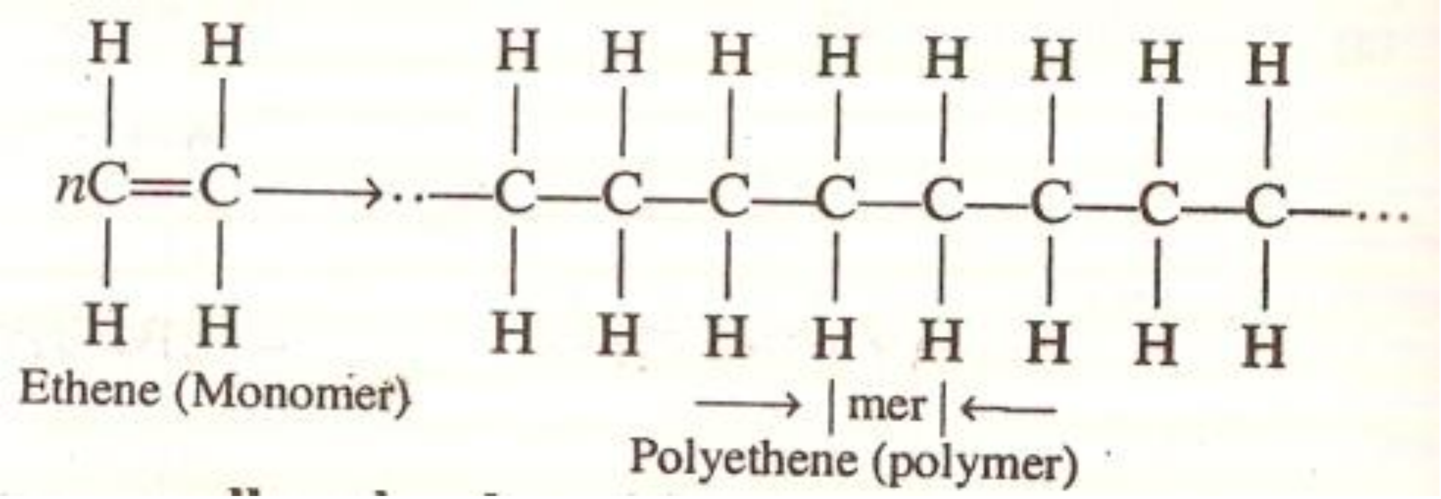
POLYMERS

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.



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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.

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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.

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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.

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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-

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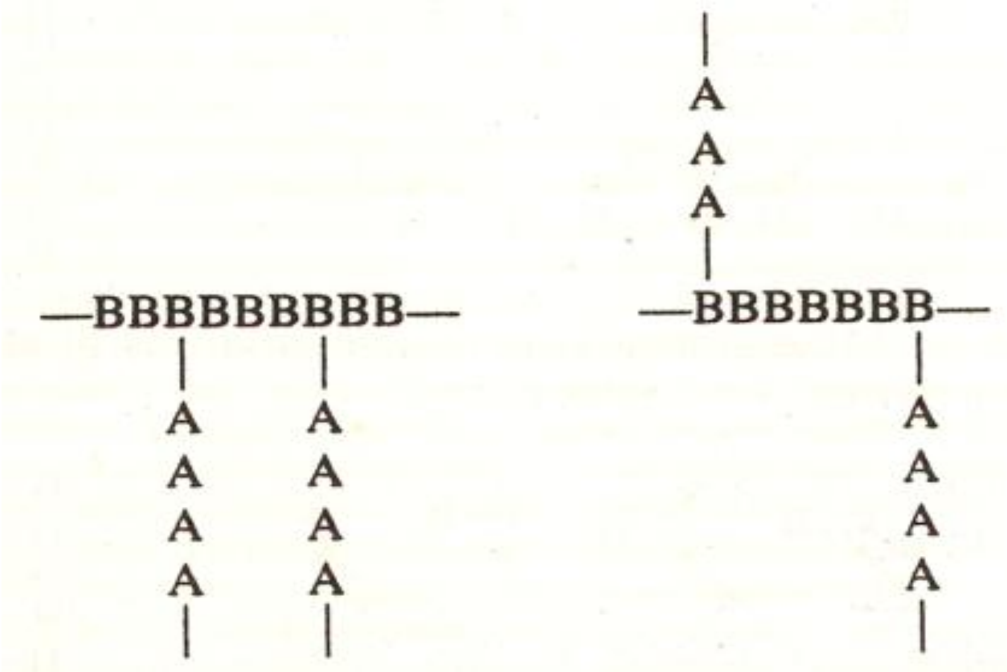
(c) Block Co-polymers: In such co-polymers, block of repeating units of one type alternate with block of another type, *e.g.*

