POLYMER CHEMISTRY

Polymers & monomers :

Polymers are macromolecules build up by the linking together of large numbers of molecules much smaller molecules. Therefore polymers are made by the repealation of small, simple chemical units.

The small molecules that combine with each other to form polymer molecules are termed monomer. The repeat unit of the polymer is usually equivalent or nearly equivalent to the monomer and its numbers may be hundreds, thousands, tens of thousands and more.

Ex —

Repeal-unit	Monomer	Polymer
$-CH_2-CHCl-$	$CH_2=CHCl$	Poly (Vinylchloride)

Degree of polymerisation :

The reactions by which monomers combine to form polymer are termed polymerisation. The length of the polymer chain is specified by the number of repeat unit in the chain. This is called the degree of polymerisation (Dp). The subscript 'n' is used on the parentheses in the foregoing structural formulas for polymers to represent this Dp.

Example :

$$-\left(CH_2-CH_2\right)_5 \qquad Dp = 5$$

Molecular weight of polymer is given by —

$$M = Dp \times M_0$$

M = p molecular weight of polymer

M_0 = Molecular weight of Monomer / formula weight of the repealing unit.

Ex —

If Dp is 1000 for poly (vinylchloride), then its molecular weight will be —

$$63 \times 1000 = 63000$$

Classifications of polymers :

Polymers are obtained from different sources and can have different chemical, structurals, physical properties, mechanical behaviors, thermal characteristics etc and can be classified in the different ways —

1. Natural and synthetic polymers :

Natural polymers :

Those isolated from natural materials are called natural polymers.

Ex — cotton, silk, wool, rubber etc.
(cellophane, cellulose, rayon, leather etc are modified natural polymers)

Synthetic polymers :

Polymers synthesized from low molecular compounds are called synthetic polymers.

Ex — Polyethylene, PVC, nylon, teflylene.

2. Organic and Inorganic polymers :

Organic polymers :

A polymer whose backbone chain is essentially made of carbon atoms is called organic polymer.

Ex — The majority of synthetic polymer is organic, Polyethylene, PVC etc.

Inorganic polymers :

Polymers which generally contain no C-atom in their backbone chain is called the Inorganic polymer.

Ex — Glass, silicone, rubber etc.

3. Thermoplastic and thermosetting polymers :

▸ Thermoplastic polymers :

Some polymer soften on heating and can be converted into any shape that they can retained on cooling. The process of heating, reshaping and retaining the same on cooling can be repeated several times. Such polymers are called thermoplastic polymers.

Ex — Polyethylene, PVC, nylon, sealing wax etc.

▸ Thermosetting polymers :

Some polymers undergo some chemical change on heating and converts themselves into an infusible mass like the yolk of the egg. They can not be reshaped, such polymers that become an infusible and insoluble mass on heating, are called thermosetting polymers.

Ex — Epoxy, silicone resin, polyurethane etc.

4. Plastics, Elastomers, Fibres & Liquid resin :

Depending on the ultimate form and use, a polymer can be classified as plastic, Elastomer, fibre or liquid resin.

▸ Plastic :

When a polymer is shaped into hard & tough utility articles by the application of heat & pressure, it is used as plastic.

Ex — Polystyrene, PVC, polymethylmethacrylate

▸ Elastomers : When a polymer is vulcanised into rubbery products ~~into~~ exhibiting good strength and elongation, it is used as plastic elastomer.

Ex — Natural rubber, synthetic rubber, silicone rubber etc.

▸ **Fibre :**

If drawn into long filament-like materials whose length is almost 100 times its diameter, polymers are called Fibres.

Ex — Nylon, dexylene etc.

▸ **Liquid resin :**

Polymers used as adhesives, sealant etc in a liquid form are called liquid resins.

Ex — Epoxy adhesives, polysulphides sealant etc.

● Based on polymer composition & structure, they are classified into condensation and addition polymers. This classification was originally done by Carothers in 1929.

▸ **condensation polymerisation :**

condensation polymers are those polymers that form from polyfunctional monomers by the various condensation reactions of organic chemistry with the elimination of some small molecules such as water.

