NEET Revision Notes
Chemistry
Polymers

Introduction:

Polymer is defined as a veritably large patch having high molecular mass $(10^{-3} - 10^7 \, \text{u})$.

● Polymers are macromolecules, which are formed by joining or repeating structural units on a large scale.

● This process of conformation of polymer from separate monomers is called polymerisation.

● The metamorphosis of ethene to polythene and commerce of hexamethylene diamine and adipic acid leading to the conformation of Nylon 6, 6 are illustration of two different types of polymerization response.

Classification of polymers

S.No	Basis of classification	Nature of polymers	Common example
1	Source of polymer	Natural polymers Semisynthetic polymers Synthetic polymers	Cotton, silk Cellulose rayon Polythene
2	Structure of polymers	Linear polymer Branched chain Cross linked or network polymer	High density polythene Low density polythene Bakelite melamine
3	Mode of polymerisation	Condensation polymer Addition Polymers	Terylene Polypropylene, polythene.
4	Molecular force	Elastomers Fibres Thermos plastic Polymers Thermosetting polymers cannot be remoulded	Buna-N Polyamides such as Nylon-6,6 Polythene, Polystyrene Bakelite, Urea-HCHO resins

5	Polarity	Cationic polymerization polymers Anionic Polymerization Polymers	Polystyrene; Polyvinyl ethers Buna type synthetic rubbers
6	Heat treatment	Thermoplastic polymers Thermosetting Polymer	Polyethylene, PVC Nyon Bakelite, Polysiloxanes
7	Organic and inorganic substance	Organic Polymers Inorganic Polymers	Leather; Cellulose Glass, Silicone rubber

Classification based on growth polymerisation

The addition and condensation polymers are nowadays also referred to as chain growth polymers and step growth polymers depending on the type of polymerization mechanism they undergo during their formation.

Types of Polymerisation Reaction

Addition polymerisation or chain growth polymerisation:
- In this type of polymerisation, the molecules of the same monomer or different monomers add together on a large scale form a polymer.
- The monomers used are unsaturated compounds, e.g., alkenes, alkadienyls and their derivation.
- This mode of polymerisation leading to an increase in chain length or chain growth can take place through the formation of either free radicals or ionic species.

A. Cationic Addition Polymerization

When the initiator is cationic in nature, in addition to the double bond, it would generate a cationic intermediate for propagation of the chain process and is termed as cationic addition polymerization.
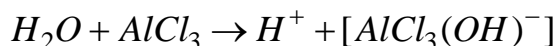- The process is initiated by a Lewis acid.
- The important chain initiators used for the cationic polymerisation are BF_3, $AlCl_3$.
- Cation polymerization is facilitated in monomers containing electron-releasing group.
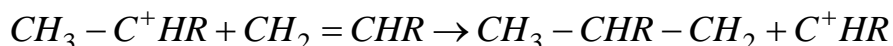
- Isobutylene undergoes cationic polymerization easily as it has two electrons releasing the $-CH_3$ group that will stabilize the intermediate cation.
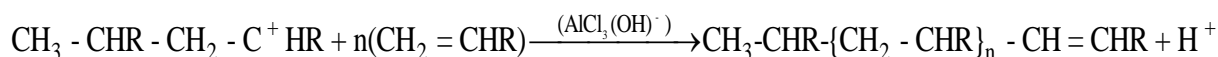
The reaction proceeds through 3 steps:
- Chain initiation step:

$$H_2O + AlCl_3 \rightarrow H^+ + [AlCl_3(OH)^-]$$

- Chain propagation:

$$CH_3 - C^+HR + CH_2 = CHR \rightarrow CH_3 - CHR - CH_2 + C^+HR$$

- Chain termination step:

$$CH_3 \text{-} CHR \text{-} CH_2 \text{-} C^+HR + n(CH_2 = CHR) \xrightarrow{(AlCl_3(OH)^-)} CH_3\text{-}CHR\text{-}\{CH_2 \text{-} CHR\}_n \text{-} CH = CHR + H^+$$
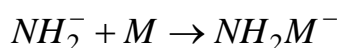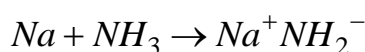
B. Anionic Addition Polymerization

