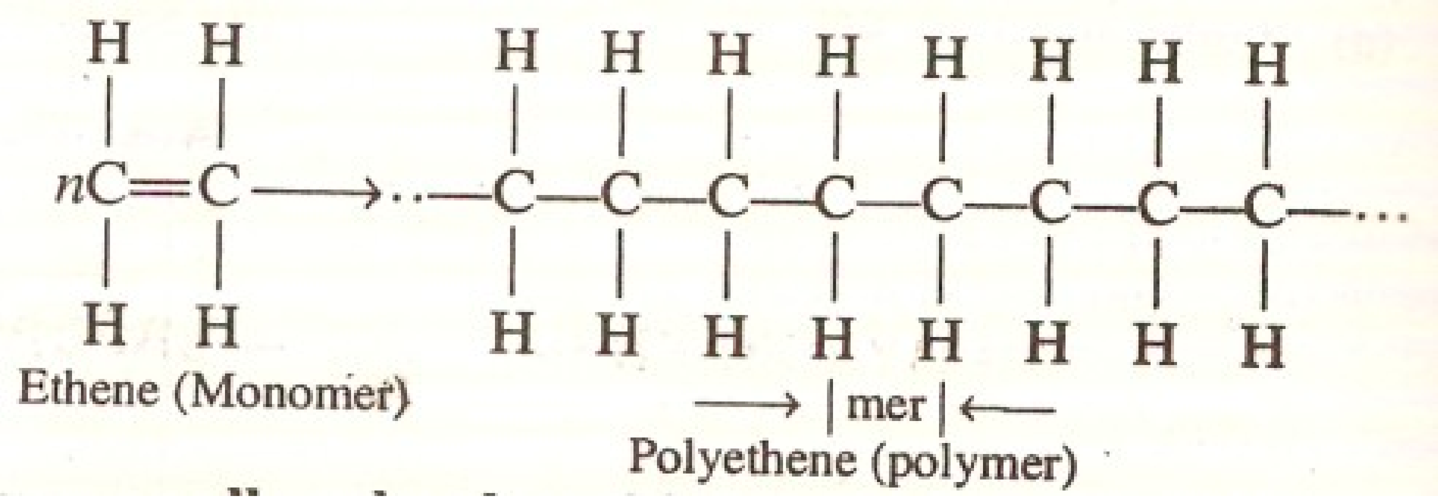
POLYMERS

Introduction : The word "**polymer**" is derived from two Greek words, **polys (= many**) and **mers (= parts or units).** A polymer is a large molecule which is formed by repeated linking of small molecules called "**monomers**". **Example:** Polyethene is a polymer formed-by linking together of a large number of ethene (C_2H_4) molecules.



$$n\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}} \longrightarrow \cdots-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\cdots$$

POLYMERS

Thus, small molecules which combine with each other to form polymer molecules, are termed monomers ; and the "re-peat unit" in a polymer is called mer.

Characteristics of Polymers :

1. Polymeric molecules are very big molecules. There 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 amor- phous regions. Crystallites provide strength and hardness and the amorphous regions provide flexibility to the polymeric material.

POLYMERS

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.

POLYMERS

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.

CLASSIFICATION OF POLYMERS :

1. 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 polymerised together.

POLYMERS

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 (c) Block co-polymers

(b) Random co-polymers (d)Graft 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.

