



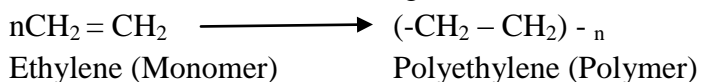
www.studentsjungle.com

UNIT II POLYMER CHEMISTRY

Part – A

1. Define polymer and polymerization.

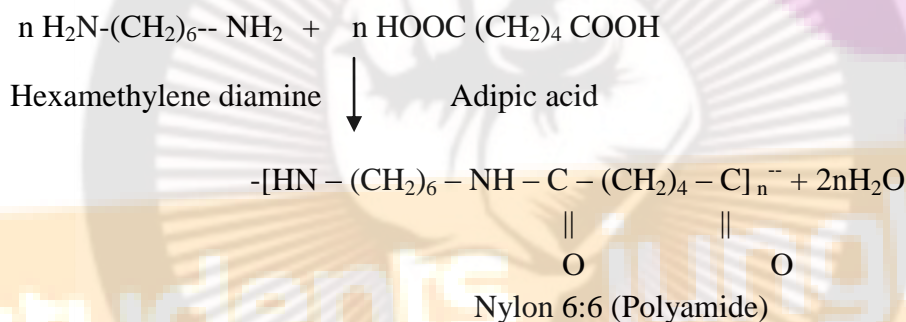
Polymers are macromolecules formed by repeated linkage of large number of small molecules called monomers. e.g.



Polymerization is the chemical process in which large numbers of monomers combine together, to form a polymer with or without the elimination of simple molecules like water, HCl, etc.

2. Define condensation polymerization with suitable example.

It is a reaction between simple polar groups containing monomers that yield polymers with the elimination of small molecules like H₂O, HCl, etc.



3. Define hetero chain polymer.

If the back bone of the polymer chain is made up of different atoms it is called heterochain polymer, e.g., polyesters, Nylon 6:6. Polyesters contain carbon and oxygen atoms in the main chain.

4. Explain functionality of a monomer with a suitable example.

The number of bonding sites or reactive sites or functional groups in a monomer is known as its functionality.

CH₂ = CH₂ (ethylene) – Functionality is 2 (Two bonding sites are due to the presence of one double bond in the monomer. Therefore ethylene is a bifunctional monomer).

5. What is degree of polymerization?

The number of repeating units (n) in a polymer chain is known as the degree of polymerization. It is represented by the following relationship,



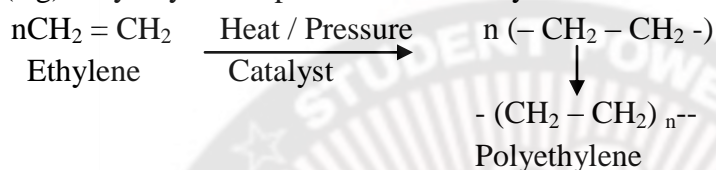
www.studentsjungle.com

$$\text{Degree of polymerization (n)} = \frac{\text{Molecular weight of the polymeric network}}{\text{Molecular weight of the repeating unit}}$$

6. What is addition polymerization?

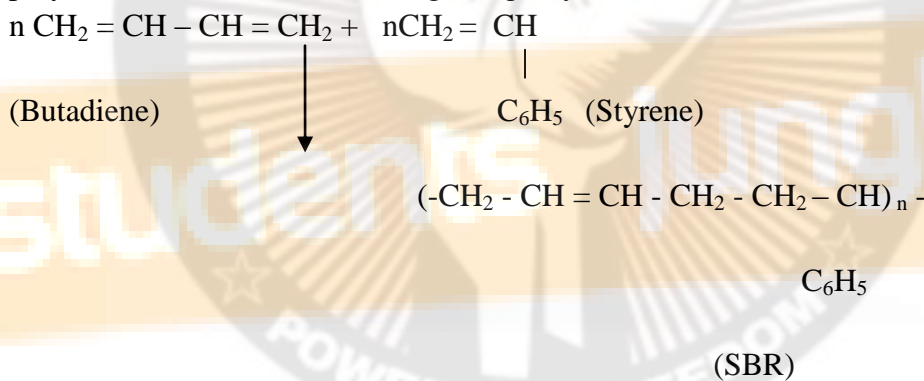
It is a reaction that yields polymer which is an exact multiple of the original monomer molecule. The monomer contains one or more double bonds. This reaction is initiated by the application of heat, light, pressure, or catalyst, for breaking down the double bonds of monomers. In addition polymerization there is no elimination of any molecule.