An anion initiator will similar generate carbanionic intermediate and the resulting polymerization is categorized as anionic addition polymerization. Here, the active centre of the propagating species is negatively charged.
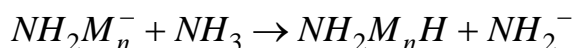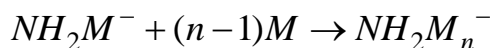
- It occurs fluently with monomers containing electron withdrawing groups similar as phenyl, nitrile etc., which are suitable to stabilized the propagation species.
- Inauguration can be brought about by reagents similar as n-butyl lithium or potassium amide.

The steps with the vinyl derivative can be written as follows:
- Chain initiation

$$Na + NH_3 \rightarrow Na^+NH_2^-$$

$$NH_2^- + M \rightarrow NH_2M^-$$

- Chain propagation

$$NH_2M^- + (n-1)M \rightarrow NH_2M_n^-$$

$$NH_2M_n^- + NH_3 \rightarrow NH_2M_nH + NH_2^-$$

C. Free radical addition mechanism

Here the chain initiator (catalyst) may be benzol peroxide, acetyl peroxide is tert-butyl peroxide, acetyl peroxide is tert-butyl peroxide.
The main steps are involved:
- Chain initiating step
- Chain propagation step

● Chain terminating step

Condensation Polymerization and step growth polymerisation:

When both the reactants are bifunctional, they undergo a series of condensation reaction in a controlled stepwise manner with the elimination of small molecule like H_2O, alcohol to form polymers, and the process is called condensation polymerization.

● This process is also called step-growth polymerization'.
● Condensation polymerisation takes place between molecules having polyfunctional groups.

Polyamides: Polymers enjoying amide liaison are important synthetic fibres.
They are made by condensation of diamines with dicarboxylic acid and also from amino acids or caprolactams the cyclic amides.

Polyesters: Dacron is the best known of the polyesters and is manufactured from ethylene glycol and terephthalic acid.

● The reaction is carried out at 420 to 460K in the presence of catalyst mixture of zinc acetate and antimony trioxide.
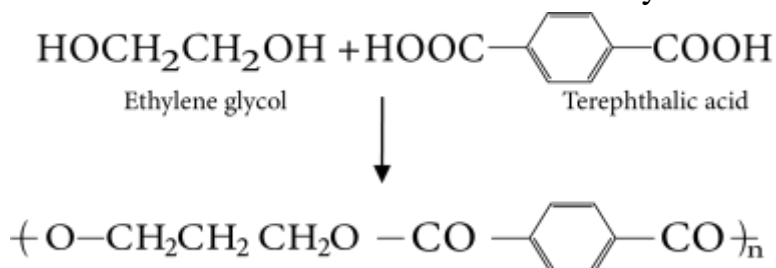
$$HOCH_2CH_2OH + HOOC\!-\!\langle\!\bigcirc\!\rangle\!-\!COOH$$

Ethylene glycol   Terephthalic acid

$$\left(\!O\!-\!CH_2CH_2\,CH_2O\!-\!CO\!-\!\langle\!\bigcirc\!\rangle\!-\!CO\!\right)_n$$

Image: Terylene

● The Terylene fibre (Dacron) is grease resistant and has low moisture absorption.
● It has high tensile strength.
● It is mainly used in making wash and wear garments, in blending with wool to provide better grease and winkle resistance.