-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.*



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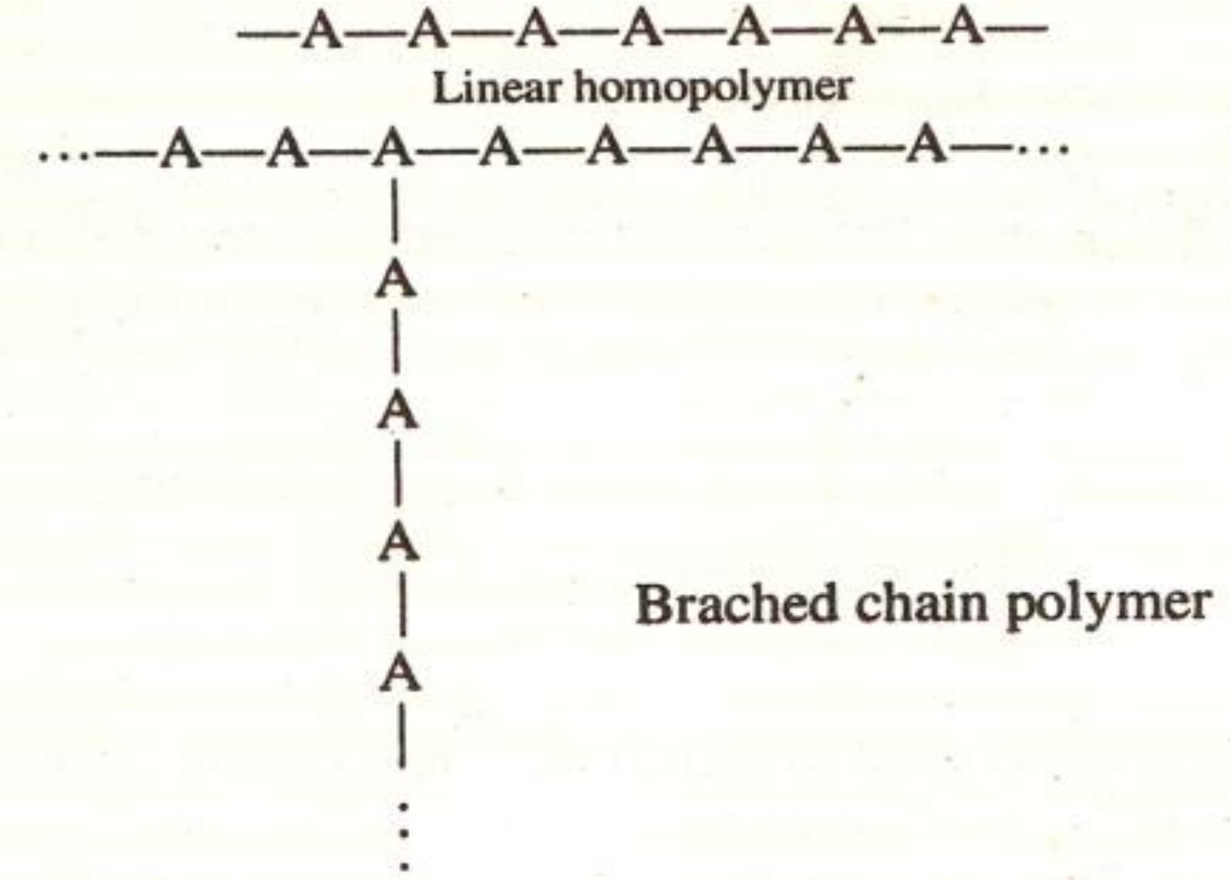
(ii) Homopolymers: If the polymers consist of monomer of identical chemical structure then they are called homopolymers, *e.g.,*