(e.g) Polyethylene is produced from ethylene:



7. Explain co-polymerization with an example.

It is the joint polymerization in which two (or more) different monomers combine to give a co-polymer. Co-polymerization is mainly carried out to vary the properties of polymers such as hardness, strength, rigidity, heat resistance, etc.



8. Why thermosetting plastics cannot be remoulded?

Thermosetting Plastic consists of three dimensional network structure where the polymer chains are connected by strong covalent bonds by cross linking. They get hardened on heating and cannot be remoulded.

9. What is Tacticity?

The orientation of monomeric units or functional groups in a polymer molecule can take place in an orderly or disorderly manner with respect to the main chain is known as tacticity



www.studentsjungle.com

10. Define T_g.

Glass transition temperature (T_g) is the temperature at which the amorphous solid state (glassy state) is transformed to the melt state.

11. What is poly dispersity index?

The ratio of the weight – average molecular weight (M_w) to that of number – average molecular weight (M_n) is known as polydispersity index (PDI).

$$\text{PDI} = M_w / M_n$$

12. How are the polymers classified on the basis of their tacticity?

1. Isotactic polymers

Here functional groups are arranged on the same side of the main chain.

2. Syndiotactic polymers

Here functional groups are arranged in an alternating fashion.

3. Atactic polymers

Here functional groups are arranged randomly.

14. What are the advantages of solution polymerization?

1. Exothermic heat evolved during polymerization is controlled easily.
2. Viscosity built up is negligible.
3. The mixture can be agitated easily.

15. What are the factors affecting T_g?

1. The value of T_g depends on chain length, extent of cross linking, the barrier which hinders the internal rotation of the chain links.
2. The values of T_g of a given polymer varies with the rate of heating or cooling.
3. Below T_g the polymer is hard and brittle.

Part – B

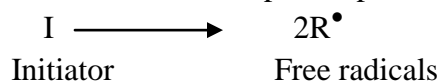
1. Explain the mechanism of free radical polymerization.

Free radical mechanism

Polymerization by free radical mechanism occurs by the following three steps, namely, initiation, propagation, and termination.

1. Chain Initiation

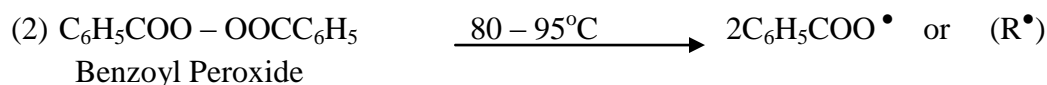
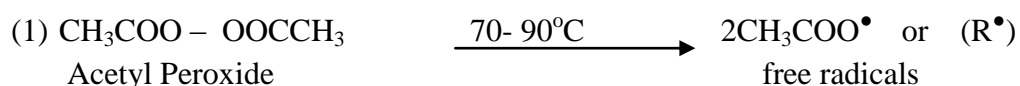
1. Production of a pair of primary free radicals (R[•]) by homolytic cleavage of an initiator:



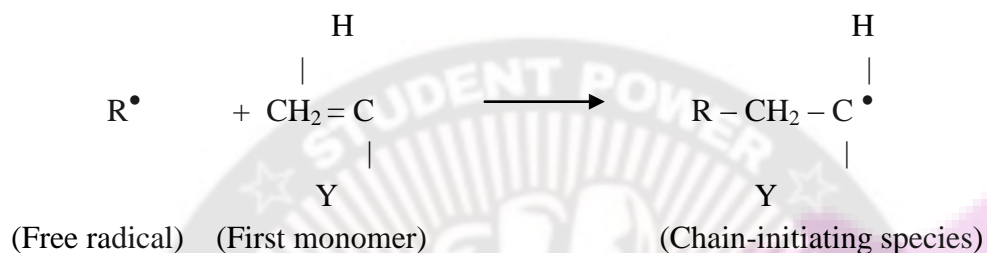


www.studentsjungle.com

Heat is used to produce free radicals by homolytic cleavage of weaker O-O bond of the peroxide molecule

