Unit - I st

INTRADUCTION OF POLYMERS :-

POLYMER :

Defination :- The word "polymer" is derived from the greek 'poly' → Many and 'meras' → parts

"A polymer molecule may be defined as a number of repeating units held together by chemical bonds."

or

A polymer may be defined as a high molecular weight compound formed by the combination of a large number of one or more types of molecules of low molecular weight.

In other words, polymers are giant molecules of high molecular weight, called macromolecules.

Monomers ⇒ The simple molecules which combine together are called Monomers.

Polymerisation ⇒

The reaction by which monomers combine to form polymers is known as polymerisation.

OR

In other words, polymerisation is the union of two or more smaller and simple molecules of similar or diff. types, with or without the elimination of water etc. leading to the

formation of New C-C bonds.

Classification of polymers

S.No	Basis of classification	Polymer types
(1)	On the basis of origin.	(i) Natural polymers (ii) semi synthetic polymers (iii) Synthetic polymers
(2)	Thermal Response	(i) Thermoplastic polymers (ii) Thermosetting polymers
(3)	Mode of formation	(i) Addition polymers (ii) Condensation polymers
(4)	Line structure	(i) Linear polymers (ii) Branched polymers (iii) cross-linked polymers
(5)	Application of physical properties	(i) Rubber (ii) plastics. (iii) Fibres.
(6)	Tacticity	(i) Isotactic (ii) syndiotactic (iii) atactic
(7)	crystallinity	(i) Non crystalline (ii) semi crystalline (iii) Crystalline

(8) On the basis of Composition	(i) Homo polymers. (ii) Co-polymers.
(9) Bases of polarity	(i) Ionic polymers. (ii) Non-ionic polymers.
(10) Presence of Carbon in polymer	(i) Inorganic polymers (ii) Organic polymers.

(1) ON THE BASIS OF ORIGIN :-

(i) Natural polymers ⇒ They are available in nature. and also known as biological polymers. Eg, Exo: 1,4 Cis-isoprene, natural silk, cellulose, starch, proteins.

(ii) Semi synthetic polymer ⇒ They are chemically modified natural polymers such as hydrogenated, halogenated or hydro-halogenated natural rubber, cellulosics, i.e. esters and ethers of cellulose such as cellulose nitrate, methyl cellulose etc.

(iii) Synthetic polymers ⇒ They are man made polymers prepared synthetically. Eg: polyethylene, polystyrene, polyesters, phenol formaldehyde resins.

(2) ON THE BASIS OF THERMAL RESPONSE :-

(i) Thermoplastic polymers : These are the polymers which soften on heating and stiffen on cooling.

Ex: Such polymers are polyethylene, PVC, nylon and sealing wax.

(ii) Thermosetting polymers ⇒ Thermosetting polymers are those which change irreversibly into hard and rigid materials on heating. After cooling, if the set article is again heated, it will not soften again, hence it is irreversible.

They are permanent setting resins

Ex: Bakelite plastic, amino plastic, ebony plastic.

★ Thermosetting resin are usually, harder, stronger and more brittle than thermoplastic resins.

(3) ON THE BASIS OF MODE OF FORMATION ⇒

① Addition polymers:- These are the products formed when the monomer units are repeatedly added to form long chains without elimination of any by product molecules.

→ The monomer units are generally unsaturated compounds usually derivatives of alkenes.

Ex:- PVC, Polystyrene, polyethene

★ Addition polymerisation is also known as chain growth polymerisation.

(ii) Condensation polymers:- When a monomer contains active functional group (generally two) which react together with the elimination of a simple molecule such as H_2O then the product formed is called condensation polymers.

Exa: Nylon-66, [Hexamethylene diamine + adipic acid]

* Condensation polymerisation is also known as step growth polymerisation.

(4) ON THE BASIS OF LINE STRUCTURE :-

(1) Linear polymer :- In which the repeating units are similar to the links in a very long chain. A linear polymer usually has end groups which are different from the repeating unit because it is necessary in some way to terminate the polymerisation.

Although the end gps have no effect on the mechanical properties of a polymer, they may have profound effect on the stability, solubility and adhesive properties of the polymers

Exa: ~~~ -A-A-A-A-A-, polyethylene

(2) Branched polymer ⇒ In which some of the molecules are attached as side chains to the linear chains.