Phenol-formaldehyde polymer (Bakelite and related polymer)

● Phenol is condensed with formaldehyde in the presence of either an acid or a base.
● The reaction starts with the initial formation of O and/or P-hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with $-CH_2$ groups.
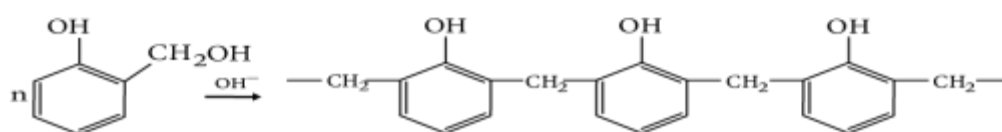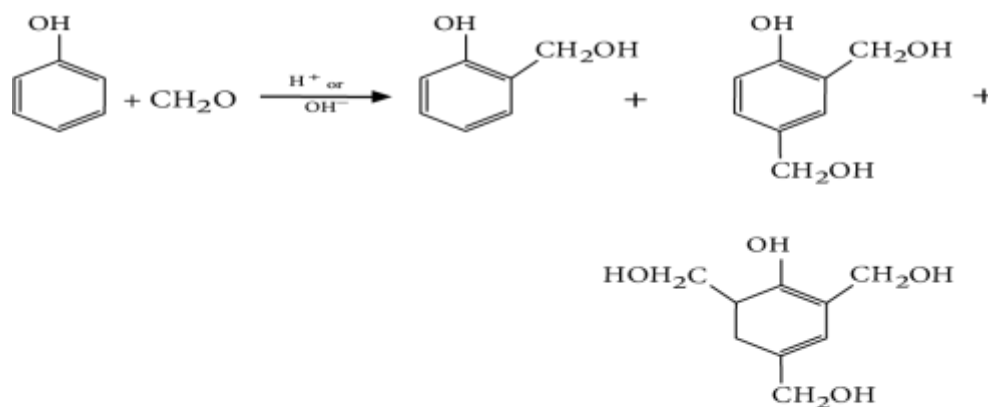● The initial product could be a linear product Novolin used in paints.

Image: Novolac

On further heating with formaldehyde, novolac undergoes cross-linking to crystallize an infusible common sense called Bakelite.
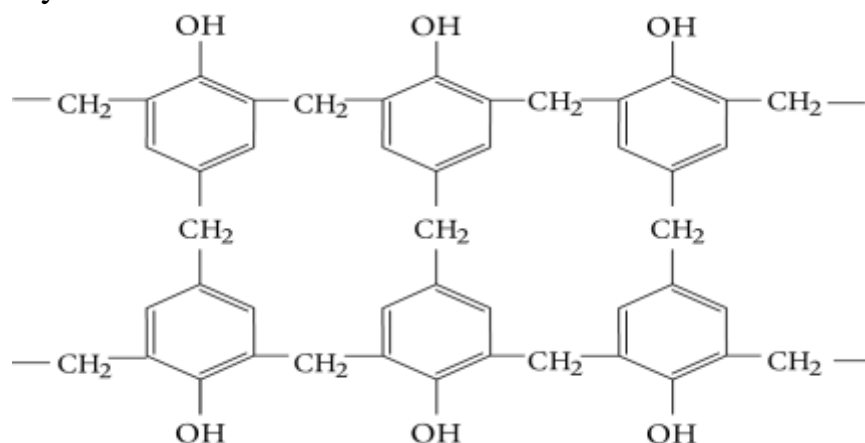

Image: Bakelite

- This polymer called Bakelite is hard, scratch and water resistant.
- It possesses excellent electrical insulating character and hence, it finds major use in making electrical goods.

Copolymerization: If a mixture of more than one monomeric species is allowed to polymerise, a co-polymer is formed and it contains multiple units of each monomer used in the same polymeric chain. The co-polymer can be made not only by chain growth polymerisation, but by step growth polymerisation also.

Co-polymers are further classified into four categories depending on the nature of the different monomers in the chain.

Random copolymers are formed by the random arrangement of monomer units in the polymer chain.

Alternating copolymer chains contain the monomer units in alternate.

Natural Rubber

- It is a natural polymer and possesses remarkable elasticity.
- Latex is a conflation of poly hydrocarbon driblets in a waterless result (oil in water emulsion). 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 CH_3COOH or $HCOOH$.
- This solid is crude rubber: This is refined by
    a. Break down i.e., masticating the raw rubber and
    b. Compounding i.e., the addition of necessary agents to the rubber

Structure of Rubber:

- The empirical formula of Natural rubber is C_5H_8.
- Natural rubber may be considered as a linear 1, 4- addition polymer of isoprene.
- The residual double bonds are located between C_2 and C_3 of isoprene units in the polyme the position of double bonds is detected by ozonolysis.

