

## Unit-1

### INTRODUCTION TO POLYMERS

Monomers, Oligomers, Polymers and their characteristics. Classification of polymers: Natural, synthetic, linear, cross linked and network, Plastics, elastomers, fibers, Homopolymers and Co-polymers. Bonding in polymers: Primary and secondary bond forces in polymers, cohesive energy. Determination of Molecular mass of polymers: Number Average molecular mass ( $M_n$ ) and weight average molecular mass ( $M_w$ ) of polymers.

#### Introduction

##### 1. What are polymers?

Polymers are high molecular weight compounds whose structures are made up of a large number of simple repeating units. The interlinking of many units has given the polymer its name 'Poly' means many, mers means units = polymers. Small molecules are combined to form a big molecule i.e., polymers. It can be formed from one or more chemical compounds.

Eg: Butadiene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ )

butadiene + butadiene + ... + → polybutadiene (m.w-54)(4000 times)

##### 1.1 DEGREE OF POLYMERISATION:

The number of repeating units in a polymer is known as degree of polymerization.

- If  $n = \text{low}$ , Mol.Wt = 500 – 5000 Dalton units, it is Oligo polymer.
- If  $n = \text{High}$ , Mol.Wt = 10,000 – 2,00,000 Dalton units, it is High polymer.

##### 1.2 Monomer:

The repeating units are usually obtained from low molecular weight simple compounds referred to as monomers. The reaction by which monomers are converted into polymers is known as polymerization. The formation of polyethylene from ethylene is an example of polymerization reaction.

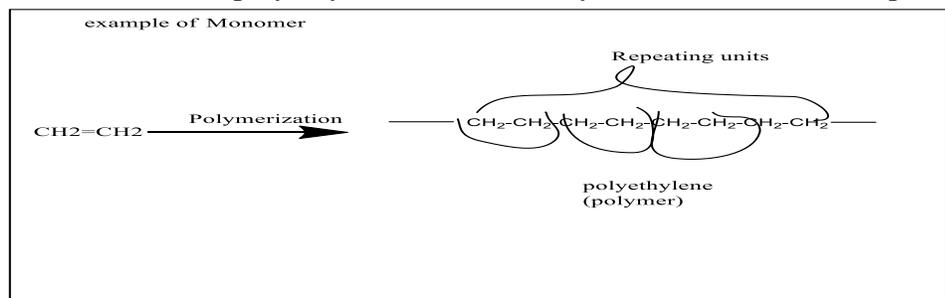


Fig1.2 Example of ethylene monomer

### 1.2.1 Requirements of monomer

- It should possess at least
  - a) two bonding sites (multiple bonds) or
  - b) reactive functional groups.

1.3 Oligomers: Oligomers are low molecular weight polymers comprising a small number of repeating units. This process of formation is called as oligomerization. Oligomers are significantly dependent on the length of the chain. It is the intermediate of the polymerization reaction.

- Types of oligomers:
  1. Homo oligomers (multiple copies of same subunits)
  2. Hetero oligomers (different protein chains).

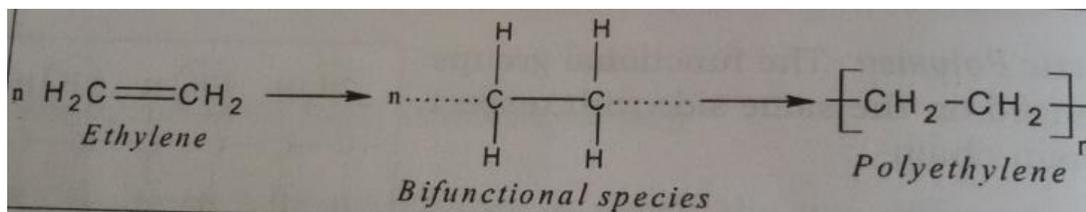
### 1.4 Characteristics of polymers:

Polymers are having Low density, Economical, Good mould ability, Corrosion resistance, Poor tensile strength, Poor temperature strength, Non-toxic in nature, Low cost.

### 1.5 Types of polymerization

The reaction in which monomers combine to give polymers is known as polymerization. It can be broadly classified into three categories as

- addition polymerization: Monomers having multiple bonds (double or triple bond) undergo addition polymerization. Monomers combine to give polymer through addition reaction without elimination of any smaller molecules. Therefore, the molecular weight of the resulting polymer will be an integral multiple of the molecular weight of monomers. Eg: Ethylene to polyethylene.