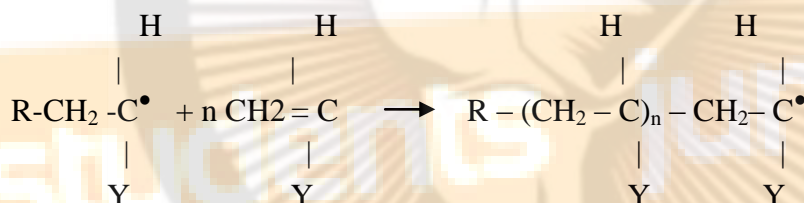


2. Addition of this free radical to the first monomer to produce chain-initiating species:



2. Chain Propagation:

Propagation step consist of the growth of the chain-initiating species by successive addition of large numbers of monomer molecules:

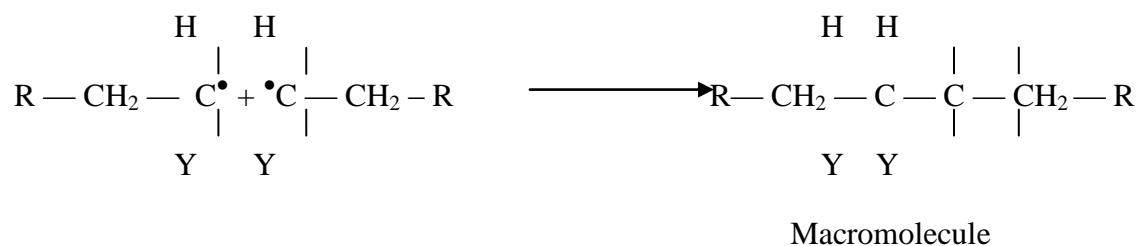


3. Chain Termination:

Termination of the long living radical polymer may occur either by coupling reaction or by disproportionation

a) By Coupling or Combination:

Coupling of free radical of one chain end to another free radical chain leads to a macro molecule.



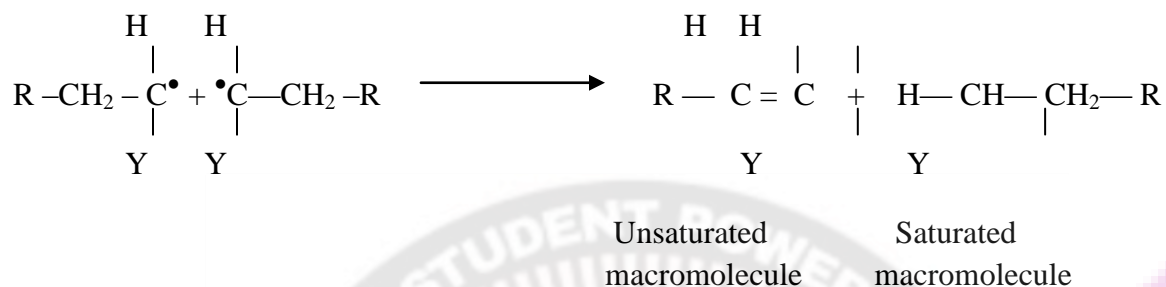


www.studentsjungle.com

(Dead Polymer)

b) By Disproportionation:

Transfer of a hydrogen atom of one radical centre to another radical centre forming two macromolecules, one saturated and another unsaturated.

**3. Distinguish thermoplastics and thermosetting plastics with suitable examples.**

Thermoplastic resin	Thermosetting resins
They are formed by addition polymerization	They are formed by condensation Polymerization
They consist of linear long chain polymers	They consist of three-dimensional network structure
Polymer chains are held together by weak Vander Waals forces	Polymer chains are held by strong covalent bonds
These polymer are usually soluble in organic solvent	They are usually insoluble in organic solvents
They can be remoulded and recycled	They cannot be remoulded or recycled
They can be softened on heating and hardened on cooling reversibly.	They get hardened on heating and they cannot be softened on reheating



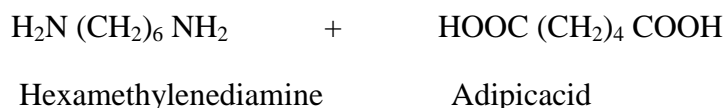
2. Distinguish between addition and condensation polymerization