All these double bonds have cis configuration and thus, rubber is cis 1, 4 - polyisoprene.

Vulcanization of Rubber

Natural rubber becomes soft at high temperatures (>335K) and brittle at low temperatures (< 283 K) and shows high water absorption capacity. It is soluble in nonpolar solvents and is non-resistant to attack by oxidising agents.

- 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, resistant to oxidation and organic solvents.

Synthetic Rubber:

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

Difference between Natural and synthetic polymers:

S.No	Distinguishing property	Natural Polymers	Synthetic Polymers
1	Source of their preparation and common example	Obtained in natural wool, silk, jute, etc	Prepared in the lab, nylon, terrene, Dacron etc.
2	Length of polymer chain	Not of uniform length	Can be of uniform length
3	Affinity for sulphur and vat dyes	Posses very high affinity	Possess low affinity
4	Fixing quality	Low	High

Determination of Molecular Mass of Polymers

The Molecular mass of a polymers can be expressed in two ways:

a. Number average molecular mass ($\bar{M}_n$)

If $N_1, N_2, N_3, ...$ are the number of molecules with molecular masses $M_1, M_2, M_3, ...$ respectively, the number average molecular mass is

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2 + ... + N_iM_i}{N_1 + N_2 + N_3 + ... + N_I} = \frac{\displaystyle\sum_{i=1}^{n} N_i M_i}{\displaystyle\sum_{i=1}^{n} N_i}$$

$\bar{M}_n$ is determined by
- End group analysis method
- Colligative properties like osmotic pressure

$\bar{M}_n$ is related to osmatic pressure by the equation

- $\left(\dfrac{\pi}{C}\right)_0 = RT . \dfrac{1}{\bar{M}n}$ or $\bar{M}n = \left(\dfrac{C}{\pi}\right)_0 RT$

C is concentration of polymer solution in gm/litre is osmatic pressure in cms

- $\left(\dfrac{\pi}{c}\right)_0$ value is calculated from the graph plotted between $\dfrac{\pi}{c}$ on y axis and

   C on X-axis by extrapolated technique, the graph is straight line with an

   intercept is $\dfrac{RT}{\bar{M}n}$ on y axis

b. Weight average molecular mass $(\bar{M}_w)$.

When the total of groups of molecules, having different molecular are multiplied with their all the, molecules, the result obtained is called the   or weight average molecular

$$\bar{M}_w = \dfrac{N_1 M_1^2 + N_2 M_2^2 + ... + N_i M_i^i}{N_1 M_1 + N_2 M_1 + ... + N_i M_i} = \dfrac{\sum\limits_{i=1}^{n} N_i M_i^2}{\sum\limits_{i=1}^{n} N_i M_i}$$

$N_1, N_2, N_3, ...$ are number of molecules

$M_1, M_2, M_3, ...$ are molecular masses

Weight average molecular weight is determined by

- Light scattering
- Ultra-Centrifugal method
- Viscosity measurements

PDI: The ratio of weight average molecular mass to the number average molecular rms is called **Poly dispersity index (PDI).**

$$PDI = \dfrac{\bar{M}_w}{\bar{M}_n}$$

- The value of PDI for polymers in between 1 and 1.5.
- For natural polymers, PDI is usually unit (natural polymers and mono dispersed) $(\bar{M}_w = \bar{M}_n)$.
- For synthetic polymer, PDI is greater than one $(\bar{M}_w > \bar{M}_n)$.
- $\bar{M}_n$ is measured on the basis of the colligative properties.
- The mass average molecular mass $\bar{M}_w$ is measured with the help of ultra-centrifugations, sedimentation etc.

Biodegradable polymers:

- These are polymers which are degraded by microorganisms with in a suitable period so that the polymers and their degraded products do not cause any serious effects on the environment. Biopolymers degrade mainly by enzymatic hydrolysis and oxidation.
- These synthetic polymers mostly have functional groups which are normally present in biopolymers and lipids.