- condensation polymerization: Monomers having same or different types of functional groups undergo condensation polymerization. The polymerization proceeds by step wise reaction between reactive functional groups and small molecules are eliminated. Eg: polymerization reaction of nylon 6,6.



Copolymerization: It is a special kind of polymerization, otherwise known as “Joint polymerization”. The product is known as ‘Co-polymers’. This is superior to other polymerization because it is used to alter the hardness, strength, rigidity and crystallinity of the monomers.



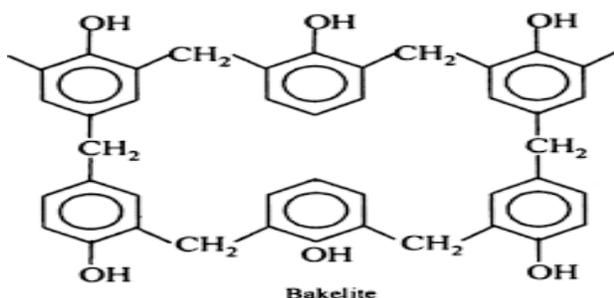
Linear polymer: In these polymers' monomers are linked with each other and form a long straight chain. These polymer chains do not consist any side chains. A linear polymer can be schematically represented by a single line. Example: polyethylene

-A-A-A-A-A-A-A-A-A-A- a polymer made of A atoms.



Cross linked polymer: They have long straight chain with different branched side chains. Molecules are irregularly packed. Example: polyethylene HDPE-High Density polymer LDPE-Low Density polymer

Network polymers: Network polymers have trifunctional monomeric units that are formed by many interconnected polymer chains. They are giant molecules in which movement of individual monomeric unit is prevented by strong cross links. It is having three active covalent bonds. It should be in three-dimensional network. Eg: Bakelite, urea formaldehyde, melamine formaldehyde, etc.



1.3Plastics: The term plastic or plastic material, is given to “organic materials of high molecular weight, which can be moulded into any desired form, when subjected to heat and pressure in the presence of a catalyst”. The term plastics are differentiated from the resin. Resins are the basic binding materials which form a major part of the plastics, and which actually has undergone polymerization and condensation reactions, during this preparation.

#### 1.3.1 Thermoplastic polymers:

These polymers are linear, long chain polymers, which can be softened on heating and cooling reversibly. This is called thermoplastics, their hardness is a temporary property, subject to change with rise or fall of temperature. Eg: polythene, polypropylene (PP), polyvinylchloride (PVC), PTFE, etc.

1.3.2 Thermosetting polymers (thermosets): Thermosets are those polymers, which during moulding (by heating) get hardened and once they have solidified i.e. they are permanent polymers. Such polymers during moulding acquire three-dimensional cross-linked structure, with strong covalent bonds.

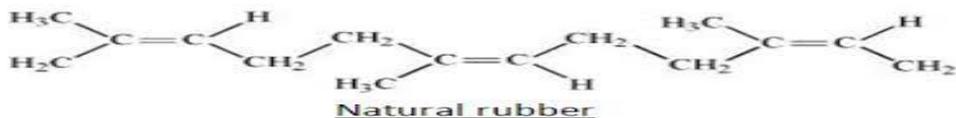
Thus, a thermosetting polymer once moulded cannot be reprocessed.

Eg: polystyrene (terylene), Bakelite, epoxy resin, melamine, urea formaldehyde etc.

## Differences between Thermoplastics and thermosetting plastics

S.No	THERMOPLASTICS	THERMOSETTING PLASTIC
1	Eg.PVC , Polyethylene	Polyester, Bakelite
2	Plastics which are melted at high temperature, solidified at low temperature They can be remelted and remoulded into any desired shapes for any number of times.	They cannot be remoulded after their first usage.
3	Scrap can be used again.	Scrap cannot be used again.
4	Formed by addition polymerization	Formed by condensation polymerization
5	The bond strength is low	The bond strength is high
6	Molecular weight is low	Molecular weight is high
7	Soluble in organic solvents.	Insoluble in organic solvents.
8	Prepared by Injection moulding	Prepared by compression moulding.
9	They have linear structure	They have complex 3D structure.