Addition Polymerization	Condensation Polymerization
The monomer should have at least one multiple bond, e.g., $\text{CH}_2 = \text{CH}_2$ (ethylene)	The monomer should have at least two identical functional groups $\text{CH}_2 - \text{OH}$ (glycol) $\text{CH}_2 - \text{OH}$ $\text{H}_2\text{N}(\text{CH}_2)_6\text{COOH}$ (6-aminohexanoic acid)
Monomer adds to give a polymer and no other by-product is formed.	Monomers condense to give a polymer and by-products such as H_2O , CH_3OH , are formed.
Number of monomeric units decreases steadily throughout the reaction as there is steady growth of polymer chain.	Monomers disappear at the early stage of reaction as oligomers are formed first and then polymers are produced
High molecular weight polymer is formed at once.	Molecular weight of the polymer rises steadily throughout the reaction.
Usually thermoplastics are produced, e.g., polyethylene, PVC, etc.	Usually thermosetting plastics are produced, e.g., Bakelite, urea-formaldehyde.
This follows a free radical mechanism.	This follows the mechanism of condensation reaction
Homochain polymer is obtained.	Hetero-chain polymer is obtained.

3. Give the preparation, properties, and uses of:

(i) Nylon – 6:6

It is obtained by the polymerization of adipic acid with hexamethylene diamine:



↓
Condensation polymerization



Properties

1. It has high chemical – resistance to water, acids, alkalis, various solvents and other chemicals.
2. They are flexible, tough and possess very good heat resisting property.
3. Due to the polar nature of the molecules, they possess excellent adhesion quality.

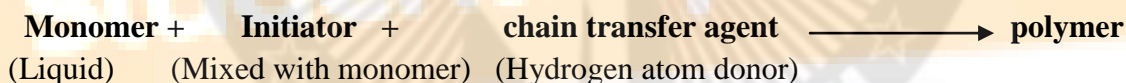
Uses:

1. It is used as surface coatings, adhesives like araldite, glass- fiber reinforced Plastics.
2. It is applied over cotton, rayon and bleached fabrics to impart crease-resistance and shrinkage control.
3. It is used as laminating material in electrical equipments.

4. Write notes on bulk and suspension polymerization techniques.

Bulk polymerization

The monomer is taken in a liquid form and the initiator, chain transfer agents are dissolved in it .The flask is placed in a thermostat under constant agitation and heated.



The reaction is slow but becomes fast as the temperature rises. After a known period of time, the whole content is poured into methanol and the polymer is precipitated out.

Examples: polystyrene, PVC, PMA.

Advantages:

1. It is simple and requires simple equipments.
2. The polymer has high optical clarity.
3. High-purity polymers are obtained.

Disadvantages:

1. During polymerization, viscosity of the medium increases hence mixing and control of heat is difficult.



www.studentsjungle.com

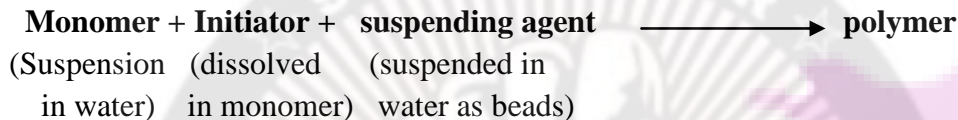
2. Polymerization is highly exothermic

Uses: It is used in casting formulations, adhesives, plasticizers and lubricant and additives.

Suspension Polymerization:

It is used only for water insoluble monomers. This polymerization reaction is carried out for heterogeneous systems.

The water insoluble monomer is suspended in water as tiny droplet and an initiator is dissolved in it by continuous agitation. The suspension is prevented from coagulation by using suspending agents like PVA, gelatin, methyl cellulose. The whole content is taken in a flask and heated at constant temperature with vigorous agitation in a thermostat in nitrogen atmosphere. After eight hours pearl-like polymers are obtained, which is filtered and washed by water.



Examples: polystyrene, polystyrene- divinyl benzene.

Advantages:

1. Products are highly pure.
2. This method is more economical.
3. Efficient heat control.
4. Isolation of product is easy.

Disadvantages:

1. It is only applicable for water insoluble monomers.
2. Control of particle size is difficult.

Uses:

1. it is used as ion exchangers.
2. This technique is used in heterogeneous system.