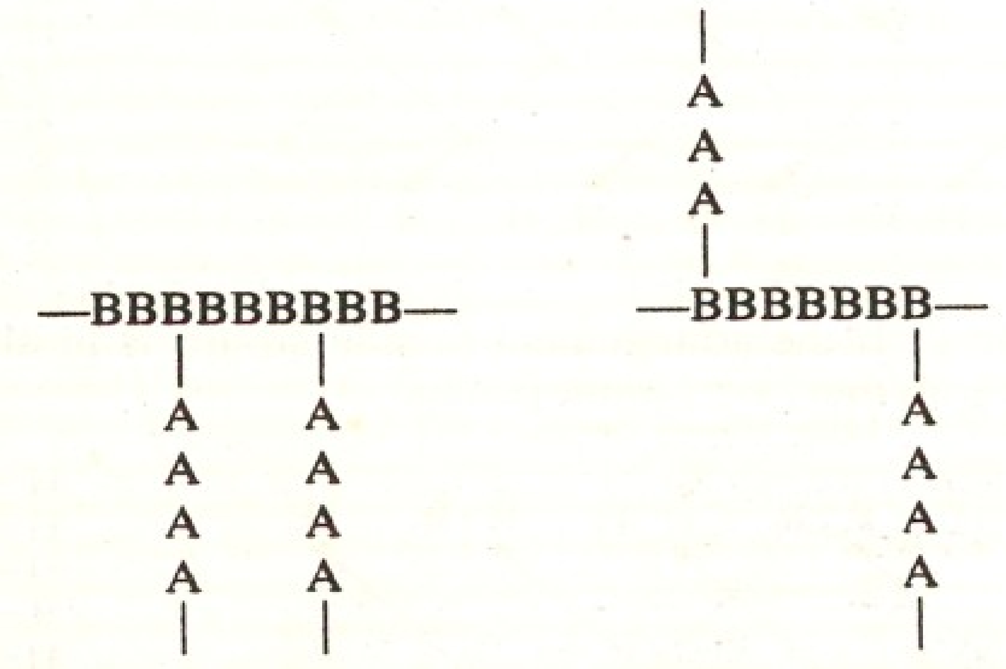
-ABAABABBAAABA-

POLYMERS

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

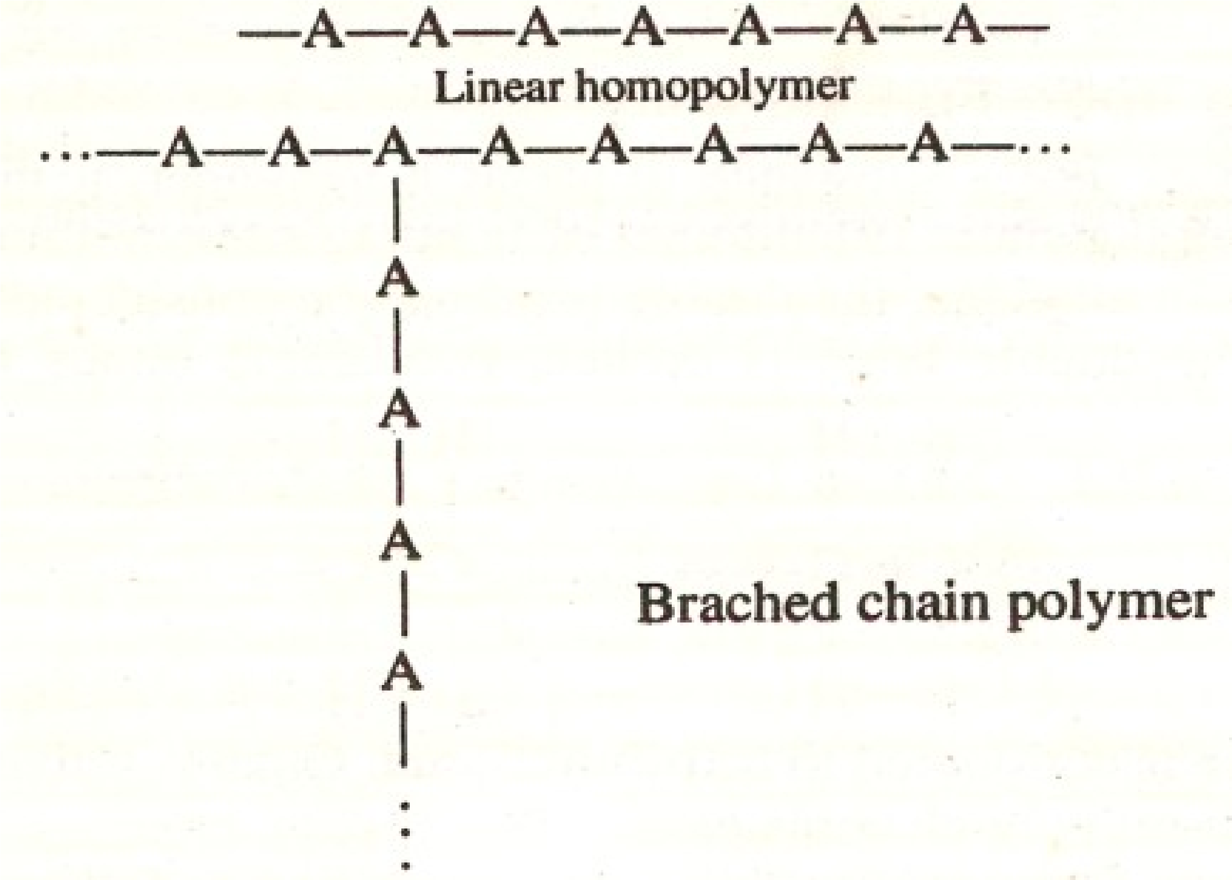
-AAAABBBBAAAABBBB-

(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.*



POLYMERS

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

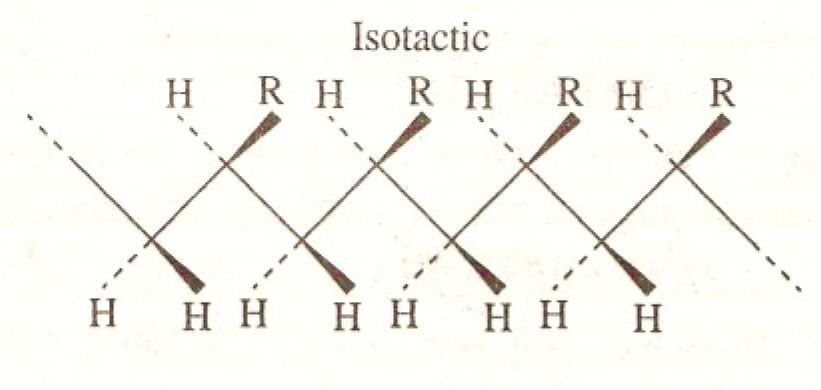


POLYMERS

2. Based on Tacticity :

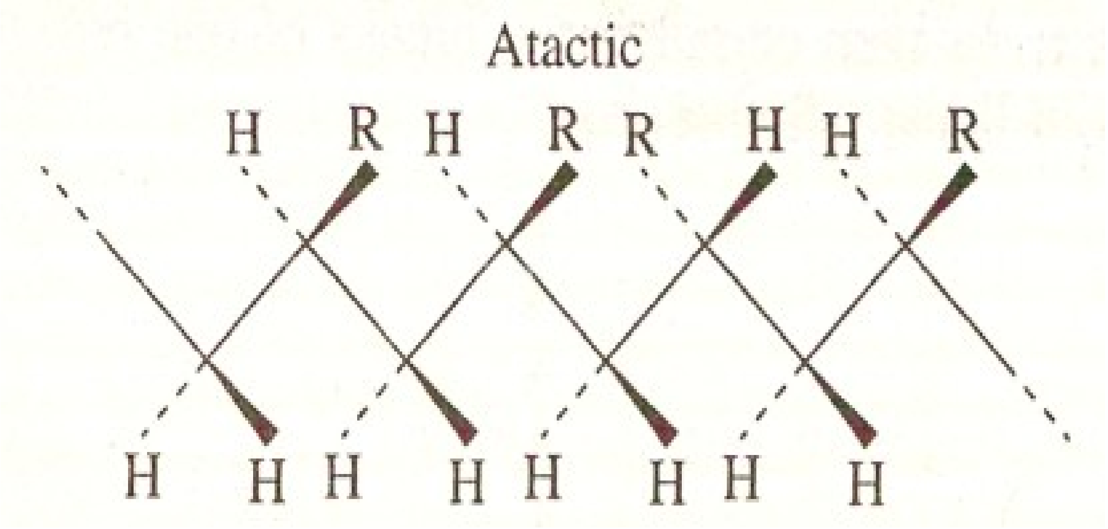
The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain. The difference in configuration (tacticity) do affect their physical properties. Based on tacticity they are classified as follows:

(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.,



POLYMERS

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



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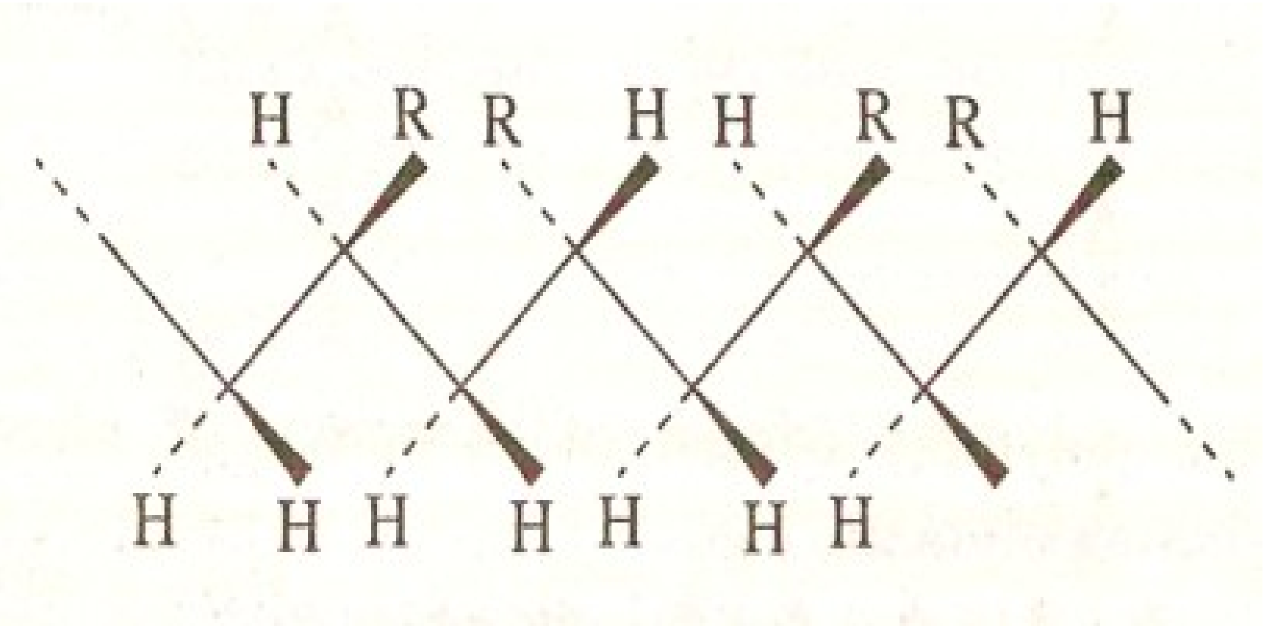
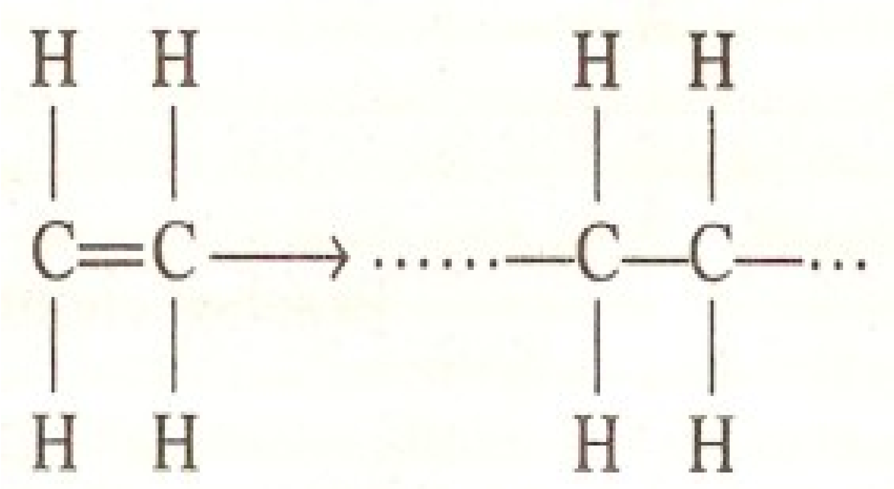
iii) Syndiotactic: If the arrangement of side groups is in **alternating** fashion, it is called **syndiotactic polymer,** *e.g.,* gutta percha.



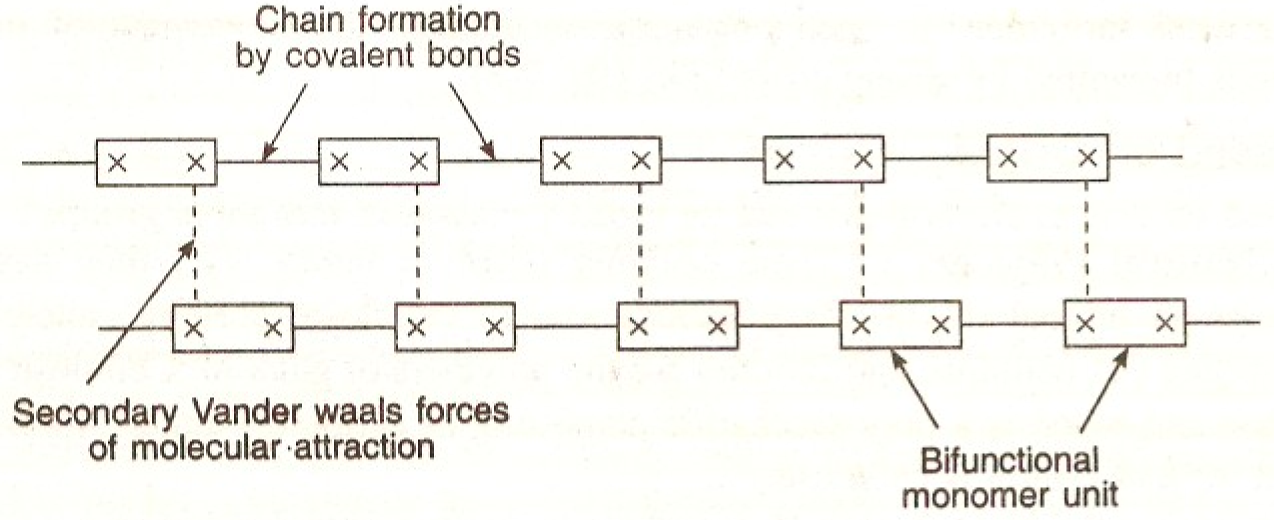
POLYMERS

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



POLYMERS

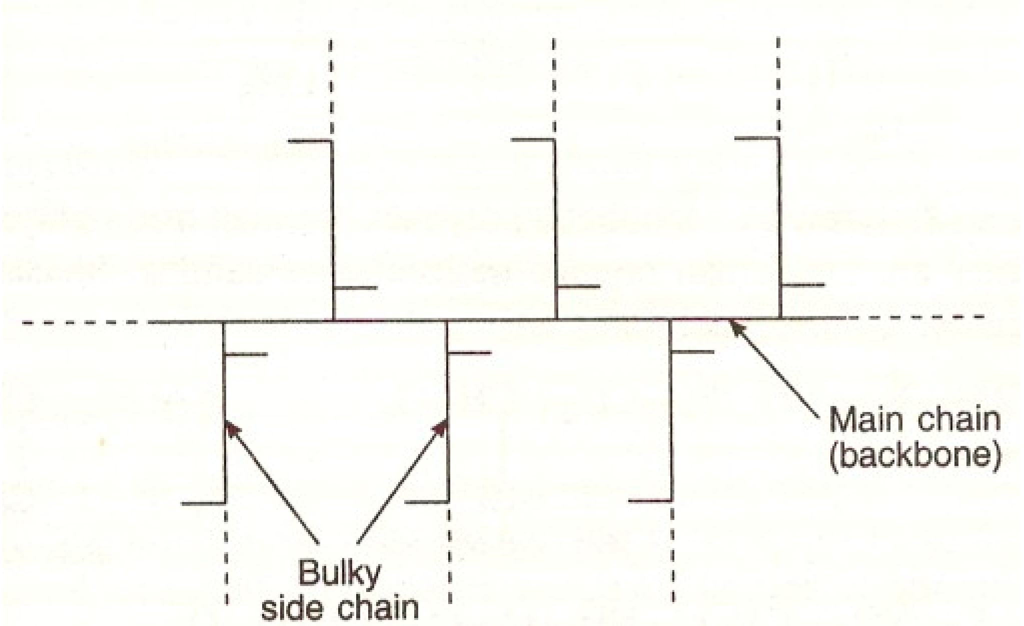
(i) Linear or Straight Chain Polymer: In case of a **bifunctional monomer,** two reactive groups attach side by side to each other forming **linear or straight chain polymer.** Linear molecules consist of monomer units linked by primary covalent bonds, but the different chains are held together by secondary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