Examples :

1. $n H_2N-R-NH_2 + n HO_2C-R'-CO_2H \rightarrow \left[-NH-R-NH-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}-\right]_n OH + (2n-1)\, H_2O$

Polyamide

where R & R' are aliphatic & aromatic groups. when $R = (CH_2)_6$ & $R' = (CH_2)_4$; we get,

2. $n H_2N-(CH_2)_6-NH_2 + n HO_2C-(CH_2)_4-CO_2H \longrightarrow$

6-carbons Hexamethylene-diamine

6-carbons adipic acid

$$H\left[-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n OH + (2n-1)\, H_2O$$

Nylon-6,6
or, Nylon 6/6
Poly(Hexamethylene adepamide)

3. $n\,HO-R-OH + n\,HO_2C-R'-COOH \longrightarrow H\left[O-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}\right]_n OH + (2n-1)H_2O$

Polyester.

4. $n\,HO-C_6H_4-R-C_6H_4-OH + n\,Cl-CO-Cl \xrightarrow{\text{Phosgene}}$

$H\left[O-C_6H_4-R-C_6H_4-O-\overset{O}{\overset{\|}{C}}\right]_n Cl + (2n-1)HCl$

Polycarbonate.

5. $H_2N-R-NH_2 + Cl-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow H\left[NH-R-NH-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}\right] Cl$

6. $HO-R-OH + OCN-R'-NCO \longrightarrow \left[O-R-O-\overset{O}{\overset{\|}{C}}-NH-R'-NH-\overset{O}{\overset{\|}{C}}\right]_n$

Polyurethane.

7. $H_2N-\overset{O}{\overset{\|}{C}}-NH_2 + H-\overset{O}{\overset{\|}{C}}-H \longrightarrow \left[NH-\overset{O}{\overset{\|}{C}}-NH-CH_2\right]_n$

urea formaldehyde $+ H_2O$

8. $C_6H_5OH + H-\overset{O}{\overset{\|}{C}}-H \longrightarrow \left[C_6H_3(OH)-CH_2\right]_n + H_2O$

Phenol formaldehyde

▸ Addition polymers :

The polymers those form from monomers without the loss of a small molecules are called the addition polymers. Unlike condensation polymers, the repealing unit of an addition polymer has the same composition as the monomer.

▸ Example :

$$n CH_2 = CHY \longrightarrow \left[- CH_2 - CHY - \right]_n$$

where Y can be any substituent group such as $-H$, $-R$, $-Ar$, nitrile, ester, acid, ketone, ether, halogen.

More examples ——

Monomer	Polymer
ⓐ $CH_2 = CH_2$	$-CH_2-CH_2-$
ⓑ $CH_2 = CH-CN$	$-CH-CH-$ (CN)
ⓒ $CH_2 = CHCl$	$-CH_2-CH-$ (Cl)
ⓓ $CF_2 = CF_2$	$-CF_2-CF_2-$
ⓔ $CH_2 = C(CH_3)-CH=CH_2$	$-CH_2-C(CH_3)=CH-CH_2-$

N.B. – 1 : In case of polyurethane, its looks like an addition polymer as the polymer has the same elemental composition as the sum of the monomers but it is consider as the condensation polymer because the urethane $\left(-NH-\overset{O}{\overset{\|}{C}}-O-\right)$ linkage has much in the common with the ester $\left[-\overset{O}{\overset{\|}{C}}-O-\right]$ and amide $\left[-NH-\overset{O}{\overset{\|}{C}}-\right]$ linkage that means it has more structural similarity to condensation polymer.

N.B.-2 : To avoid incorrect classification, polymers are classified from a consideration of chemical structure of the groups present in the polymer chain. Condensation polymers are those polymers whose repeating unit are joint together by functional unit of one kind or another such as ester, amide, urethane, etc linkage.

$$-R-Z-R-Z-R-Z-R-$$

; [R = aliphatic or aromatic group
Z = Functional unit]

Addition polymers do not contain such functional group as part of the polymer chain.

▶ Based on polymerisation mechanism polymerisation is classified into step and chain polymerisation.

Step and chain polymerisation differ in several features, but the most important difference is in the identities of the species that can react with each other. Another difference is the manner in which polymer molecular size depends on the ~~of~~ extend of conversion.

▶ Step polymerisation :

Step polymerisation proceed by the stepwise between the functional groups of reactants. The size of the polymer molecule increases at a relatively slow pace in such polymerisation. One proceeds from monomer to dimer, trimer, tetramer, pentamer, and so on until eventually large-sized polymer molecules have been formed.

Example :

Monomer + Monomer ⟶ dimer
dimer + Monomer ⟶ Trimer
Trimer + Monomer ⟶ Tetramer
Tetramer + Monomer ⟶ Pentamer.
Trimer + dimer ⟶ Pentamer etc.

The characteristic of step polymerisation is that the reaction occurs between any of the different-sized species present in the reaction system.