1.4 Elastomers: Elastomers are high polymers, which have elastic properties in excess of 300%. An elastomer (rubber) is any vulcanisable man-made rubber-like polymer. When vulcanized into the rubbery products exhibiting good strength and elongation, polymers used as elastomers. An elastomer molecule is not straight chained eg: polyethene, nylon etc., but in the case of coil, it can be stretched like a spring. Natural rubber consists of basic material latex, which is a dispersion of isoprene. The isoprene molecules polymerize to form, long-coiled chains of cis-polyisoprene. Structure of natural rubber:



1.4.1 Fibres: are those polymers whose chains are held by strong intermolecular forces like hydrogen bonding. They are crystalline in nature and of high tensile strength, due to strong intermolecular forces.

Eg: nylon, polyester

1.5 Homopolymers: When all the repeating units in a particular polymer have the same structure, that polymer is called a homopolymer. Eg: vinyl chloride

1.5.1 Copolymers: When different repeating units make up the polymer chain, the polymer is called a copolymer. A-A-B-B-B-A-B-A-A-B—

Types of copolymer:





## MECHANISM OF POLYMERIZATION

Chain growth polymerization: Cationic polymerization-anionic polymerization –free radical polymerization. Stereo regular polymers: Ziegler Natta polymerization, Step growth polymerization.

### Chain growth polymerization

- Chain growth polymerization is characterized by a self –addition of the monomer molecules, very rapidly through a chain reaction. In this polymerization no byproduct is formed. The bifunctionality is provided by the double bonds present in the monomer.i.e. compounds containing reactive double bonds undergo chain growth polymerization. Eg: vinyl,allyl, dienes, olefins. Chain polymerization mainly consists of three major steps, namely,
- Initiation
- Propagation
- termination

followed by the process is, Free radical cationic and anionic polymerization reaction.

- 
- **1.1Free radical polymerization:**The initiation of the polymer chain is brought about by free radicals produced by the decomposition of compounds called initiators.Chain growth means continuous addition of the monomer units to form polymer chain.
- Initiation:free radicals contains lone pair of electrons.A free radical is highly reactive and can attack any molecule which has a lone pair of electrons this process is calledinitiation. Eg:benzoyl peroxide,azobis isobutyronitrile.
- STEP1: Initiators is thermally unstable compounds and decompose into products called free radicals.
- The initiators can be written as R: R

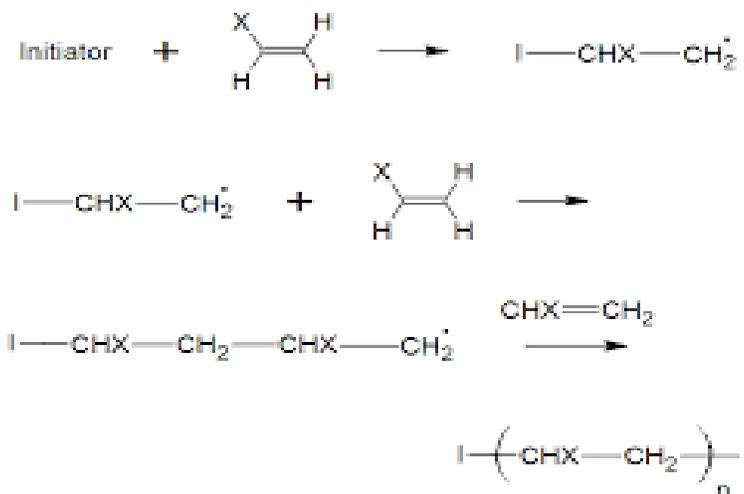
When heat is supplied in this compound, the molecule is split into two symmetrical components.



- STEP2: Propagation:In this propagation step, the radical site at the first monomer unit attacks the double bond of a fresh monomer molecule.This results in the linking up of the second monomer to the first and the transfer of the radical site from the first monomer unit to second, by the unpaired electron transfer process.

- $M1^\circ + M \rightarrow M2^\circ$
- $M2^\circ + M \rightarrow M3^\circ$
- $Mn^\circ + m \rightarrow Mn+1$
- STEP3: Termination: This process involves coupling of the two lone electrons, this kind of termination is called as termination of coupling.
- There are two types of coupling reactions.

1. disproportionation      2. dead polymer



## 1.2 Ionic polymerization:

- The ionic mechanism of chain polymerization also involves an attack on the pi electron pair of the monomer. It is a positive or negative ion.
- Two types of ionic polymerization.