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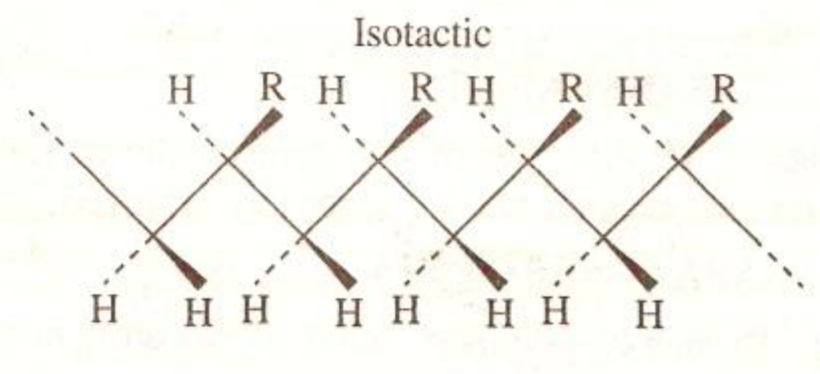
2. Based on Tacticity :

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.,



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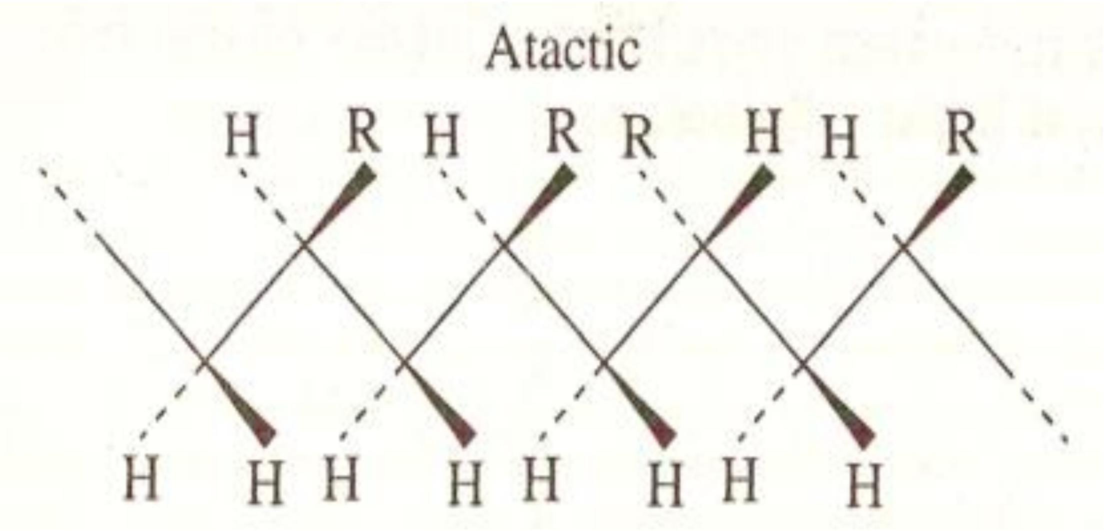
(ii) Atactic Polymer: If the arrangement of functional groups are at **random** around the main chain, it is called **atactic polymer,** *e.g.,* polypropylene.



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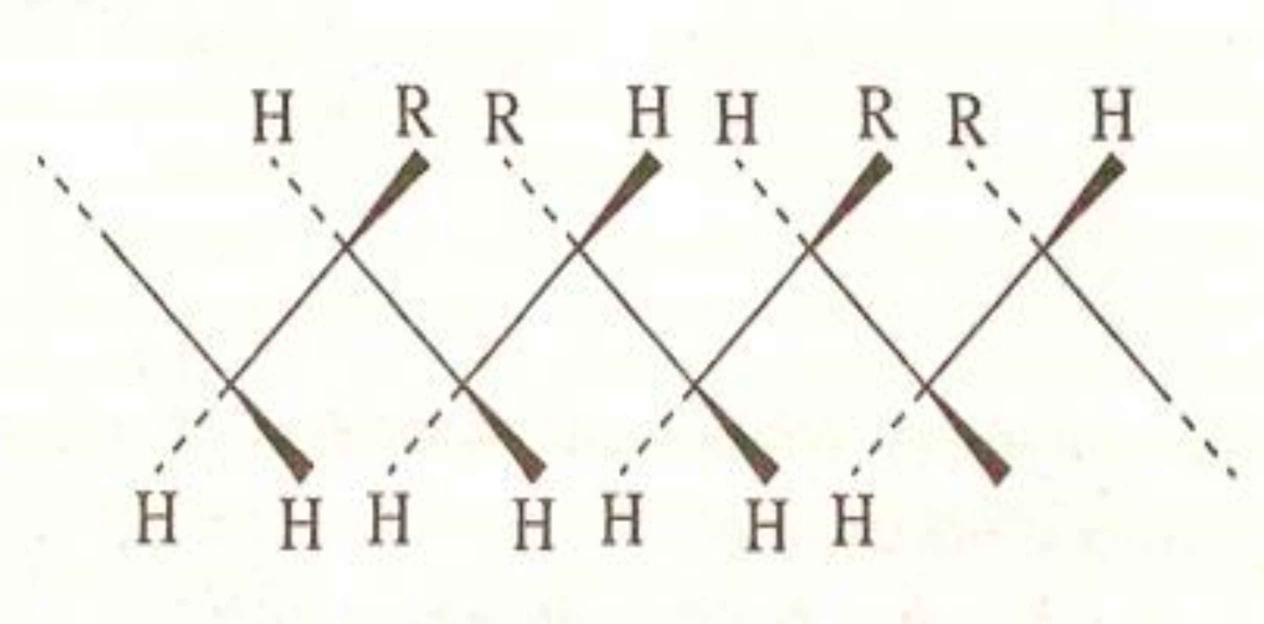
iii) Syndiotactic: If the arrangement of side groups is in **alternating** fashion, it is called **syndiotactic polymer,** *e.g.,* gutta percha.