The branching may be random and at irregular intervals. The branching may occur at regular intervals with equal length of branches.

* Branched polymers are usually more readily soluble and fusible than linear polymers.

(3) Cross-linked polymers :- They can be represented by a network structure. eg: graphite, ZnS structure 'diamond'.

→ Cross linked polymers are insoluble and infusible depending on nature and frequency of cross-links, such polymers may show different orders of swelling in solvent.

Eg: PF Resin, epoxy resins, vulcanised rubber etc.

Q→ Why branch polymer is soluble but linear polymer is not soluble.

Ans ⇒ Branched polymers are readily soluble & fusible than linear polymers of comparable chain length or m.wt

(5) ON THE BASIS OF APPLICATION and physical properties.

① Rubber ⇒ These polymers are characterized by long-chain elasticity. They are rather weak, dimensionally unstable and undergo high elongation even on application of low stress. They exhibit tensile strengths in the range 300-3000 Psi.

Exa: Natural Rubber, and synthetic rubbers.

→ They are also known as elastomers. The cross linking of rubber is commonly known as vulcanization.

② Plastics: These are polymers which can be shaped into hard and tough utility articles by the application of heat & pressure.

These are usually much stronger than rubber. ~~Some of them are hard, horny rigid, stiff~~ Plastics exhibits tensile strength ranging b/w 4,000 - 15,000 psi.

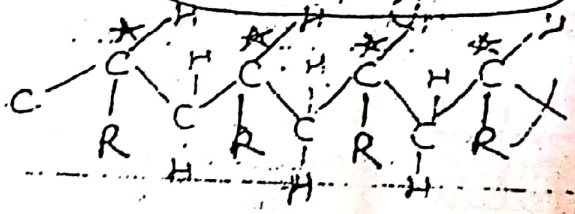
Exa: Polyethylene, polypropylene, polystyrene, PVC, PF & UF resins, polycarbonates.

(3) Fibre: They are strongest of the three diff. types of polymers.

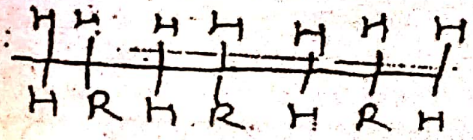
Exa: Rayon, Polyester, silk.

(6) ON THE BASIS OF TACTICITY ⇒

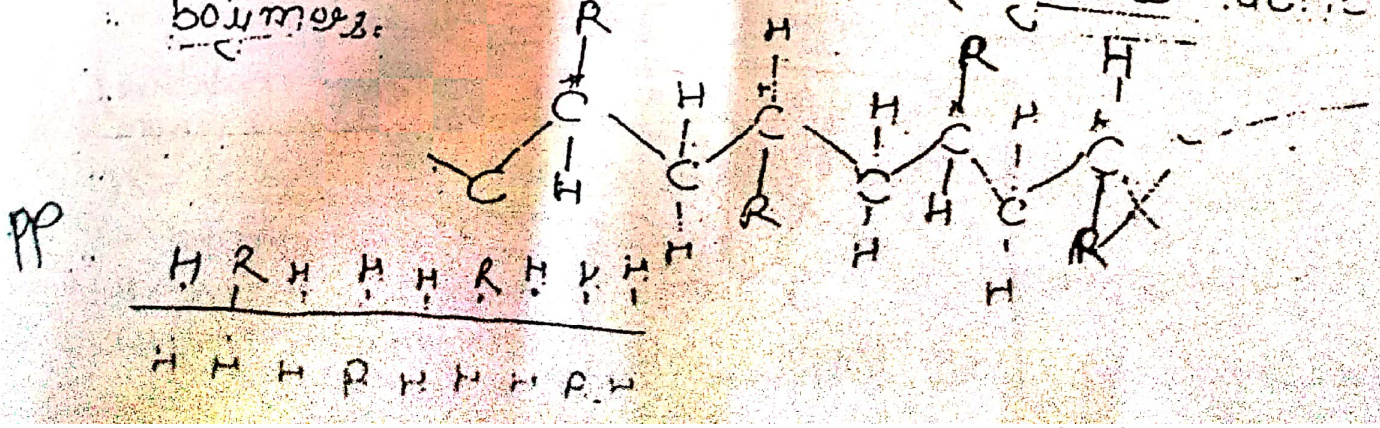
(i) Iso-tactic: Polymers where in all adjacent asymmetric carbon atoms over the chain length of the polymer chain have the same space configuration are known as Isotactic polymers.



