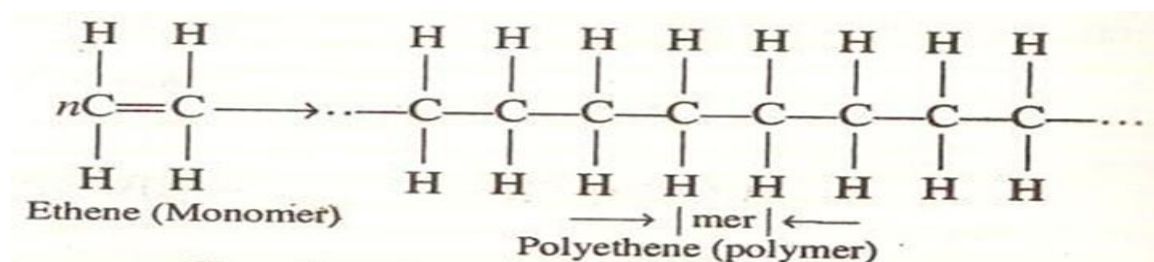
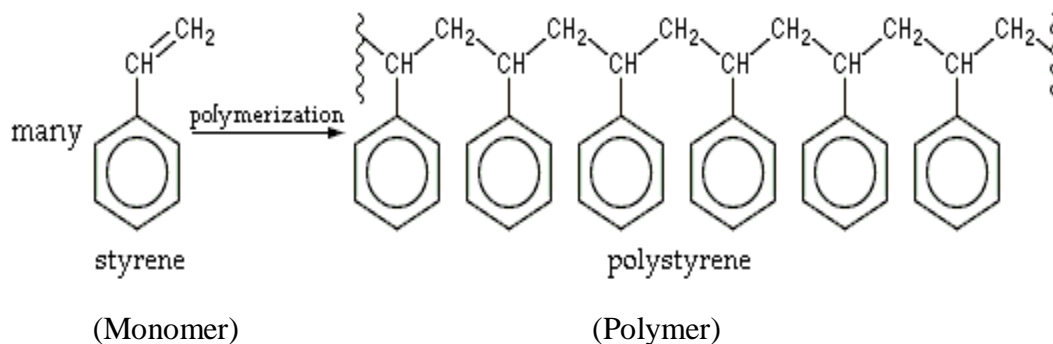


POLYMERS (HIGH POLYMERS)

Polymers (Greek term Poly-many; mers-units or parts) are ‘macromolecules (giant molecules of high molecular masses) built up by the linking together of a large number of small molecules (called monomers). For example, polythene is a polymer formed by linking together of a large number of ethene (C_2H_4) molecules. Thus



Thus, small molecules which combine with each other to form polymer molecule are termed as **monomers** and the repeating unit in a polymer is called **mer**. Thus:



The number of repeating units (n) in chain formed in a polymer is known as “degree of **polymerization (DP)**”. There may be hundreds or thousands or tens of thousands or more monomer molecules linked together in a polymer molecule. Most of the polymers, usually, fall into the **5000-200000** molecular mass range.

Characteristics of Polymers:

- (1) Polymeric molecules are very big molecules. Their average molecular weights may approach 10^5 or more. That's why, they are also known as macromolecules.
- (2) Polymers are semi-crystalline materials. It means they have both amorphous and crystalline regions. In fact, polymers have regions of crystallinity, called crystallites, embedded in amorphous regions. Crystallites provide strength and hardness and the amorphous regions provide flexibility to the polymeric material.

- (3) The intermolecular forces in polymers can be Vander Waals' forces, dipole-di-pole attractions or hydrogen bonding. These intermolecular forces are in addition to covalent bonds which connect the repeating units into a macromolecule.
- (4) The chemical, electrical, optical, mechanical and thermal properties of polymers depend on (i) size and shape of polymers, and (ii) the presence or absence of characteristic intermolecular forces. These parameters not only determine the properties of the polymers, but also the performance of these materials in a given applications.
- (5) Polymers show time-dependent properties.
- (6) Polymers are combustible materials.
- (7) Polymers have low densities and they show excellent resistance to corrosion.
- (8) Generally, polymers are thermal and electrical insulators.
- (9) Polymeric materials are easily mouldable even into complex shapes with reproducible dimensions with a minimum of fabrication and finishing cost.

NOMENCULATURE OF POLYMERS:

A polymer may consist of identical monomers or monomers of different' chemical structure and accordingly they are called **homo-polymers** and **co-polymers** respectively. Thus:

.....M-M-M-M-M-M-M-M.....

Homopolymer

.....M₁-M₂-M₁-M₂-M₁-M₂-M₁-M₂.....