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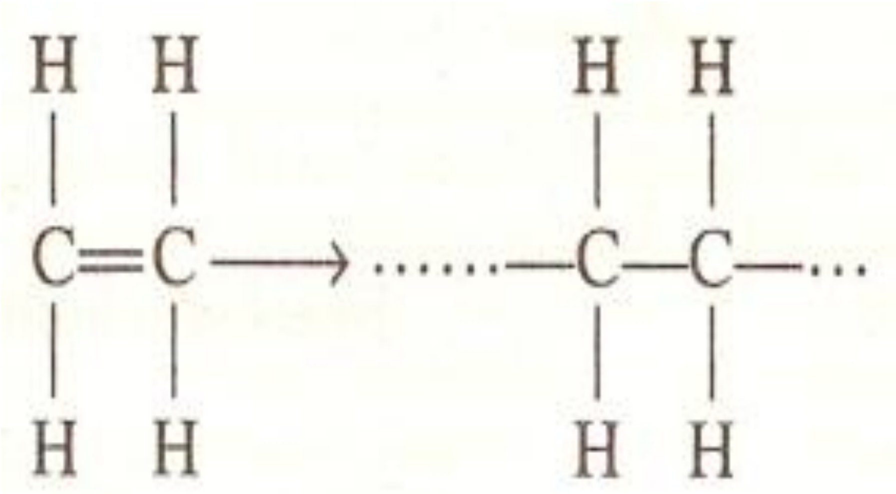
3. **Depending upon Functionality Functionality:** For a substance to act as a monomer, it must have at least two reactive sites or bonding sites. The number of bonding sites in a monomer, is referred to as its functionality. In ethylene, the double bond can be considered as a site for two free valencies.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



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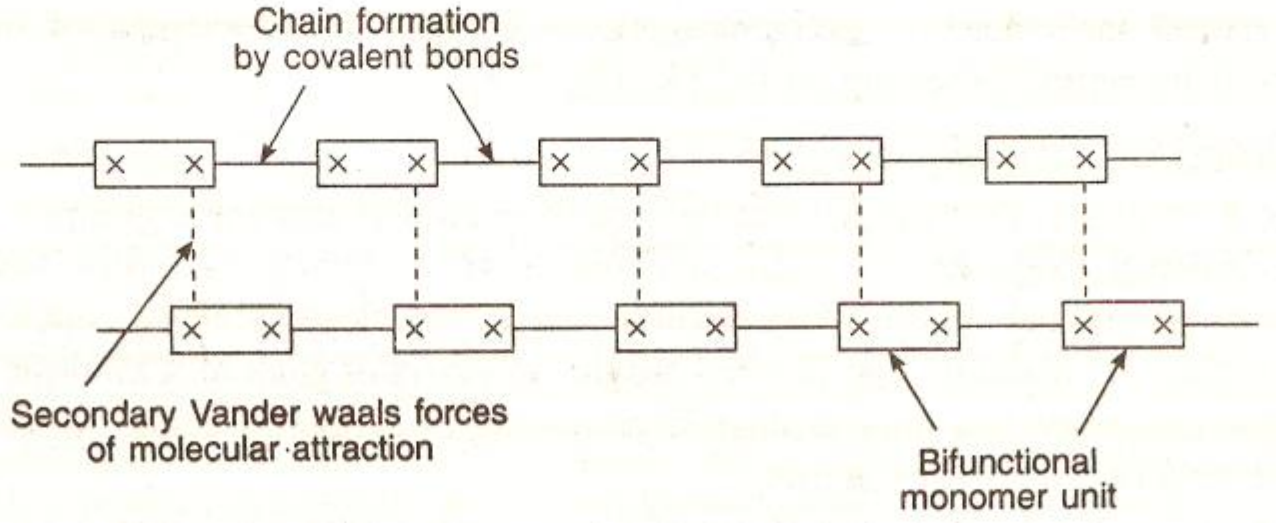
(i) Linear or Straight Chain Polymer: In case of a **bifunctional monomer,** two reactive groups attach side by side to each other forming **linear or straight chain polymer.** Linear molecules consist of monomer units linked by primary covalent bonds, but the different chains are held together by secondary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



