

Polymers

Classification: Natural and synthetic methods of the polymerization

- * The large molecules formed by the combination of a large number of small same molecules or different molecules are called polymer.
- * A polymer always consists of hundreds to thousands of repeating structural units but a micro molecule may or may not contain repeating structural units, Ex. Proteins & nucleic acids should be regarded as macro molecules but not polymers since their molecules do not contain repeating structural units, i.e. polyethene may be regarded both a macro molecule as well as polymer since it contains a large no. of repeating structural units, thus all polymers are macro molecules but all macro molecules are not polymers.
- * The smallest repeating unit combines to form the polymer is called monomer.
- * Polymers isolated from natural materials are called natural polymers. Ex: Cotton, Silk, wool, rubber etc
- * Polymers obtained by the combination of low molecular weight compounds are called synthetic polymers. Ex: Polythene, PVC, nylon, terylene etc
- * Polymers formed by the addition of large number of same or different molecules without the loss of any simple molecules are called addition polymers. Ex: Polythene, PVC, neoprene, polyvinyl pyrrolidone, etc
- * Polymers formed by the combination of a large number of same or different molecules with the elimination of small molecules such as H_2O , NH_3 , HCl are called condensation polymers. Ex: Terylene, nylon-66, Bakelite etc.
- * Polymers which contain a chain of carbon atoms are called organic polymers.
- * Polymers which contain no carbon chains are called inorganic polymers. Ex: Glass, silicone rubber etc.

- * Polymers which are soft on heating and become rigid on cooling are called thermoplastics. The polymers in which the intermolecular forces of attraction are in between those of elastomers and fibers are called thermo plastics.

Ex: Polythene, nylon, PVC, Polypropene, Polythene, Polystyrene, teflon, Polyvinyl acetate (PVA), poly acrylonitrile, Nylon - 6, Nylon - 6, 6.....

- * Fibers: Polymers in which the intermolecular forces of attraction are strongest are called fibers.

- * These forces are either due to Hydrogen bonding (or) dipole - dipole interactions.

- * Thiokol: It is prepared by copolymerisation of 1, 2 - dichloroethane (ethylene dichloride) with sodium tetra sulphide in presence of $Mg(OH)_2$

- * Polymers which are not soft on heating and become hard on heating are called thermosetting polymers. Ex: Bakelite, silicones, urea formaldehyde resins etc.

- * Polymers which are formed by cationic polymerization are called cationic polymerization polymers. Ex: Polystyrene, Poly vinyl ethers, poly isobutene etc

- * Polymers which are formed by anionic polymerization are called anionic polymerization polymers. Ex: Buna rubbers, poly isoprene, poly acrylonitrile etc

- * The process of combination of large number of same or different molecules with the elimination of small molecules such as H_2O , NH_3 , HCl etc is called condensation polymerization or step wise polymerization.

- * Adipic acid is heated with hexamethylenediamine to form nylon-6, 6.

- * Ethylene glycol is heated with terephthalic acid to form polyethylene terephthalate (PET).

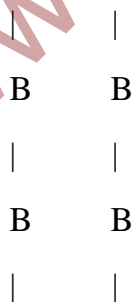
- * The process of combination of a large number of same or different molecules without elimination of small molecules is called addition polymerization or chain polymerization.

- * Ethylene undergoes polymerization to form polythene.

- * Vinyl chloride undergoes polymerization to form poly vinyl chloride (PVC).

- * Polymers which are formed from only one kind of monomer units are called homopolymers. Ex: Polythene, PVC, orlon, Polypropylene, polyisoprene, Neoprene, Poly acrylonitrile, Nylon-6, Ploybutadiene, Teflon, Cellulose, Starch.
- * Polymers which are formed from more than one kind of monomer units are copolymers. Ex: Nylon-6, 6, terylene, Bakelite, Buna-S, Bona - N, Polyesters, Alkyd resins, Bakelite, Melamine, Formaldehyde polymer.
- * Copolymers are classified into four types depending on the nature of the distribution of the different monomers of the chain
 - 1) Random copolymers
 - 2) Alternating copolymers
 - 3) Block copolymers
 - 4) Graft copolymers
- * Random copolymers are formed by the random management of monomer units in the chain -A-B-A-A-B-B-A-B-A-A-B-B-B-
- * Alternating copolymers are formed by the alternate arrangement of monomer units in the chain -A-B-A-B-A-B-
- * Blocks copolymers contain a block of one monomer unit is followed by a block of another monomer units in the chain -A-A-A-A-B-B-B-B-A-A-A-A-B-B-B-B-
- * In graft copolymers main chain contain one type of monomer units and branched chains contain another type of monomer units.