POLYMERS

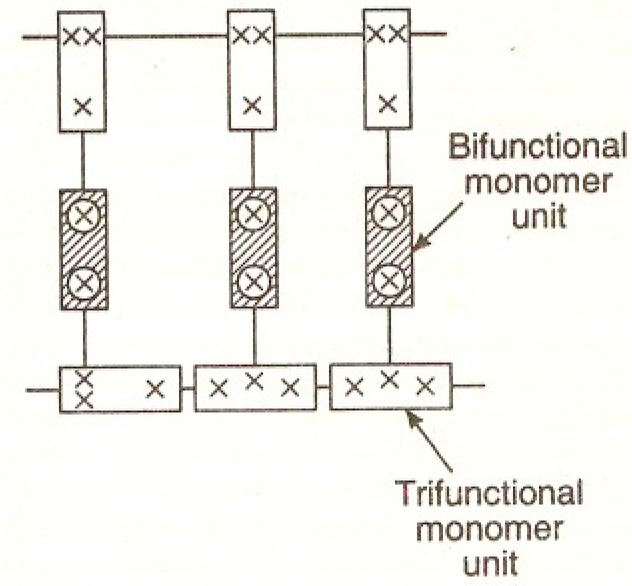
(ii) Branched Chain Polymers: During the chain growth, side chains may also form, resulting in branched-chain polymers. Such a molecule is a linear, but the movement in brached-chain molecules is, generally, more restricted than that of simple straight-chain molecules. A branched-chain polymer also results,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

polymerised.



POLYMERS

(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 netwrork polymer. In such polymeric molecules the movement of individual molecules is prevented by strong cross-links.



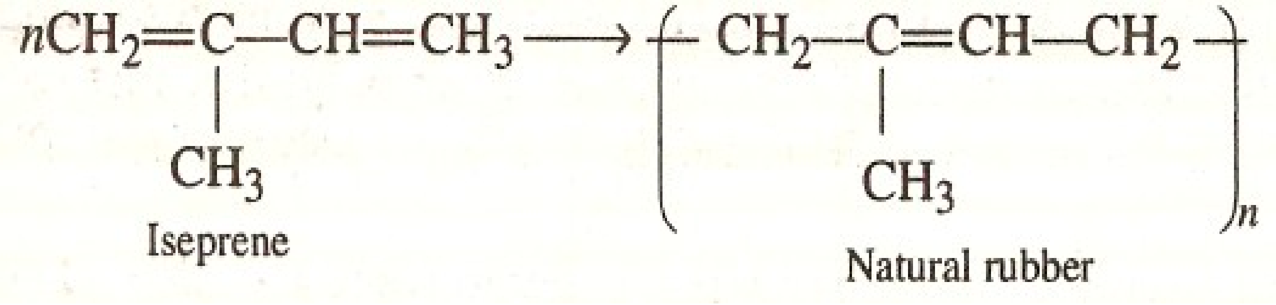
POLYMERS

4. Based on Origin :

Based on origin, the polymer can be broadly classified into three groups:

(i) **Natural Polymers:** These polymer occur in nature, *i.e.,* they have either vegitable or an animal origin. They include starch, cellulose, proteins, nucleic acids, natural rubbber etc. cellulose and starches are the polymers of glucose.

Natural rubber contains isoprene (2-methyl-1, 3-butadiene) repeat unit.



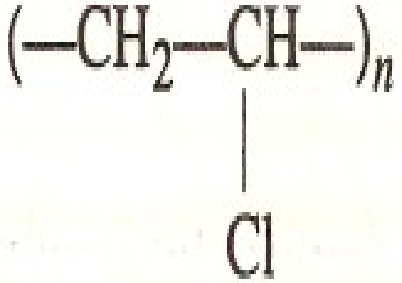
$$n\mathrm{CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_3} \longrightarrow \left(\mathrm{CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH{-}CH_2} \right)_n$$

POLYMERS

(ii) Synthetic Polymers: Synthetic polymers are man made polymers. Most of the synthetic polymers are long-chain organic molecules containing thousands of monomer units. Most common synthetic polymers are :

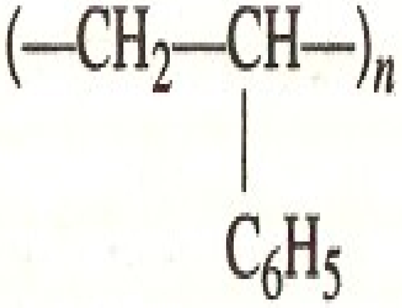
$(\text{—CH}_2\text{—CH}_2\text{—})_n$

Polyethylene



$$(\text{—CH}_2\text{—}\underset{\displaystyle \text{Cl}}{\underset{|}{\text{CH}}}\text{—})_n$$

Polyvinyl chloride

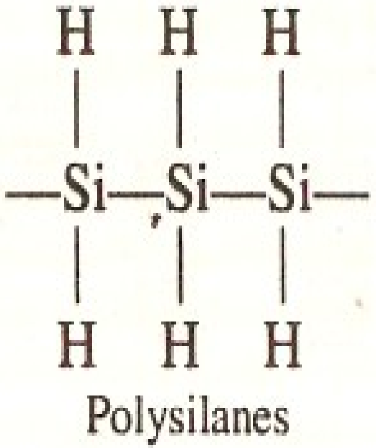


$$(\text{—CH}_2\text{—}\underset{\displaystyle \text{C}_6\text{H}_5}{\underset{|}{\text{CH}}}\text{—})_n$$

Polystyrene

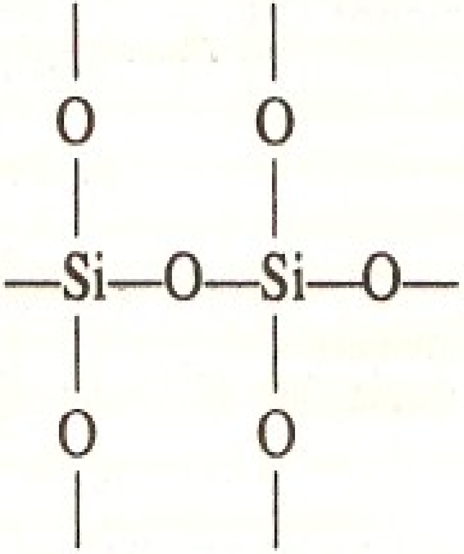
POLYMERS

(iii) 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.,*



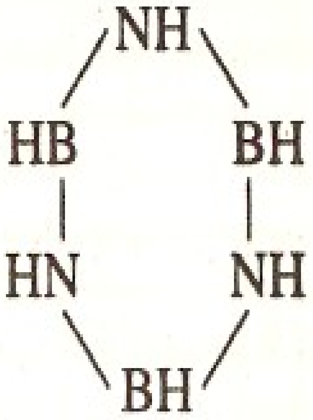
$-\underset{H}{\overset{H}{\mathrm{Si}}}-\underset{H}{\overset{H}{\mathrm{Si}}}-\underset{H}{\overset{H}{\mathrm{Si}}}-$