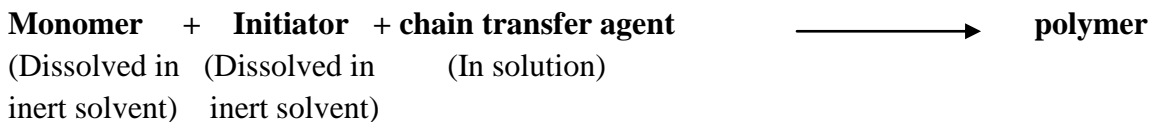
5. How are solutions and emulsion polymerization carried out? Mention some applications

Solution polymerization:



www.studentsjungle.com

The monomer, initiator and the chain transfer agents (Hydrogen atom donor) are taken in a flask and dissolved in an inert solvent. The whole mixture is kept under constant agitation. After some time, the polymer is precipitated by pouring it in a suitable non-solvent.



Examples: Polyacrylic acid, polyisobutylene and polyacrylonitrile.

Advantages:

1. Heat control is easy.
2. Viscosity built up is negligible.
3. The mixture can be easily agitated

Disadvantages:

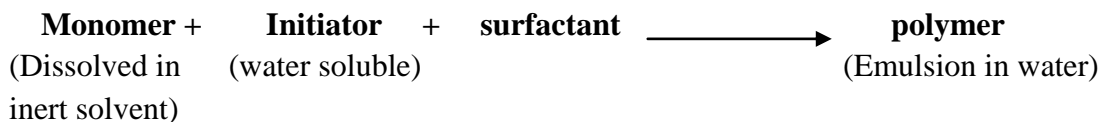
1. It requires solvent recovery and recycling.
2. It is difficult to get very high molecular weight polymer.
3. The polymer formed is isolated from the solution either by evaporation of the solvent or by precipitation in a non- solvent.

Applications:

It can be directly used as adhesives and coatings.

Emulsion polymerization:

The monomer is dispersed in a large amount of water and then emulsified by the addition of soap. Then initiator is added. The whole content is taken in a flask and heated at a constant temperature with vigorous agitation in a thermostat with nitrogen atmosphere. After 4 to 6 hours, the pure polymer can be isolated from the emulsion by addition of de-emulsifier like 3% solution of $\text{Al}_2(\text{SO}_4)_3$.



Advantages:

1. The rate of polymerization is high.
2. Heat can be easily controlled and hence viscosity is low.

- High molecular weight polymer can be obtained.

Disadvantages:

- It is very difficult to remove entrapped emulsifier.
- Polymer needs purification.
- It requires rapid agitation

Applications:

- It is used in production like water based paints, adhesives, plastics, etc.,
- It is used for the manufacturing polymers like butadiene and chloroprene.

6. Explain the mechanism of anionic polymerization with an example.

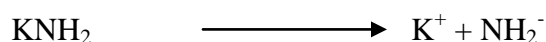
This type of polymerization takes place when electron withdrawing groups like Cl, CN is present in a monomer. These groups stabilize the carbanion.

Examples: Vinyl chloride, styrene, acrylonitrile.

The catalyst used to initiate the reaction are Lewis bases like NaNH_2 , LiNH_2 etc.,

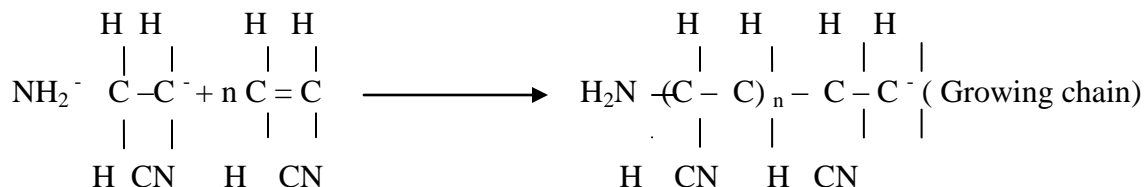
(i) Initiation

It involves the formation of chain initiating species.

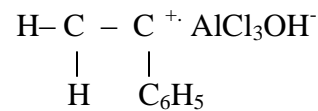
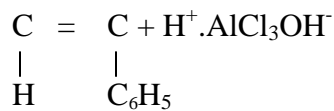


ii) Propagation

It involves the growth of chain initiating species by successive addition of large number of monomers and the negative charge simultaneously shifts to the newly added monomer.