Hetero/Co-polymer

Staudinger Herman a German Chemist, one of the pioneers in polymer Chemistry, awarded Noble prize in Chemistry in the year 1953

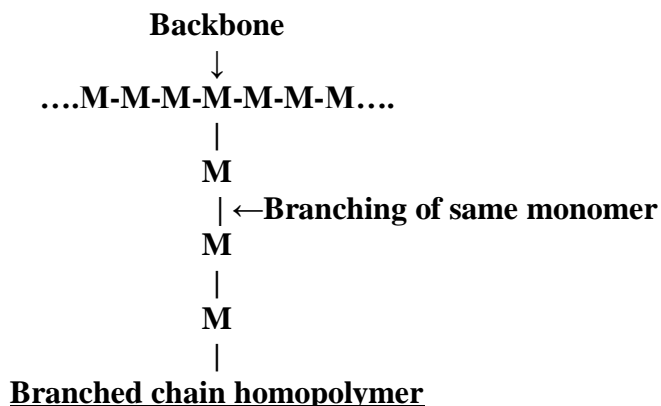
The monomeric unit in a polymer may be present in linear, branched or cross linked (three dimensional) structure. Thus:

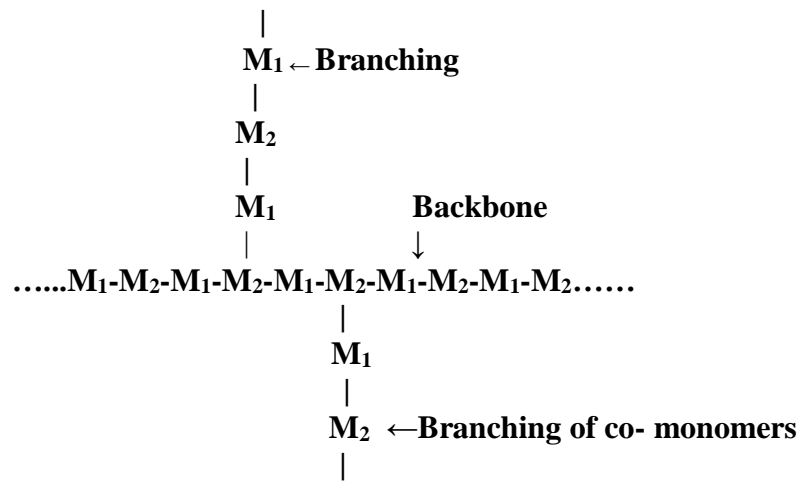
....M-M-M-M-M-M-M-M.....

Linear homopolymer

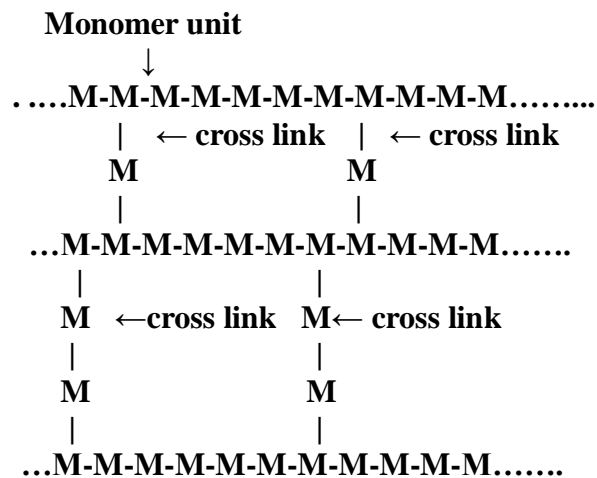
.....M₁-M₂-M₁-M₂-M₁-M₂-M₁-M₂.....

Linear copolymer



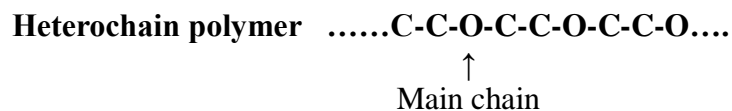
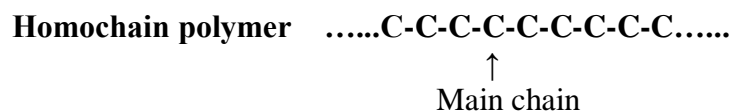


Branched chain copolymer



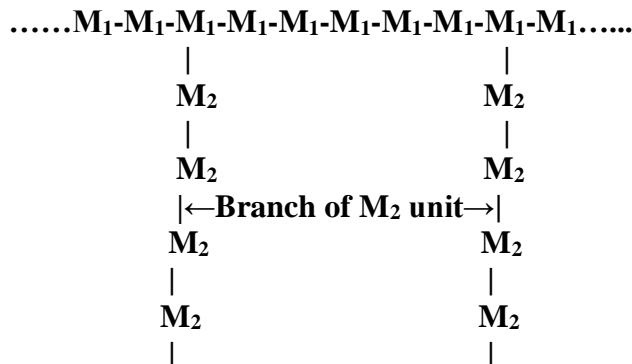
Crossed linked homo-polymer

If the main chain is made up of same species of atoms, the polymer is called “**homochain polymer**” and if the main chain is made up of different atoms, then it is called as “**heterochain polymer**”. Thus:



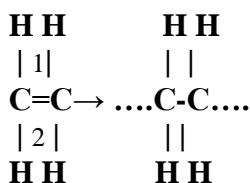
Graft copolymers are branched structures in which the monomer segments on the branches and the backbone differ. Thus:

Graft copolymer



FUNCTIONALITY (No. of bonding sites):

For a substance to act as monomer, it must have at least **two reactive or bonding sites**. The number of bonding sites in a monomer is referred to as its **functionality**. In an olefin, the double bond can be considered as a site for two free valency. When the double bond is broken, two single bonds become available for combination. Thus:



Thus, ethylene is considered to be bifunctional. Other reactive groups are hydroxyl, acid, amino acid, poly alcohols, di-amino acids, di-acids etc.

(i)**Linear or Straight Chain Polymer:** In case of a **bifunctional monomer**, two reactive groups attach side by side to each other forming **linear or straight chain polymer**. Linear molecules consist of monomer units linked by primary covalent bonds, but the different chains are held together by secondary vander waals forces of molecular attraction. This gives the possibility of **chain movement** in one direction.