Polysilanes



$-\underset{O}{\overset{O}{\mathrm{Si}}}-O-\underset{O}{\overset{O}{\mathrm{Si}}}-O-$

Silicon di-oxide



Borazole

POLYMERS

Classification Based on Molecular Forces :

(i) **Elastomers:** 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 nonplastic and give it greater elasticity and ductility.

(ii) **Fibres:** Strong intermolecular hydrogen bonding, *e.g.,* nylon-66.

(iii) **Thermoplastics:** Some polymers soften on heating and can be converted into any shape that they can retain on cooling. The process of heating, reshaping and retaining the same on cooling can be repeated several times. Such polymers, that soften on heating and stiffen on cooling are termed 'thermoplastics' *e.g.,* polyethylene, PVC, nylon and sealing wax.

POLYMERS

(iv) Thermosetting: Some polymers undergo some chemical change on heating and convert themselves into infusible mass. They are like Yolk of egg, which on heating sets into a mass and once set cannot be reshaped. Such polymers, that become infusible and insoluble mass on heating, are called 'thermosetting' polymers *e.g.,* bakelite.

POLYMERS

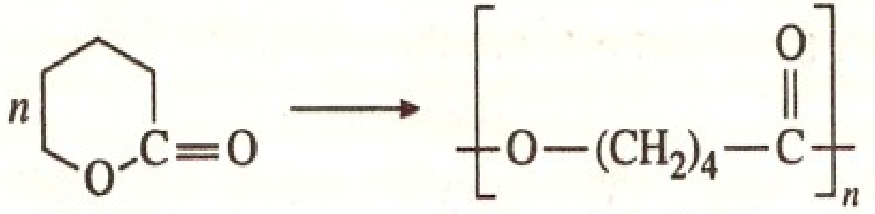
POLYMERIZATION : Polymerization is the process by which simple (monomer) molecules join together to form very large (polymer) molecules. Hence, the synthesis of large molecular weight polymers by the combination of monomer molecules is termed as polymerization. There are three different ways for doing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

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

$$\underset{\text{Ethene}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{Polyethene}}{(-CH_2-CH_2)_n}$$

POLYMERS

(b) By opening a ring e.g.

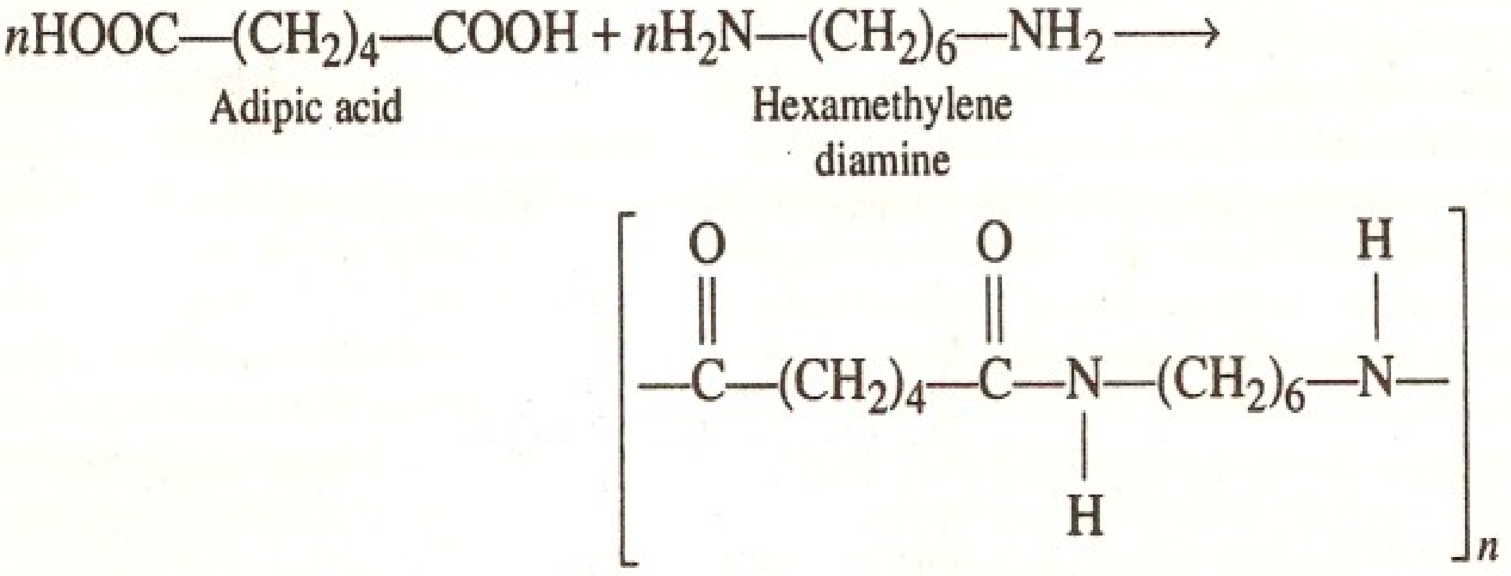


δ-valerolactone

Polyether

$$\left[-O-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}- \right]_n$$

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



$$nHOOC-(CH_2)_4-COOH + nH_2N-(CH_2)_6-NH_2 \longrightarrow$$

Adipic acid

Hexamethylene diamine

$$\left[-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-(CH_2)_6-\overset{\overset{\displaystyle H}{|}}{N}- \right]_n$$

Nylon 6, 6

POLYMERS

Types of Polymerization :

(1) 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.