1. cationic polymerization

2. anionic polymerization

1.2.1 **Cationic polymerization:** The proton pulls the pi electron pair towards it and positive charge of the proton is transferred to the end of the monomer molecules, forming carbonium ion. In this process, a sigma bond is formed between the proton and the monomer unit and the polymer chain growth initiated. The carbonium ion attacks the pi electron of the second monomer molecules and pulls it over. the positive charge is transferred to the second monomer unit.

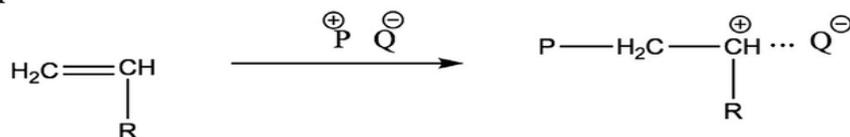
Three steps are involved in this process.

Initiation

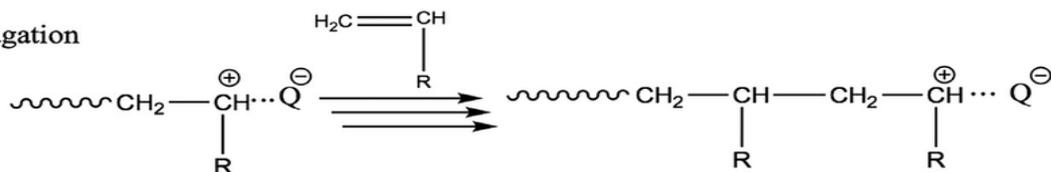
Propagation

termination

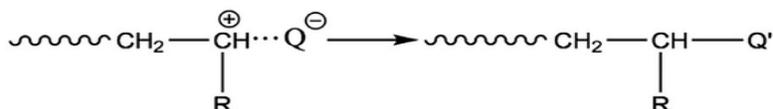
·Initiation



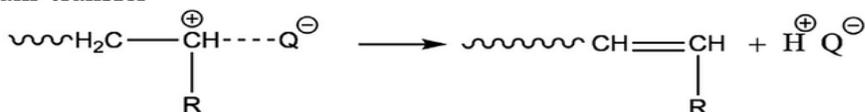
·Propagation



·termination

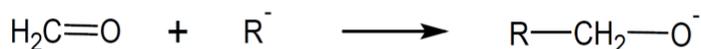


·Chain transfer

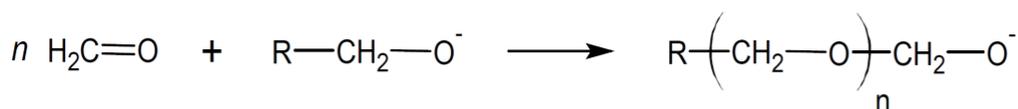


- **1.2.2 Anionic polymerization:** Monomer is done by negatively charged ion, an anion. Such a system has electrons and extra electrons and the resultant negative charge attacks the pi electron pair pushing it to the end of the molecule. It forms sigma bond with the monomer molecules. Next carbanion is formed and now propagates the chain growth by attacking the second monomer unit followed by termination process.

*Initiation*



*Propagation*



*Termination*

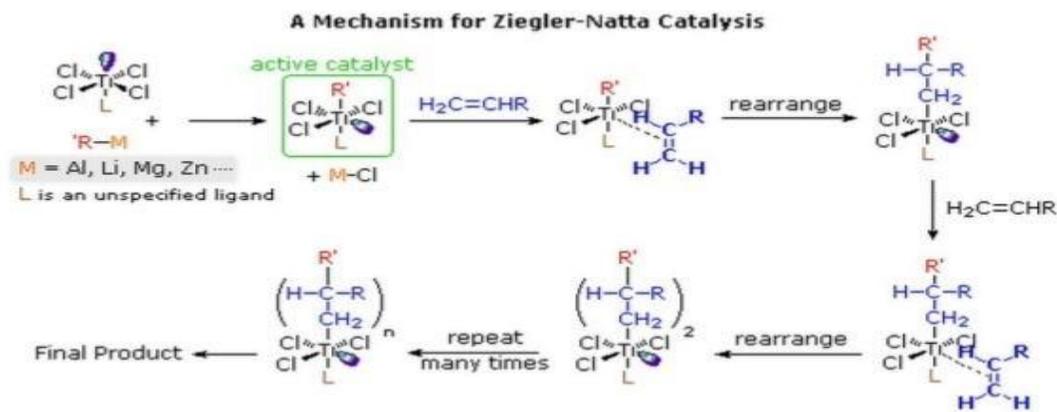


**Stereo regular polymers (stereo specific polymers):**

- Each monomer segment is in a regular configuration giving a definite structural regularity to the polymer molecules. The structural regularity in a polymer are termed as Optical and geometrical isomerism of the main chain atoms or substituent's in the polymer molecule.