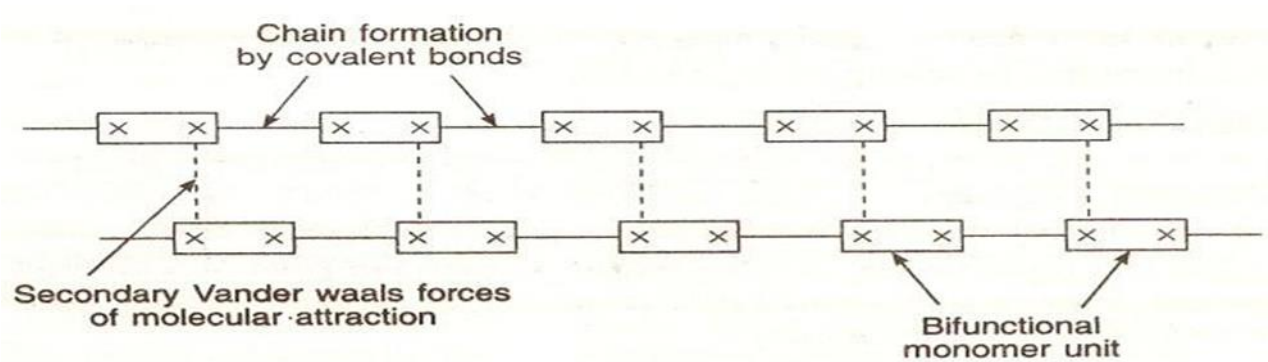


Fig: Linear chain polymer from a bifunctional monomer

(ii)**Branched Chain Polymers:** During the chain growth, side chains may also form, resulting in **branched-chain polymers**. Such a molecule is a linear, but the movement in branched-chain molecules is, generally, **more restricted** than that of simple straight-chain molecules. A branched-chain polymer also results, when a trifunctional monomer is mixed in **small amounts** with a bifunctional monomer and polymerized.

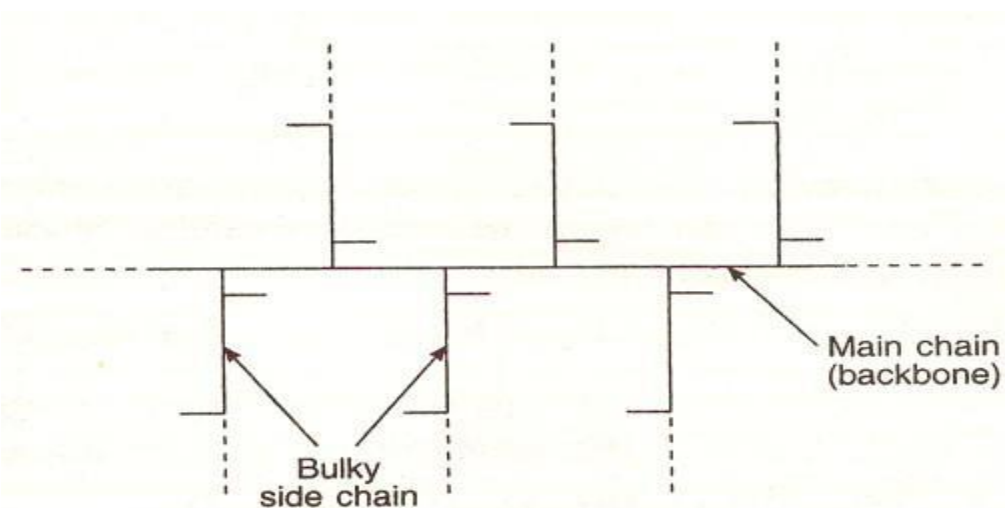


Fig: Branched chain polymer

(iii)**Network Polymer:** In case of **polyfunctional groups**, monomer molecules are connected to each other by covalent bonds, resulting in the formation of a **three-dimensional network** polymer. In such polymeric molecules, the movement of individual molecules is **prevented by strong cross-links**.

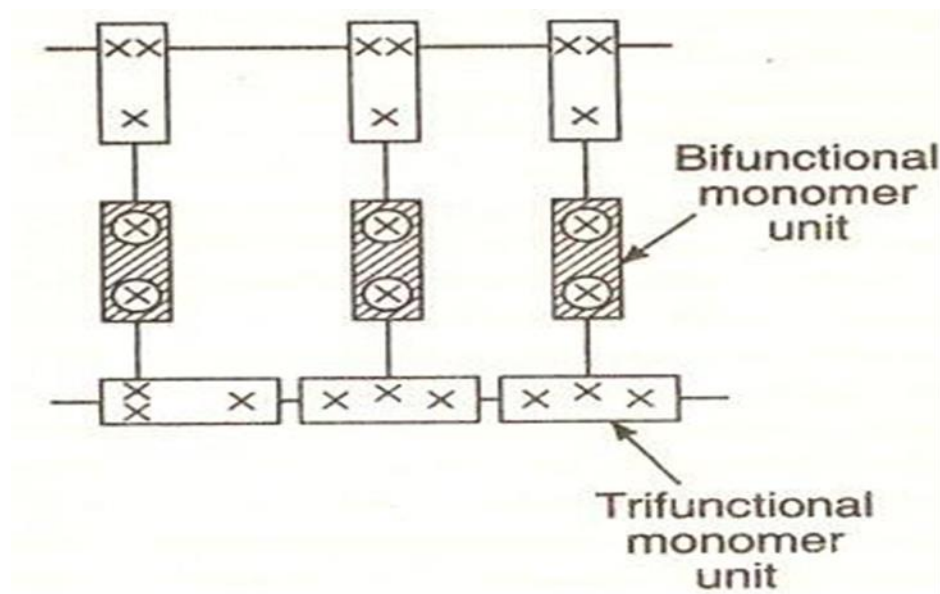


Fig.: Reaction between two and three functional molecules

CLASSIFICATION OF POLYMERS:

Polymers can be classified in a number of ways:

(1) Classification based on Number of Monomers: Polymers can be homopolymer or copolymer when the number of monomers are one and two respectively.