A-A-A-A-A-A-A-A-



Addition Polymerization

- * When the molecules of same monomer or different monomers add together to form a polymer, this process is called addition polymerization.
- * The monomers used here are unsaturated compounds such as alkenes, alkadienes and their derivatives.
- * This process is also called chain growth polymerization because it takes place through stages leading to increase in chain length.
 - . Addition polymers are same empirical formula as their monomers.

Ex: Polyethene, PVC, Teflon, Polypropylene.

- * This mode of polymerization can take place through the formation of either radicals or ionic species such as carbanions or carbocations.

- * **Free radical mechanism**

Three main steps are involved

1. Chain initiating step
2. Chain propagating step
3. Chain terminating step

- * Here the chain initiator (Catalyst) may be benzoyl peroxide, acetyl peroxide or tert-butyl peroxide.

- * Preparation of some important addition polymers

Ex: - Polythene

There are two types

a) Low density polythene (LDPE)

- * It is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes.

- * b) **High density polythene (HDPE)**

- * It is used for manufacturing buckets, dustbins, bottles, pipes.

- * Ziegler-Natta catalyst is



B. Cationic Addition Polymerization

When the initiator is cationic in nature, on addition to the double bond, it would generate a cationic intermediate for propagation the addition chain process and is termed as cationic addition polymerization.

- * The process is initiated by a Lewis acid.
- * The important chain initiators used for the cationic polymerisation are or
- * Cation polymerization is facilitated in monomers containing electron-releasing groups.
- * Isobutylene undergoes cationic polymerization easily as it has two electron releasing - groups that will stabilize the intermediate cation.
- * The reaction proceeds through three steps as given below:
 - i) Initiating step
 - ii Propagation step
 - iii) Termination step

C. Anionic Addition Polymerization

An anionic initiator will similarly generate carbanionic intermediate and the resulting polymerization is categorized as anionic addition polymerization. Here, the active centre of the propagating species is negatively charged.

- * It occurs easily with monomers containing electron-withdrawing groups such as phenyl, nitrile etc., which are able to stabilize the propagating species.
- * Initiation can be brought about by reagents such as n-butyl lithium or potassium amide.

Natural Rubber

It is a natural polymer and possesses remarkable elasticity

- * It is manufactured from rubber latex which is a colloidal suspension of rubber in water and is obtained by making incisions in the bark of rubber trees.
- * Latex is an emulsion of polyhydrocarbon droplets in an aqueous solution. It consists of negatively charged particles of rubber.
- * The latex contains about 35% rubber. The rubber present in the latex is coagulated by the addition of or
- * This solid is crude rubber: This is refined by
 - a) Break down i.e., masticating the raw rubber and
 - b) Compounding i.e., addition of necessary agents to the rubber.
- * The empirical formula of Natural rubber is C_5H_8
- * Natural rubber may be considered as a linear polymer of isoprene.
- * The residual double bonds are located between and of isoprene units in the polymer.
- * All these double bonds have cis configuration and thus, rubber is cis 1, 4 - polyisoprene.
- * X-ray studies carried out by Bunna (1942) established that rubber is composed of long chains of isoprene units arranged in cis form as shown below
- * The transform of rubber is called gutta percha. The weight average molecular weight of rubber varies between 1, 30,000 to 3, and 40,000.\

Vulcanization of Rubber

- * Rubber as such is used in the temperature range 283 to 335 K as it becomes soft at higher temperatures and brittle at low temperatures.
- * Addition of sulphur to hot rubber causes changes that improve its physical properties. This process is called **Vulcanization**.
- * It was performed by heating a mixture of raw rubber and sulphur at 373 to 415 K.

- * This process is slow and additives such as zinc oxide, zinc stearate etc., are used to accelerate the rate of vulcanization.
- * The Vulcanized rubber has excellent elasticity, low water- absorption tendency, resistance to oxidation and organic solvents.
- * The allylic - CH_2 -(- CH_2 - group next to double bond) is also very reactive.