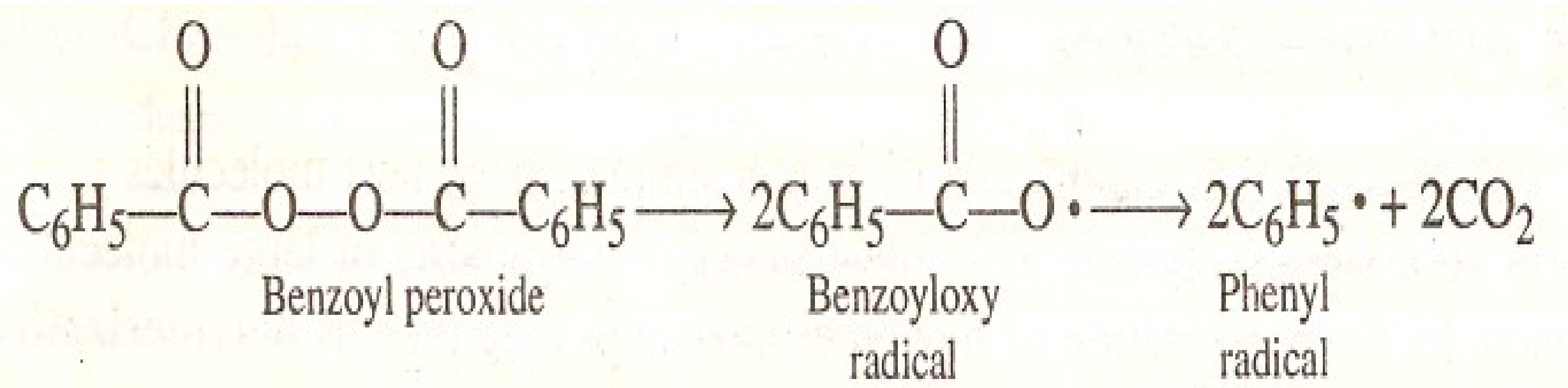
The three different types of active centres have been found to be formed during the addition polymerization, *viz.,* free radical, carbonium ion and carbanion. So the mecha-nisms involving these reactive species in polymerization constitute the mechanism of addition polymerization.

POLYMERS

(a) Free radical polymerization :

Free-radical polymerization form only linear molecules.

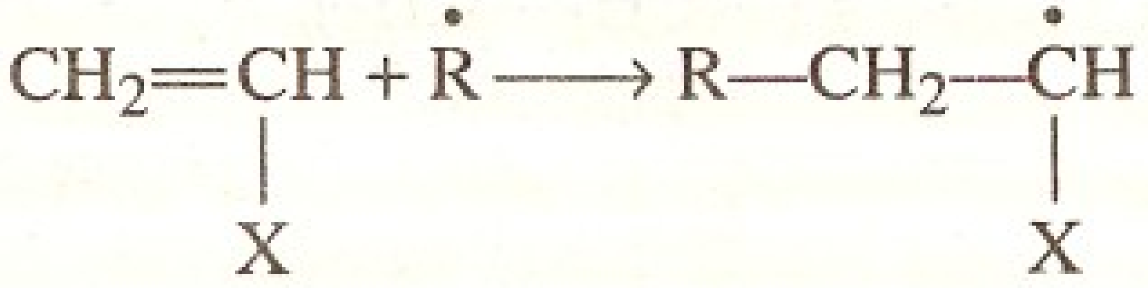
(i) Initiation step: It involves the formation of a free-radical from a radical initiator such as benzoyl peroxides, and other materials that can generate free radicals.



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \longrightarrow 2C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O\cdot \longrightarrow 2C_6H_5\cdot + 2CO_2$$

POLYMERS

The radical so formed then adds to the monomer to form a new free radical, *e.g.,* it adds to vinyl monomer in the following way



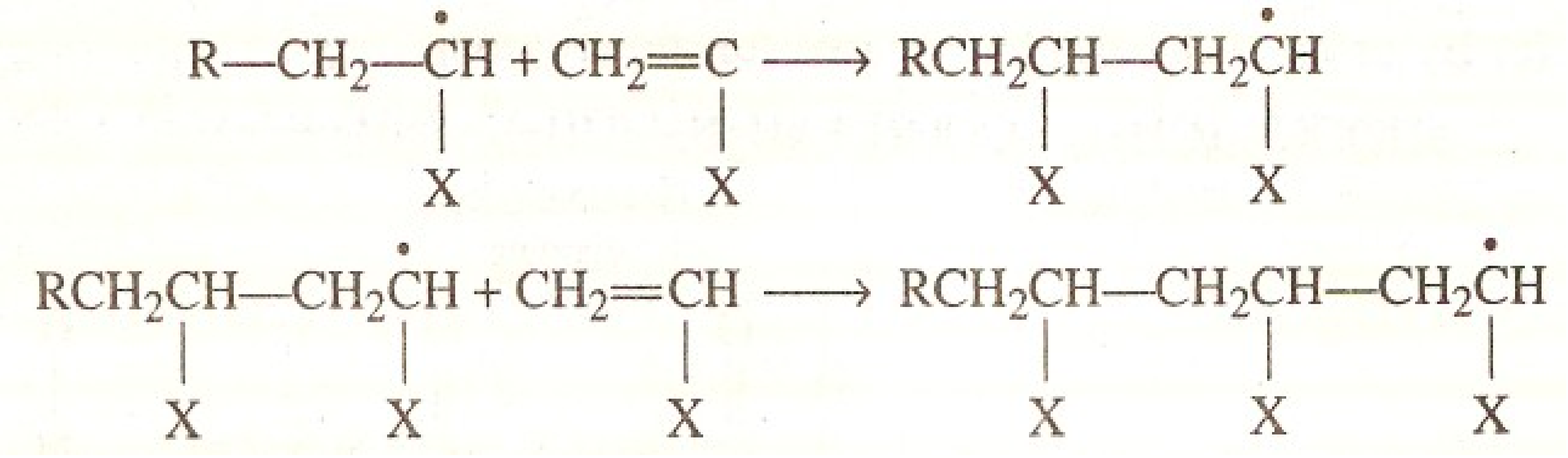
$$CH_2{=}\underset{\displaystyle X}{\underset{|}{CH}} + \dot{R} \longrightarrow R{-}CH_2{-}\underset{\displaystyle X}{\underset{|}{\dot{C}H}}$$

New free radical

$[\dot{R}{=}C_6\dot{H}_5\,]$

POLYMERS

(ii) Propagation step: The new free radical now adds to another molecule of monomer to form another new free radical until a large free radical is formed .



$$R{-}CH_2{-}\underset{X}{\dot{C}H} + CH_2{=}\underset{X}{C} \longrightarrow RCH_2\underset{X}{CH}{-}CH_2\underset{X}{\dot{C}H}$$