(i) Copolymers: Molecules which are built up of at least two different kinds of monomer are known as co-polymers. Thus, a co-polymer is obtained when two or more suitable monomers are polymerized together.

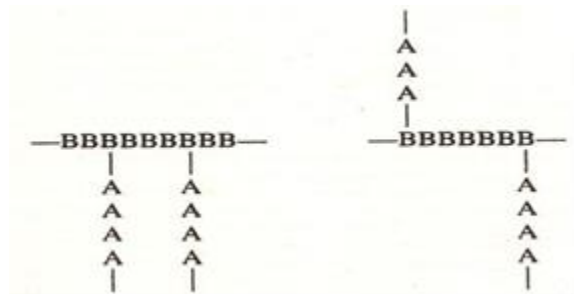
The chains of co-polymer consist of repeating units derived from each monomer. Following are some common types of co-polymers:

(a) Alternating co-polymers: In such Co-polymers, the different repeating units alternate in each chain. If A and B represent two different units then an alternating co-polymer will be represented as, **-ABABABAB-**

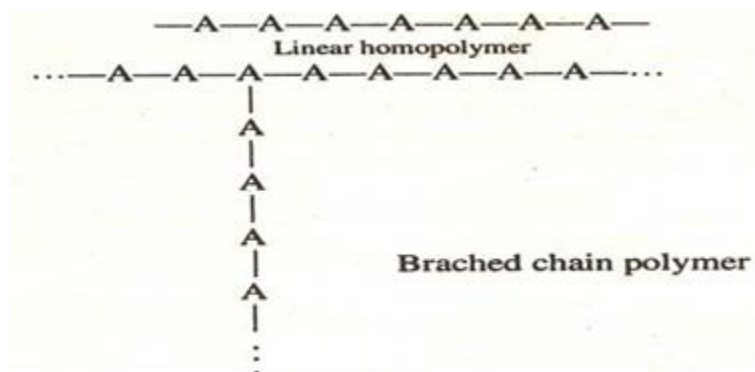
(b) Random co-polymers: In this type of copolymers, the different repeating units are not arranged in a systematic manner but are randomly arranged, e.g. **-ABAABABBAABA-**

(c) Block co-polymers: In such co-polymers, block of repeating units of one type alternate with block of another type, e.g. **-AAAABBBBAAAABBBB-**

(d) Graft co-polymers: In such co-polymers, blocks of one repeating units are attached or grafted to a block of linear polymer, e.g.



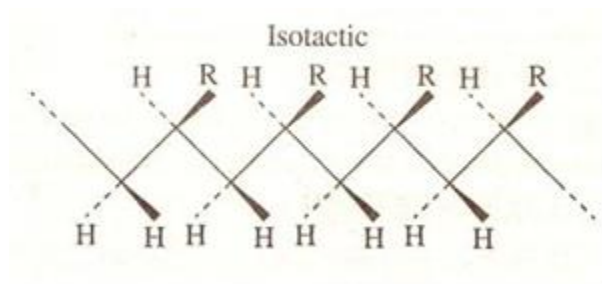
(ii) Homopolymers: If the polymers consist of monomer of identical chemical structure then they are called homopolymers, e.g.,



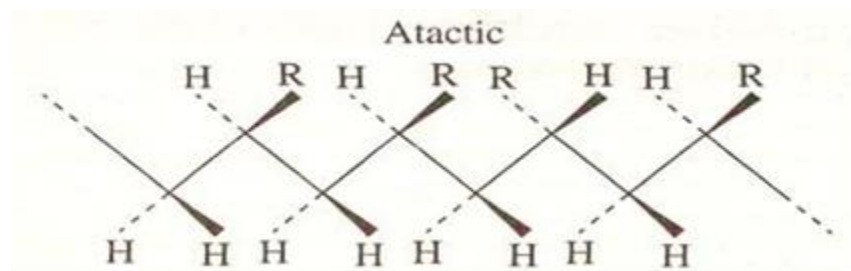
(2) Classification based on Tacticity:

The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain. The difference in configuration (tacticity) do affect their physical properties. Based on tacticity they are classified as follows:

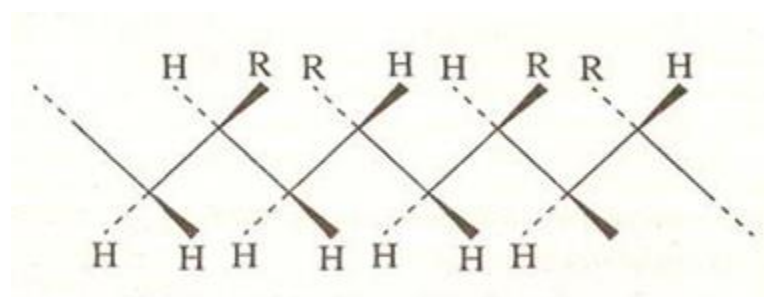
(i) Isotactic Polymer: The head-to-tail configuration, in which the functional groups are all on the same side of the chain, is called isotactic polymer, e.g.,



(ii)Atactic Polymer: If the arrangement of functional groups are at random around the main chain, it is called atactic polymer, e.g., polypropylene.