Iso-tactic

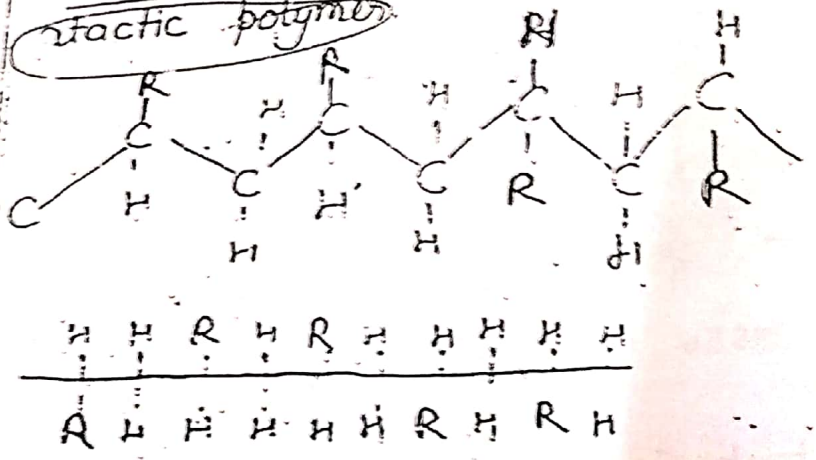


(ii) Syndio-tactic ⇒ Polymers in which chain is made up of units having opposite space configuration of each symmetric carbon atom are known as (Syndio-tactic polymers.



~~(ii) Syndiotactic~~ ⇒

(iii) Atactic polymer ⇒ Polymer in which gps are arranged randomly in space over the chain are known as atactic polymer



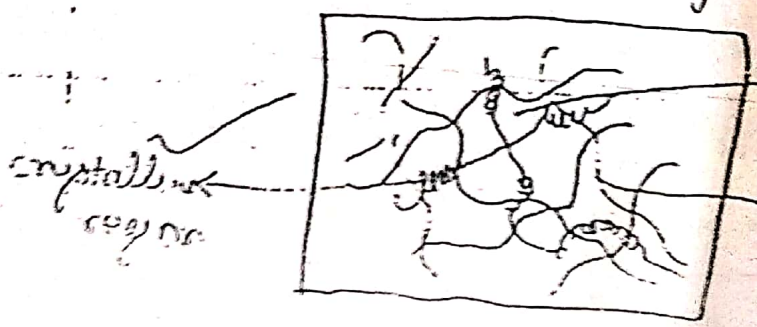
(7) ON THE BASIS OF CRYSTALLINITY ⇒

When polymers cooled from molten state they exhibit diff. tendency to crystallize at different rates depending on many factors.

(1) Crystalline ⇒ Polymer showing a high extent of crystallinity more than 60% are commonly known crystalline polymers

(2) Semi crystalline ⇒ those showing a significant but relatively lower degree of crystallinity are termed as (semicrystalline polymers.)

(3) Non crystalline ⇒ No crystal formation



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2078 (2½) - Chemical

(8) ON THE BASIS OF composition ⇒ On this basis the polymers can be classified as-

(i) Homo-polymer ⇒ When a polymer is obtained from a single monomer unit it is called homopolymer e.g. polystyrene which is formed from monomer styrene.

→ Some other examples of homopolymers are polyethylene, polypropylene.

With some exceptions, polymers made in chain reactions often certain only carbon atoms in main chain (homo chain-polymers).

(ii) Co-polymers ⇒ When a polymer contains two and more monomer units in the chain then it is known as a copolymers

It is possible to designate copolymers as

(a) Random copolymers ⇒ when monomer units are arranged in an irregular manner, the co-polymer molecule is called Random co-polymer Exa: -A-B-B-A-B-A-B-A-A-B

(b) Alternate co-polymers ⇒ When monomer units in a copolymer molecule are arranged in the chain in regular manner, the molecule is called alternate - copolymer.

Exa: -A-B-A-B-A-B-A-B-A-

(c) Block-Copolymer ⇒ Linear copolymes in which the like monomeric units occur in relatively long sequences are called block co-polymers.

