a free radical or persulphate catalyst at high pressures.	It is chemically inert and resistant to attack by corrosive reagents.	In making oil seals and gaskets, for non-sticky pans.
3	**Polyacrylonitrile (PAN)** $-[CH_2-CH(CN)]_n-$	Acrylonitrile (Cyanoethene) $CH_2 = CHCN$	Polymerisation of **acrylonitrile** in presence of a peroxide catalyst	--	In making of synthetic wool, fibres (orlon).
4	**Polypropene** $-(CH_2-CH(CH_3))_n-$	Propene	--	--	In making of ropes, toys, pipes, fibres, etc.
5	**Polystyrene** $-(CH_2-CH(C_6H_5))_n-$	Styrene (Phenylethene)	--	--	As insulator, making of toys, television cabinets etc.
6	**Polyvinyl chloride (PVC)** $-(CH_2-CH(Cl))_n-$	Vinyl chloride	--	--	In making of rain coats, vinyl flooring, water pipes.
IMPORTANT CONDENSATION POLYMERS					
7	**Nylon 6,6** (Simultaneously prepared in New York & London) $-[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO]_n-$	(a)Hexamethylene diamine $nNH_2(CH_2)_6NH_2$ (b) Adipic acid $HOOC(CH_2)_4COOH$	Polymerisation of **hexamethylenediamine** with **adipic acid** under high pressure and at 553K.	--	In making sheets, brushes, rope and in textile industry.
8	**Nylon 6 (*Perlon*)** $-[CO-(CH_2)_5-NH]_n-$	Caprolactum 	Heating caprolactum with water at 533-543 K	--	In making tyre cords, fabrics and ropes
9	**Terylene (Dacron-** a polyester**)** 	(a) Ethylene glycol HOH_2C-CH_2OH (b) Terephthalic acid 	Heating **ethylene glycol** and **terephthalic acid** at 420 -460 K in the presence of **zinc acetate - antimony trioxide** catalyst	Blend with cotton, wool fibres and also as glass reinforcing material.	In the making of fabrics, safety helmets.
10.	**Bakelite (Phenol - formaldehyde resin)** 	(a) Phenol  (b) Formaldehyde CH_2O	Reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst.	Electrical insulator	For making combs, electrical goods, handles of utensils and computer discs.
11.	**Melmac (Melamine - formaldehyde resin)** 	(a) Melamine  (b) Formaldehyde CH_2O	Formed by the polymerisation of melamine and formaldehyde	--	In making of unbreakable crockery

12	**Urea-formaldehyde resin** $\left(NH-CO-NH-CH_2 \right)_n$	(a) Urea (b) Formaldehyde	--	--	For making unbreakable cups and laminated sheets.
13	**Glyptal** 	(a) Ethylene glycol (b) Phthalic acid	--	--	In making paints and lacquers.
IMPORTANT RUBBERS					
14	**Natural rubber** 	Isoprene (2-methyl-1,3-butadiene) $H_2C=C(CH_3)-CH=CH_2$	--	Can be stretched	--
			Vulcanised rubber - Natural rubber is heated with 3-5% sulphur at a 373 - 415 K.	The rubber gets hardened (as sulphur forms cross links between the units)	--
15	**Neoprene (Polychloroprene)** $\left[CH_2-C(Cl)=CH-CH_2 \right]_n$	Chloroprene (2-chloro-1,3-butadiene) $CH_2=C(Cl)-CH=CH_2$	Polymerisation of chloroprene in the presence of Ziegler-Natta catalyst	--	In making conveyor belts, gaskets and hoses
16	**Buna – S** (Styrene butadiene rubber) 	(a) 1,3-butadiene $CH_2=CH-CH=CH_2$ (b) Styrene 	Formed by the co-polymerisation of 1,3-butadiene with styrene	Tough and is a good substitute for natural rubber	In making autotyres, floor tiles, footwear components, etc.
17	**Buna – N** (Nitrile rubber) $\left[CH_2-CH=CH-CH_2-CH_2-CH(CN) \right]_n$	(a) 1, 3 – butadiene $CH_2=CH-CH=CH_2$ (b) Acrylonitrile $CH_2=CH(CN)$	Copolymerisation of 1, 3 – butadiene and acrylonitrile in the presence of a peroxide catalyst.	Resistant to the action of petrol, lubricating oil and organic solvents.	In making oil seals, tank lining, etc.
BIODEGRADABLE POLYMERS					
18	**Poly β-hydroxybutyrate – co-β-hydroxy valerate (PHBV)** $\left(O-CH(CH_3)-CH_2-C(=O)-O-CH(CH_2CH_3)-CH_2-C(=O) \right)_n$	(a) 3- hydroxybutanoic acid (β-hydroxy butyric acid) $CH_3-CH(OH)-CH_2-COOH$ (b) 3 - hydroxypentanoic acid (β-hydroxy valeric acid) $CH_3-CH_2-CH(OH)-CH_2-COOH$	Copolymerisation of 3-hydroxybutanoic acid and 3 - hydroxypentanoic acid	--	In packaging, orthopaedic devices and in controlled drug release.
19	**Nylon 2–nylon 6** $\left[C(=O)-CH_2-NH-C(=O)-(CH_2)_5-NH \right]$	(a) Glycine H_2N-CH_2-COOH (b) Amino caproic acid $NH_2-(CH_2)_5-COOH$	Copolymerisation of glycine and amino caproic acid	--	Surgical sutures, food wrappers