(iii)Syndiotactic: If the arrangement of side groups is in alternating fashion, it is called syndiotactic polymer, e.g., gutta percha.



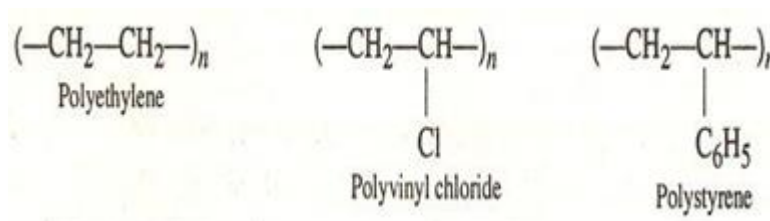
(3) Classification on the basis of source:’

- (i) **Natural polymers:** Which are found in nature in animals and plants. For e.g., starch (a polymer of α D-glucose), cellulose (a polymer of β -D glucose), proteins (poly peptides and polyamides), nucleic acids, natural rubber (a polymer of cis -isoprene)

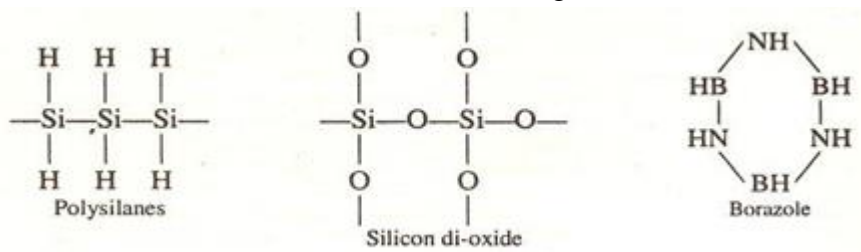


2 Methyl -1,3 butadiene (isoprene) Polyisoprene (Natural Rubber)

- (i) **Synthetic polymers (Man-made polymers):** like polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), nylon, terylene, Bakelite etc.



- (ii) **Inorganic Polymers:** These are polymers containing no carbon atoms. The chains of these polymers are composed of different atoms joined by chemical bonds, while weaker inter-molecular forces act between the chains, e.g.,



(4) Classification on the basis of structure:

- (i) **Linear polymers or straight chain polymers:** In which monomeric units are joined in the form of long straight chain. For e.g., high density polythene (**HDPE**), nylons, polyesters etc. These polymers possess high melting point, density, tensile strength due to close packing of polymer chain.
- (ii) **Branched chain polymers:** are mainly linear in nature, but also possess some branches along the main chain. For e.g., Low density polymer (**LDPE**), glycogen, amylopectin etc. These polymers possess low melting point, density and tensile strength compared to linear polymers, due to poor packing of polymer chain in presence of branches.
- (iii) **Three -dimensional network polymers:** contains monomers molecules connected to each other by only **covalent bonds**. They, are giant molecules in which movement of individual monomeric units is prevented by strong cross links. Due to presence of strong cross links, they are hard, brittle, and do not melt but burn on strong heating. Example: are Bakelite, urea-formaldehyde, melamine formaldehyde etc.

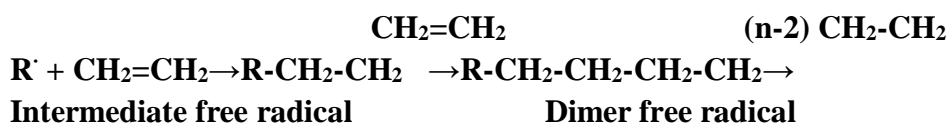
(5) Classification on the basis of their methods of synthesis:

- (i) **Addition polymers:** are obtained by addition polymerization method, which involves the repeated addition of monomers (unsaturated derivatives of ethene) to yield long chain. There, empirical formula is same as that of their monomers. Example, polyethylene, polypropylene, polystyrene, polyvinyl chloride etc.
- (ii) **Condensation polymers:** are obtained by a series of condensation reactions, generally involving two monomers. The condensation reactions usually, results in the loss of small molecules (like

H₂O, HCl, NH₃ etc.). Example: nylon-6 (from adipic acid and hexamethylene diamine), bakelite (from phenol and formaldehyde), polyester (from terephthalic acid and ethylene glycol) etc.

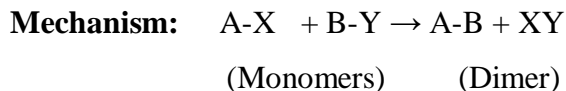
(6) Classification on the basis of growth polymer chain:

- (i) **Chain growth polymers:** are formed by the successive addition of monomer units to the growing chain carrying a reactive intermediate. Example: are polyethene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC) etc. **Mechanism**

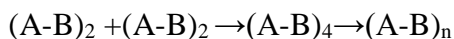


Chain growth polymer (polythene)

- (ii) **Step-growth polymers:** are formed through a series of independent reactions involving bond formation (condensation) between two different monomers with loss of small molecules like H₂O, HCl, NH₃ etc.