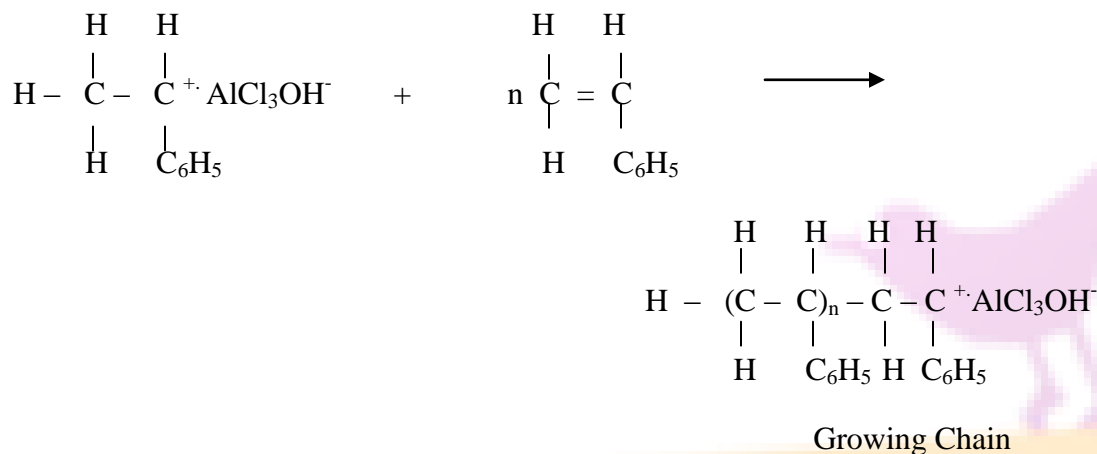
(iii) Termination



Chain initiating species

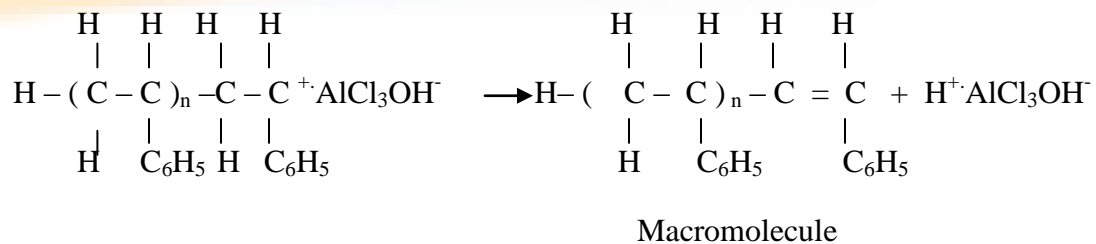
Propagation:

It involves the growth of chain initiating species by successive addition of large number of Monomers.



Termination

Termination of the growing chain involves removal of the catalyst by the addition of proton to the counter ion AlCl_3OH^-



8. Explain Glass transition temperature (T_g) and mention its factors influencing it.

Glass transition temperature is the temperature at which the amorphous solid state is transformed into glass state. Below the glass transition temperature (T_g) the polymer is hard and above which is soft. The hard brittle state is called glassy state and soft flexible state is called as rubbery or viscoelastic state. Thus the glass transition temperature is an important property of a polymer.

Factors influencing T_g

- 1. Molecular weight:** The glass transition temperature of a polymer is influenced by its molecular weight. As the molecular weight increases the T_g also increases.
- 2. Flexibility:** A free rotational motion of the polymer chain imparts flexibility to the polymer. As flexibility decreases the T_g of the polymer increases.
- 3. Crystallinity:** Higher the crystallinity, larger is the T_g value of a polymer. In crystalline polymer, the linear or stereo-regular chains are lined up parallel to each other and are held by strong cohesive forces. This leads to a high T_g value of the polymer.
- 4. Plasticisers:** This when added to polymer improves the flexibility and reduces brittleness and T_g .