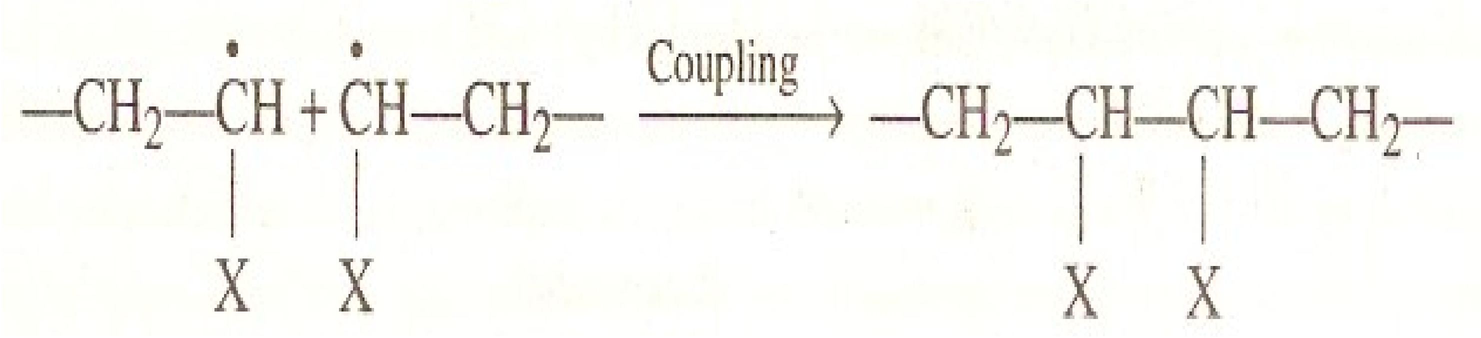
$$RCH_2\underset{X}{CH}{-}CH_2\underset{X}{\dot{C}H} + CH_2{=}\underset{X}{CH} \longrightarrow RCH_2\underset{X}{CH}{-}CH_2\underset{X}{CH}{-}CH_2\underset{X}{\dot{C}H}$$

After the first few steps the addition of a monomer unit proceeds at a constant specific rate independent of the chain length of free radical formed.

POLYMERS

(iii) Termination step: Termination of chains usually occurs by radical coupling or disproportionation reactions.

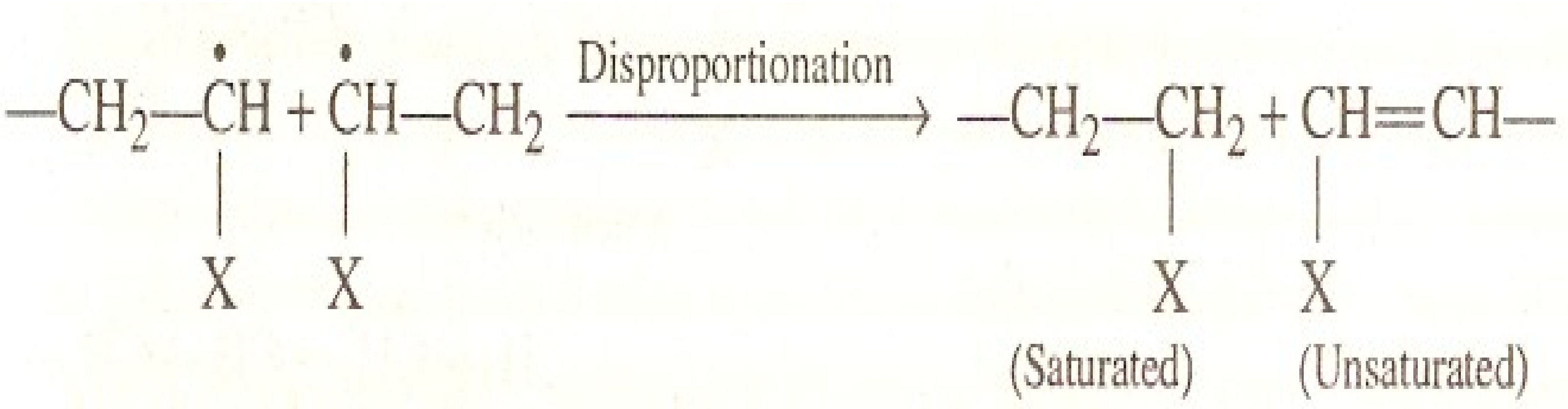
By coupling or combination, *e.g.,*



$$-CH_2-\underset{X}{\underset{|}{\dot{C}H}} + \underset{X}{\underset{|}{\dot{C}H}}-CH_2- \xrightarrow{\text{Coupling}} -CH_2-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH}}-CH_2-$$

POLYMERS

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 **other unsaturated,** *e.g.,*



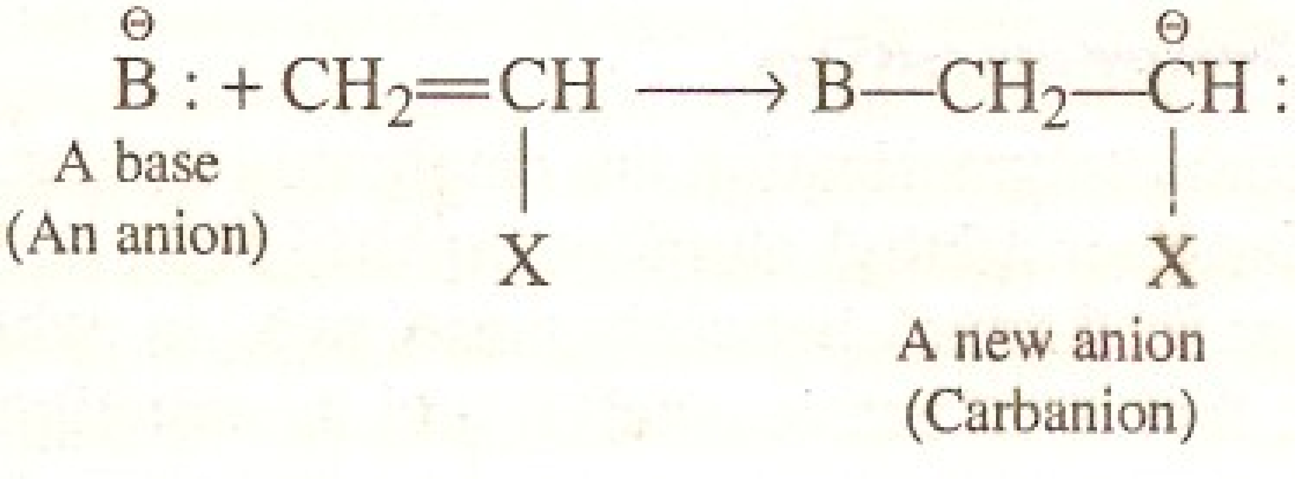
$$-CH_2-\underset{X}{\underset{|}{\dot{C}H}}+\underset{X}{\underset{|}{\dot{C}H}}-CH_2 \xrightarrow{\text{Disproportionation}} \underset{\text{(Saturated)}}{-CH_2-\underset{X}{\underset{|}{CH_2}}}+\underset{\text{(Unsaturated)}}{\underset{X}{\underset{|}{CH}}{=}CH-}$$

POLYMERS

(b) Ionic Polymerization :

(i) Anionic Polymerization: Anionic polymerization involves following steps:

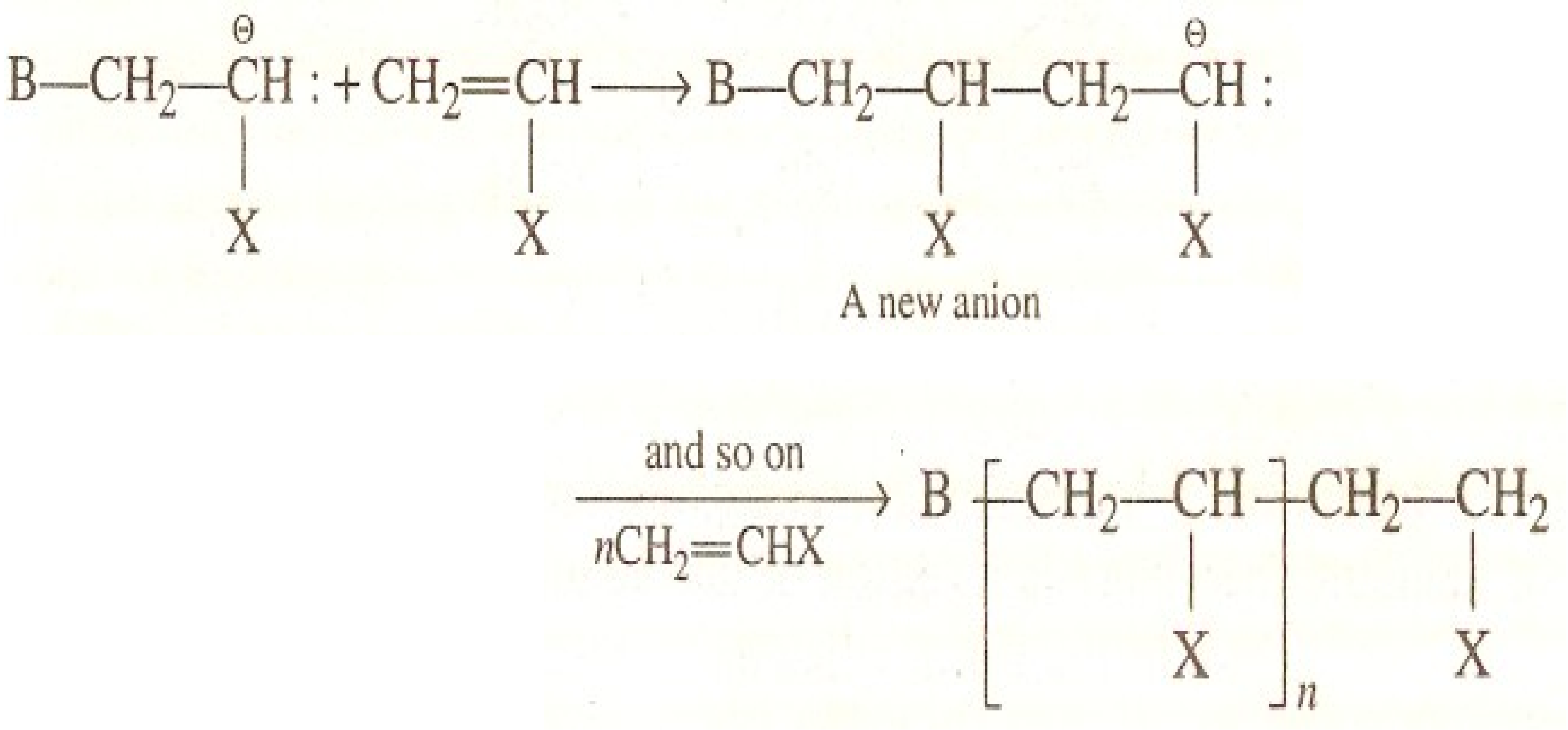
Initiation: A number of reagents are used to bring about initiation the most important being n-butyl lithium and lithium amide.



$$\overset{\ominus}{B}: + CH_2{=}\underset{\substack{|\\ X}}{CH} \longrightarrow B{-}CH_2{-}\overset{\ominus}{\underset{\substack{|\\ X}}{CH}}:$$

POLYMERS

Propagation :

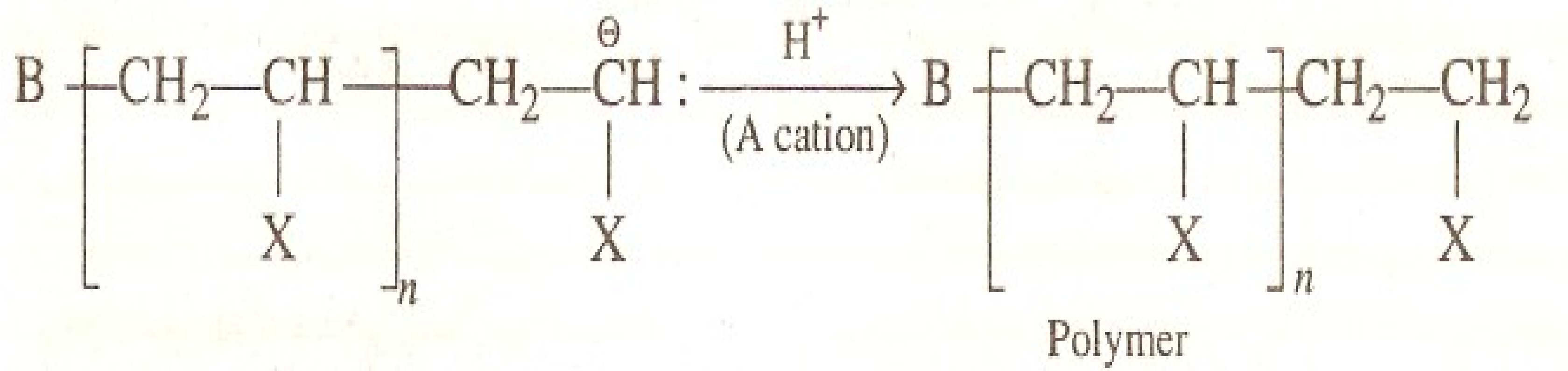


$$B-CH_2-\underset{\displaystyle X}{\overset{\ominus}{CH}}: + CH_2{=}\underset{\displaystyle X}{CH} \longrightarrow \underbrace{B-CH_2-\underset{\displaystyle X}{CH}-CH_2-\underset{\displaystyle X}{\overset{\ominus}{CH}}:}_{\text{A new anion}}$$

$$\xrightarrow[nCH_2{=}CHX]{\text{and so on}} B\left[-CH_2-\underset{\displaystyle X}{CH}-\right]_n CH_2-\underset{\displaystyle X}{CH_2}$$

POLYMERS

Termination: Termination occurs by a hydride transfer or by the action of reactive centres with solvent or with - nctional group of the monomer,



$$B\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{\overset{\ominus}{C}H}:\ \xrightarrow[\text{(A cation)}]{H^+} B\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{CH_2}$$