(Tetramer)



(Condensation polymer)

(7) Classification based on molecular forces: on the basis of magnitude of intermolecular forces present in polymers:

- (i) **Thermoplastic polymers:** are linear, long chain polymers, which can be softened on heating and hardened on cooling reversibly. i.e., their hardness is a temporary property, subject to change with rise or fall of temperature. Thus, they can be processed again and again

Examples: Polythene (PE), Polypropylene (PP), Polyvinylchloride (PVC), Polystyrene (PS), Nylons, **Polytetrafluoro ethylene** (PTFE) or Teflon) etc.

- (ii) **Thermosetting polymers (Thermosets):** are those polymers, which during moulding (by heating etc.) get hardened and once they have solidified, they **cannot be softened**, i.e., they are permanent setting polymers. Such polymers during moulding acquire three-dimensional cross-linked structure, with predominantly strong covalent bonds. Thus, a thermosetting polymer **once moulded cannot be reprocessed**.

Examples: Polyester(terylene), bake-lite, epoxy-resin, melamine, urea-formaldehyde etc.

- (iii) **Elastomer (Synthetic Rubber):** is any rubber like elastic polymer, which can be stretched to at least thrice its length but it returns to its original shape and dimensions as soon as stretching force is released. The elastic deformation in an elastomer arises from the fact that in an unstressed condition, an elastomer molecular chain is in the form of a coil and consequently it can be stretched like a spring. The chain reverts back to their original coiled state as the deforming stress is released.

Held together by the weakest intermolecular forces e.g., Vulcanized Rubber. Vulcanization is a process of treating natural rubber with sulphur. Rubber is vulcanized to render it non-plastic and give it greater elasticity and ductility.

- (iv) **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.

Examples: Nylons, Polyester etc.

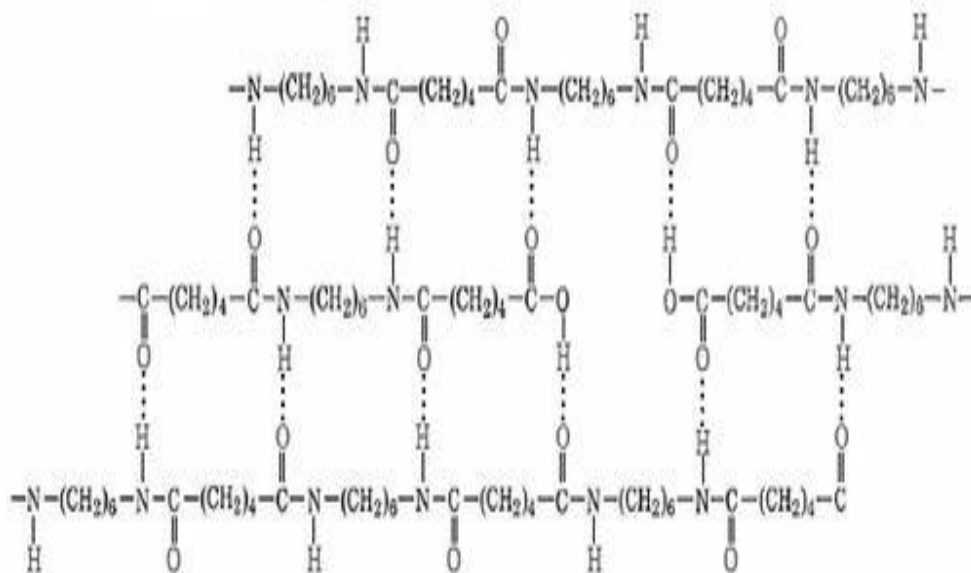
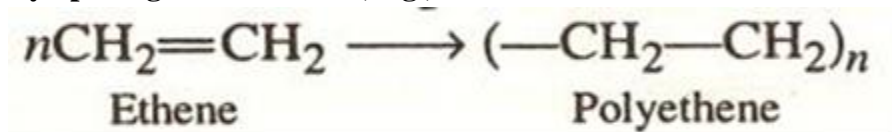


Fig.:Hydrogen bonding in Nylon-66

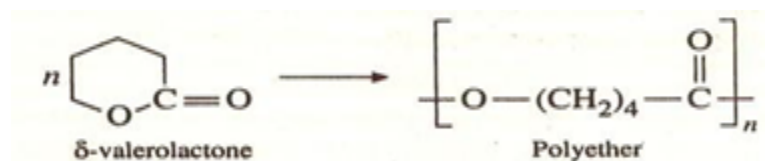
Thermoplastic Polymers	Thermosetting Polymers
1.They soften on heating readily.	They do not soften on heating. On prolong heating, however they burn.
2.They consist of long chain linear macromolecules.	Their set molecules have three-dimensional network structure, joined by strong covalent bonds.
3.They are formed mostly by addition polymerization.	They are formed mostly by condensation polymerization.
4.By reheating to a suitable temp. they can be softened, reshaped and thus reused.	They retain their shape, structure, even on heating. Hence, they cannot be reshaped and reused.
5.They are usually soft, weak and less brittle.	They are usually hard,strong and more brittle.
6.These can be reclaimed from wastes.	They cannot be reclaimed from wastes.
7.They are usually, soluble in some organic solvents.	Due to strong bonds and cross linking, they are insoluble in almost all organic solvents.