Thus, about 5% sulphur is used for making tyre rubber, a 30% of it for making battery case rubber and 40-45% of it for making ebonite.

Synthetic Rubber

- * The Polymers are derived from butadiene derivatives and contain carbon- carbon double bonds so that they can also be vulcanized.
- * Synthetic rubbers are either homopolymers of 1, 3- butadiene derivatives or copolymers, of which one of the monomers is 1,3-butadiene.
- * Commonly used synthetic rubbers are Buna-S, Buna-N, Neoprene and Butyl rubber.

Ex1) Neoprene or polychloroprene is formed by the free radical polymerization of chloroprene

Ex: 2) Buna - s is obtained by the addition polymerization from 1, 3 - butadiene and styrene

Ex: 3) 1, 3-butadiene and acrylonitrile undergo co-polymerization to give Buna-N. This is used in making oil seals and tank linings.

**SOME IMPORTANT POLYMERS NATURAL AND SYNTHETIC LIKE
POLYMERS LIKE POLYESTERS, BAKELITE, RUBBER, BIODEGRABLE AND
NON-BIODEGRABLE POLYMERS**

- The Molecular mass of a polymer can be expressed in two ways.
- If are the number of molecules with molecular masses respectively, the number average molecular mass is
- When the total mass of groups of molecules having different molecular masses are multiplied with their respective molecular masses, the products are added and the sum is divided by the total mass of all the molecules, the result obtained is called the mass or weight average molecular mass.
- The ratio of mass average molecular mass to the number of average molecular mass is called polydispersity index (PDI).

PDI gives an idea about the homogeneity of a polymer

For natural polymers, PDI is usually unity (Natural polymers are mono dispersed)

For synthetic polymers, PDI is greater than one is measured on the basis of colligative properties. (Number average molecular mass)

The mass average molecular mass “ ” is measured with the help of ultra centrifugation, sedimentation etc.

Experimental Determination of number average molecular weight:

A solution of (1g/1 Ltr) is prepared.

A series of solutions of known concentrations (C) are prepared from the above solution by diluting with a suitable solvent.

The osmotic pressure of each of the solution is measured.

The value of is plotted π / C against C

A straight line is obtained. It is extra plotted to zero concentration.

Then, $\pi / C = RT$

Ex: - In a polymer sample, 30% molecules have a molecular mass 20, 000, 40% have molecular mass 30,000 and rest have 60,000. Calculate mass average and number average molecular masses.

Biodegradable Polymers

The large scale use of synthetic polymers has been based on their relative inertness to environmental processes so that degradation reactions leading to any change in the properties of the polymer does not occur.

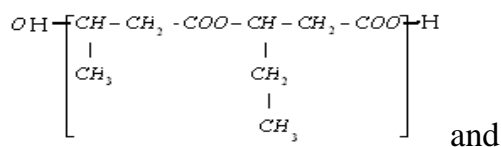
Bio-polymers degrade quickly in living systems by enzymatic chemical reactions like oxidation or hydrolysis.

The bio-degradable polymers have functional groups that are mostly present in bio-polymers and lipids.

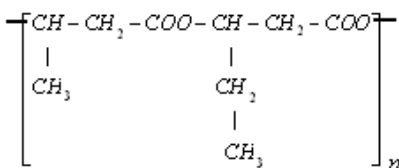
Ex:1 :- Poly- - Hydroxybutyrate-co--Hydroxyvalerate (PHBV):

It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid, in which the monomer units are connected by ester linkages.

The properties of PHBV vary according to the ratio of both the acids. 3-hydroxybutanoic acid provides stiffness and 3-Hydroxypentanoic acid imparts flexibility to the copolymer. It is used in specialty packaging, orthopedic devices and it is used in the field of medicine for making capsules.



Monomer unit



Polymer Unit

Ex 2 : Polyglycolic acid and polylactic acid

They constitute commercially successful biodegradable polymers. Both of the above polymers are biodegradable polyesters, useful for post-operative stitches. They are of commercially degradable polymers used as sutures. Dextron was the first polymer used as a biodegradable material.

Ex:3. Nylon-2-Nylon-6: (step growth polymer)

It is an alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.



Glycine Aminocaproic acid