9. Discuss about Stereo specific polymer (or) Tacticity

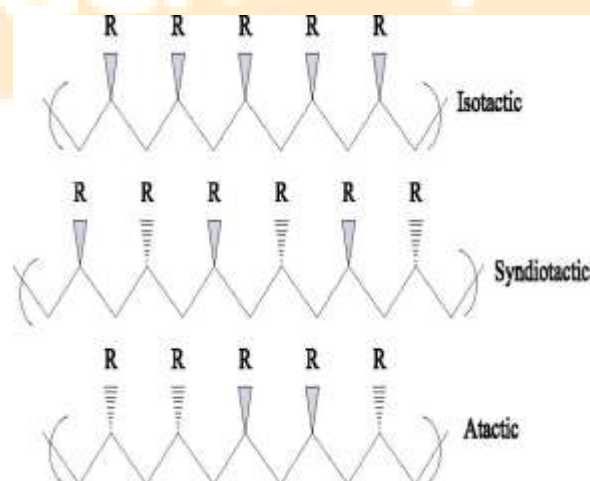
The special orientation of groups in a polymer molecule can be in an order (or) disorder with respect to main chain and this is known as Tacticity.

The three types of stereo - regular polymers are

Isotactic polymer: If the groups attached to the carbon are arranged on the same side of the main chain, the polymer is called Isotactic polymer.

Syndiotactic polymer: If the groups attached to the carbon chain are arranged in an alternating side of the main chain, the polymer is called Syndiotactic polymer.

Atactic polymer: If the groups attached to the carbon chain are arranged randomly, the polymer is called Atactic polymer.



12. Explain about number average and weight average concept of Molecular weight of a Polymer.

Assume that there are total n number of molecules in a polymer sample and n_i of them have

M_1 molecular weight; n_2 have M_2 molecular weight and so on till we get n_i having M_i molecular weight.

Now we have total number of molecules (n) is given by

$$n = n_1 + n_2 + \dots + n_i = \sum n_i$$

Number of Polymer molecules in fraction 1 = n_1

Number fraction of fraction 1 = $\frac{n_1}{\sum n_i}$

Polymer Molecular weight contribution by fraction 1 = $\frac{n_1 M_1}{\sum n_i}$

Similarly molecular weight contribution by other fractions will be

$$= \frac{n_2 M_2}{\sum n_i}, \frac{n_3 M_3}{\sum n_i}, \dots, \frac{n_i M_i}{\sum n_i}$$

Number average molecular weight of the whole polymer will be given by

$$\bar{M}_n = \frac{n_1 M_1}{\sum n_i} + \frac{n_2 M_2}{\sum n_i} + \frac{n_3 M_3}{\sum n_i} + \dots + \frac{n_i M_i}{\sum n_i} = \frac{\sum n_i M_i}{\sum n_i}$$

Similarly, Total weight of the polymer = $W = \sum n_i M_i$

Weight of polymer fraction 1 = $W_1 = n_1 M_1$

Weight of polymer fraction of fraction 1 = $\frac{n_1 M_1}{W} = \frac{n_1 M_1}{\sum n_i M_i}$

Polymer Molecular weight contribution by the other fractions will be

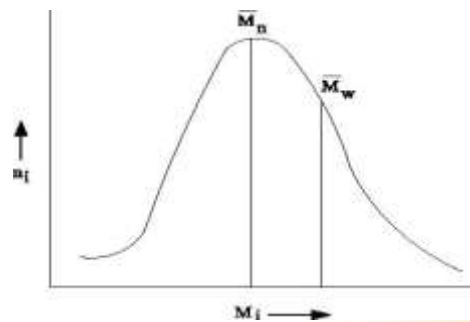
$$\frac{n_2 M_2^2}{\sum n_i M_i}, \frac{n_3 M_3^2}{\sum n_i M_i}, \dots, \frac{n_i M_i^2}{\sum n_i M_i}$$

The weight average molecular weight for all polymer fractions will be then (M_w)

$$\frac{n_1 M_1^2}{\sum n_i M_i} + \frac{n_2 M_2^2}{\sum n_i M_i} + \dots + \frac{n_i M_i^2}{\sum n_i M_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

12. Explain the Polydispersity index of a polymer

A simple chemical compound contains molecules of same molecular weight, such system is called mono dispersed system. For example water contains H_2O molecules of molecular weight of 18. A polymer which contains molecules of different molecular weight is called as polydispersed system. This is due to the variation in the degree of polymerization. The polydispersity of a polymer can be well understood by a simple molecular weight distribution curve (n_i Vs M_i).



The ratio of the weight – average molecular weight (M_w) to that of number – average molecular weight (M_n) is known as polydispersity index (PDI). The PDI is always more than 1

$$PDI = \frac{\overline{M}_w}{\overline{M}_n}$$