POLYMERIZATION: Polymerization is the process by which simple (monomer) molecules join together to form very large (polymer) molecules. Hence, the synthesis of large molecular weight polymers by the combination of monomer molecules is termed as polymerization. There are three different ways for doing polymerization:

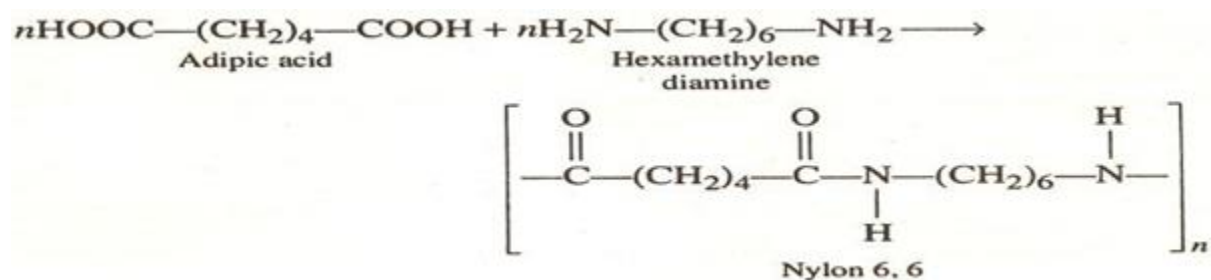
(a) By opening a double bond, e.g.,



(b) By opening a ring e.g.

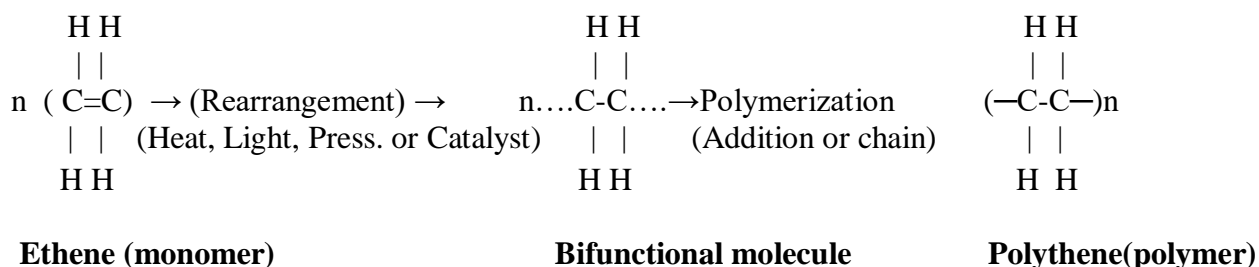


(c) By using molecules having two functional groups e.g.



TYPES OF POLYMERIZATION:

(1) **Addition or Chain Polymerization:** is a reaction that yields a product, which is an exact multiple of the original monomeric molecule. Such a monomeric molecule, usually contains one or more double bonds, which is intermolecular rearrangement, may make molecule *bifunctional*. The addition polymerization reaction must be instigated by the application of heat, light, pressure or a catalyst for breaking down the double covalent bonds of monomer. Thus:



Addition /Chain Polymerization	Condensation Polymerization
1.Only growth reaction adds repeating units one at a time to the chain.	Any two molecular species present can react.
2.Number of units decreases steadily throughout the reaction.	Monomer disappears early in the reaction.
3.High molecular mass polymer is formed at once.	Polymer molecular mass or (DP) rises steadily throughout the reaction.
4.Longer reaction times have a little effect on molecular weight but gives higher yields.	To obtain high molecular weight, longer reaction time is essential.
5.The reaction mixture contains only monomers, high polymers and about 10-8 part of growing chains.	All types of molecular species are present at any stage.

MECHANISM OF ADDITION POLYMERIZATION:

In addition, polymerization, the polymer is formed from the monomer, without the loss of any material and the product is an exact multiple of the original monomeric molecules.

Addition polymerization reactions proceed by a chain reaction mechanism consisting of three important steps,

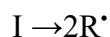
- (i) **Initiation or the formation of an active centre,**
- (ii) **Propagation or the formation of a polymer having the active centre**
- (iii) **Termination or removal of the active centre.**

The three different types of active centres have been found to be formed during the addition polymerization, viz., free radical, carbonium ion and carbanion. So, the mechanisms involving these reactive species in polymerization constitute the mechanism of addition polymerization.

Polymerization of ethylene and its substituted compounds $\text{CH}_2=\text{CHX}$ can be carried out using any of the four mechanisms:

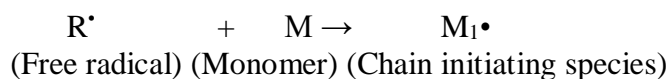
(1) **Free radical polymerization mechanism** involves the following steps:

- (i) **Initiation step:** is considered to involve two reactions: The first is the production of free radical by homolytic dissociation of an initiator (or catalyst) to give a pair of radicals R^\bullet

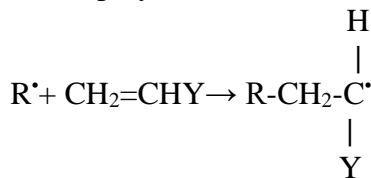


(Initiator) (free radical)

The second part of initiation involves the addition of this radical to the first monomer molecule (M) to produce the chain initiating species, M_1^\bullet

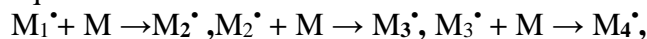


Thus, the polymerization of monomer $\text{CH}_2=\text{CHY}$ takes in the form:



(The radical R^\bullet is often referred as an initiator radical or a primary radical)

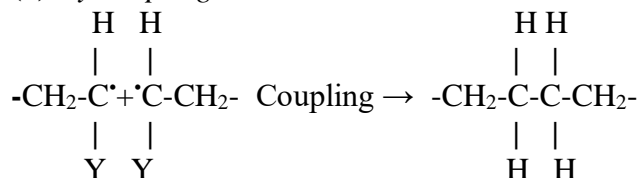
- (ii) **Propagation step:** consists of the growth of M_1^\bullet by successive additions of large number (hundreds and perhaps thousand) of monomer molecules according to equations:



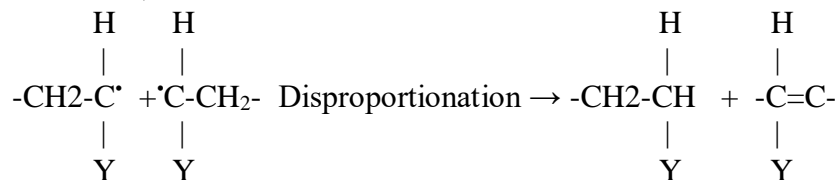
In general terms: $\text{M}_n^\bullet + \text{M} \rightarrow \text{M}_{n+1}^\bullet$

- (iii) **Termination step:** At some point the propagating polymer chain growing and terminates:

(a) *By coupling or combination:*

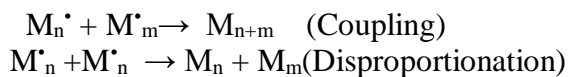


- (b) More rarely *by disproportionation* in which a hydrogen atom of one radical centre is transferred to another radical centre, this results in the formation of two polymer molecules, one saturated and one unsaturated:



(Saturated) (Unsaturated)

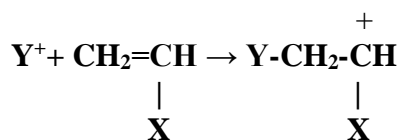
The two different modes of termination can be represented in general terms by:



The terms “*dead polymer*” signifies the cessation of the growth of the propagating radical

- (2) **Cationic Mechanism of polymerization** involves the following steps:

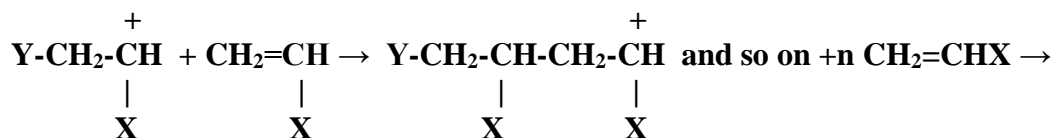
- (i) **Initiation:**



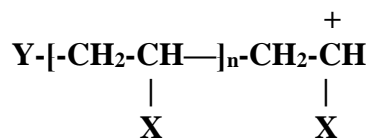
An acid (A cation)

A new cation (Carbocation)

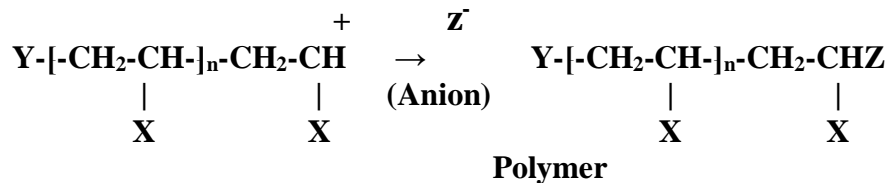
- (ii) **Propagation:**



A new cation (Carbocation)

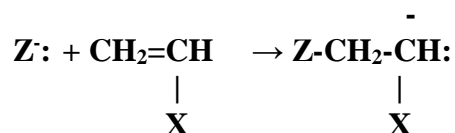


(iii) Termination:



(3) Anionic Mechanism of polymerization involves the following steps:

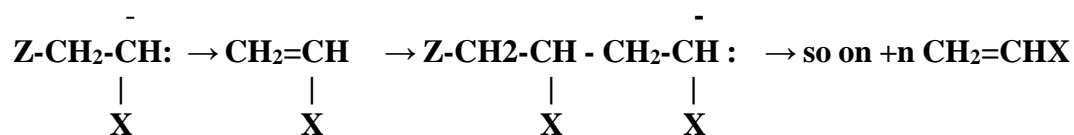
(i) Initiation:



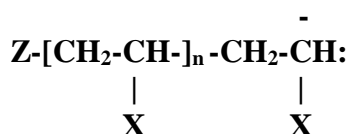
(A base (Anion))

(A new anion(carbanion))

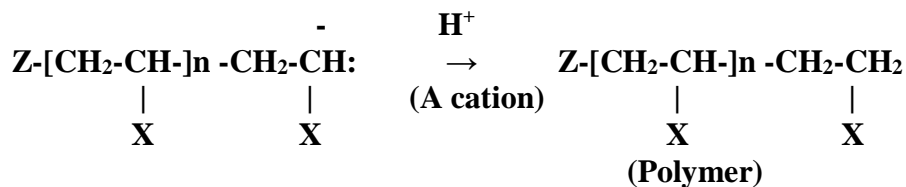
(ii) Propagation:



(A new anion)



(iii) Termination:



(3) **Coordination polymerization or Zeigler -Natta Polymerization:** Zeigler (1953) and Natta (1955) discovered that in