- **1.3.1 Ziegler –Natta polymerization:** Ziegler-Natta process for the polymerization of olefins used as a catalyst formed from  $\text{TiCl}_4$  to  $\text{TiCl}_3$  and  $\text{Al}(\text{C}_2\text{H}_5)$ . The rate of polymerization reaction is proportional to the total amount of  $\text{TiCl}_3$  ( $\text{Al}(\text{C}_2\text{H}_5)$  reduces to  $\text{TiCl}_4$  to  $\text{TiCl}_3$  and in the presence of the olefin and is independent of  $\text{AlEt}_3$  concentration.
- These are special type of coordination catalyst comprising two components as against single -component organometallic compounds.
- The two components are generally referred to as the catalyst and the co-catalyst. The monomer is complexes with the metal ion of the active center before its insertion into the growing chain. When the catalyst and cocatalyst components are mixed there occurs a chemisorption of aluminum alkyl on the titanium chloride solid surface, resulting in the formation of an electron deficient bridge complex of the structure.
- This complex now active center. The monomer is then attracted towards the Ti-C bond is the active Centre. When it forms a  $\pi$  complex with the  $\pi$ . the bond between R and olefins up producing an electron deficient Ti and a carbanion at R.

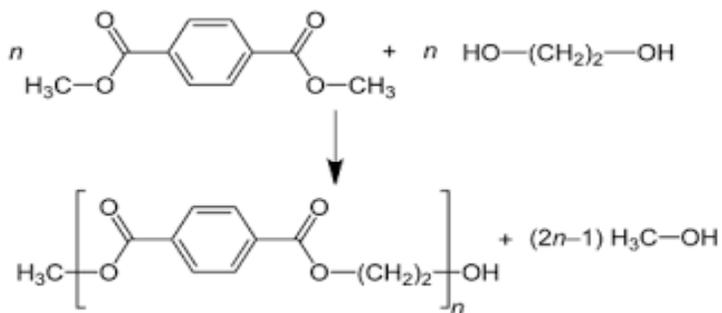
## Mechanism Of Ziegler Natta Catalysis



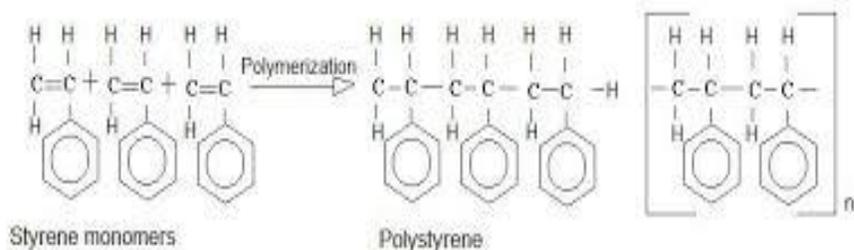
### Step growth polymerization:

- The polymer buildup proceeds through a reaction between functional groups of the monomers. Organic functional groups can be made use of this polymerization. Step growth polymerization are mostly accompanied by the elimination of small molecules.
- Polycondensation reaction: This is brought about by monomers containing two or more reactive functional groups condensing with each other. Basic reactions the same as between various functional groups in low molecular weight organic compounds. Foreexample, the reaction between a hydroxyl group and a carboxylic group, giving an ester and a water molecule.
- Step polymerization regarding,
- That monomers should have two functional groups for polymerization to proceed.

- That polymerization proceeds by step wise reaction between functional groups. that only one type of reaction
- The polymer formed still contains both the reactive functional groups at its chain ends and it also active and dead as in chain polymerisation.
- Example polycondensation reaction of polyethylene terephthalate.



- Polyaddition reaction: This is brought about by migration of atoms from one another, or to the intermediate product.
- Vinyl monomers as well as monomers pairs with reactive functional groups can undergo polyaddition polymerization.
- Styrene, for example can be polymerized in the presence of perchloric acid by this method.



Reference:

Textbook of polymer chemistry.,Gowarikar.,Viswanathan.,