Eg: -A-A-A-A-B-B-B-B-A-A-A-A-B-B-B-B-

Block copolymers

Block copolymers may be produced by the following four tech.

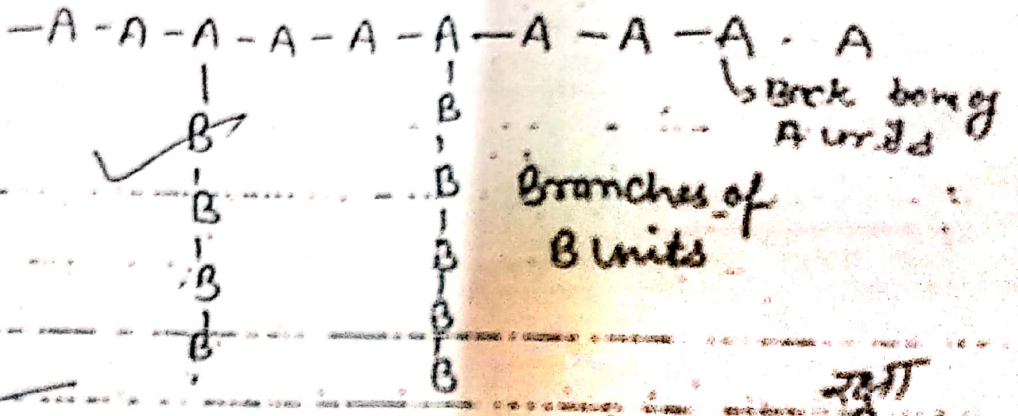
(a) Utilise reactive end groups

(b) Activate end gps

(c) fragment a chain to produce active end gps

(d) Transport reactive end gps into a diff. media

(e) Graft copolymers ⇒ These are branched copolymers in which the branches have diff. chemical st. to that of main chain.



graft

The importance of the block and graft co-polymers is that the resultant material tends to exhibit the properties of each homopolymer

They also have same unique property arising from the chemical linkage b/w the homopolymer sequence.

Eg: Pure polystyrene is quite brittle, whereas polymerisation of about 5% of Rubber produced material which is strong and tough

→ 90 part of vinyl chloride & 10 part of vinyl acetate, the random co-polymerisation

formed has toughness of polyvinyl chloride, thermal stability of polyvinyl acetate. These combination of properties makes it useful as a paint.

(9) ON THE BASIS OF POLARITY ⇒

(i) Ionic polymers

(ii) Non ionic polymers

(10) ON THE BASIS OF Presence of Carbon in polymers

(i) Inorganic polymers :- An inorganic polymer may be defined as a polymer whose backbone chain is not having carbon atom. Exa. of Inorganic polymers are glass, Silicone rubber etc.

(ii) Organic polymer :- A polymer whose back bone chain is essentially made of Carbon atom.

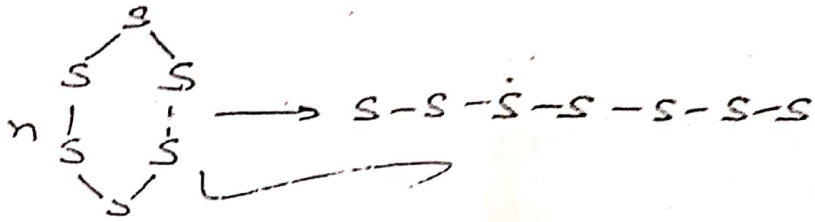
The majority of synthetic polymers are organic polymers

(11) ON THE BASIS OF presence of atom in the polymer chain ⇒ These are of two types

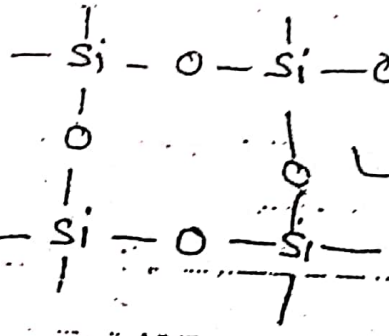
(i) Homo-chain polymers ⇒ Sulphur and selenium have a high tendency to form homo-chain polymeric compounds.

ordinary rhombohedric Sulphur has cyclic

molecules containing eight sulphur atoms. when sulphur is heated in the molten state, the ring appears into a linear polymer.



(ii) Heterochain polymers ⇒ Silicone. form the branched polymers, as represented as



Silicone dioxide

valent Bond
nic bond
valent bond
pole bond
action bond
ession bond
Hydrogen bond

← Primary bonds (1–1.5 Å°) length
← Secondary bonds (3–4 Å°) length

← Bonding in polymers →

There are two kinds of bond which characterised by structural features of polymers.

(i) The atom in the chain are joint to each other by strong bond about 1-1.5 A° length known as pri bond

A ↔ A
Atom

(ii) The force act b/w the chain at distance of about 3 to 4 A° is known as secondary bond.

M ↔ M
molecule

(iii) The pri as well as secondry bond can be subdivided into diff. types of bond.

1. Primary bond
   (i) Ionic bond (ii) covalent bond (iii) co-ordinate bond (iv) metallic bond

(i) Ionic bond ⇒ Ionic bond is formed by the donation of an e⁻ by one atom to another. it is a polar bond.

Li + F → Li⁺ F⁻

Ionic bonds are not usually formed in macro-molecular substance except in the use of divalent ions to provide cross linkage b/w carboxylic grps in natural resins & in ionomers.

Energy of Ionic interaction $\propto \frac{1}{r^2}$

(ii) Covalent bond ⇒ These bonds are formed when one or more pairs of valence e's are shared b/w two atoms.

H + H → H_2

e.g. H_2 is composed of two electrons each atom provides one electron for sharing so that each atom experiences filled shell.

The covalent bond is the predominant bond in polymer, and is extremly non polar covalent bonds are characterised by high energy

(iii) Co-ordinate bond ⇒ In the co-ordinate bond both of the shaired e⁻ come from one atom called the donar which loser an e⁻ and carries a +ve charge whereas the acceptor become -ve charge.

(iv) Metallic bond ⇒ The metallic bond is not utilized in polymeric system.

(2) Secondary Bose forces ⇒

when all the primary valences within covalent molecules are saturated, there are still forces acting b/w the molecules These are generally known as secondry valence or intermolecular forces, or van der waals forces.

(i) Dipole forces ⇒ When different atoms in a molecule carry equal and opposite electric charges, the molecule is said to be polar or to have a dipole moment.

At large distances such a molecule acts like an electrically neutral system, but at molecular distance the charge separation becomes significant, and leads to a net inter molecular force of attraction.

Ans ⇒ The dipole force is strongly depends upon the temperature.

orientational interaction Energy

$$U_{(orient)} = \frac{2}{3} \frac{\mu_1 \mu_2}{KT\, r^6}$$

μ_1 & μ_2 = are dipole moment of two molecules
T = Temperature
K = Boltzmann constant
r = Distance b/w two molecule

(ii) Induction-forces ⇒ (Interaction b/w polar & Non-polar molecule) .. A polar molecule also influences surrounding molecules that do not have permanent dipoles.

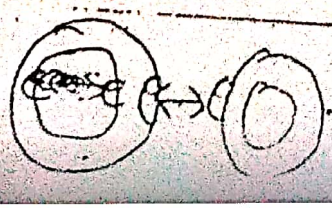
The intermolecular force b/w the permanent and induced dipoles is called induction forces. The energy of the induction force is always small and independent of temp.

$$U = -\frac{2\mu^2\alpha}{r^6}$$

μ = constant dipole moment of molecule
α = polarizability of Non-polar molecule
r = Distance b/w polar - non-polar molecule

Note ⇒ Dipole-forces & Induction-forces occurs only at small distance because Energy is inversely proportional 6th power distance of molecule.

(iii) Dispersion-forces ⇒ It caused by an interaction of the electron in the atom of diff molecules. This forces of attraction exist b/w all atoms the nearer the atom,



stronger the force of attraction these are short range forces. In non polar material only dispersion force exist.

Dispersion interaction can occur in any molecule but in case of polar molecule it is superimposed by orientational interaction.

Hydrogen bond ⇒ The bond in which a hydrogen atom is associate with two other atoms is particularly important in many polymers, including proteins, and is held by many to be essential to life processes.

The Hydrogen bond occurs b/w two functional gps in the same or diff molecules.

Typically hydrogen bonds range b/w 2.4 and 3.2 Å in length and b/w 12 and 30 KJ/mole in dissociation energy. Only fluorine, Nitrogen oxygen, and chlorine are electronegative enough to form hydrogen bonds.