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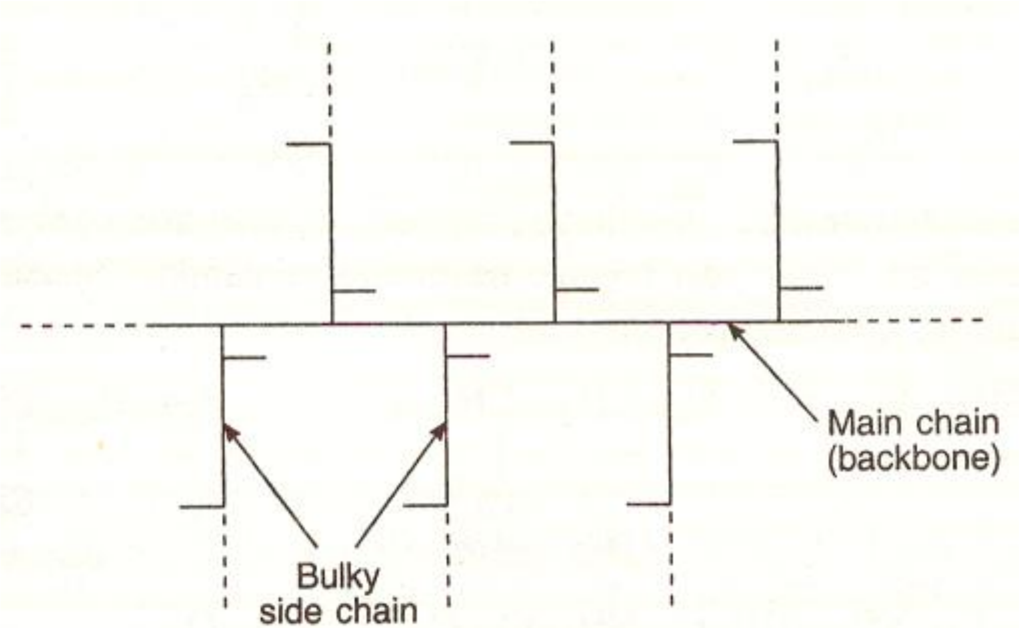
(ii) Branched Chain Polymers: During the chain growth, side chains may also form, resulting in branched-chain polymers. Such a molecule is a linear, but the movement in brached-chain molecules is, generally, more restricted than that of simple straight-chain molecules. A branched-chain polymer also results,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



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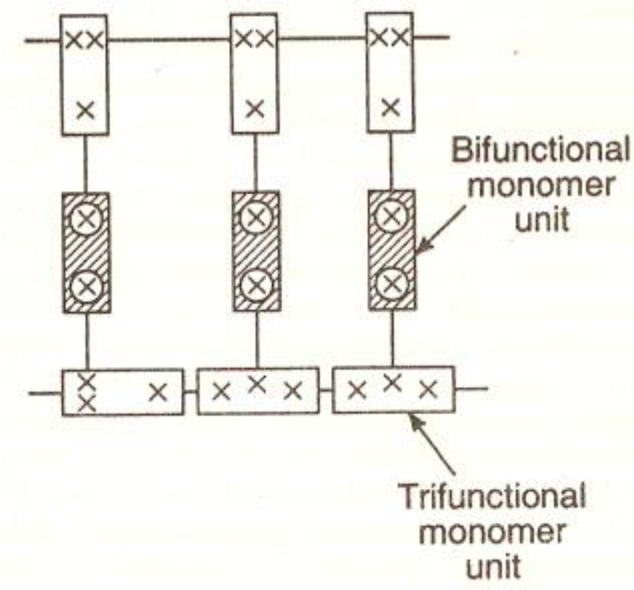
(iii) Network Polymer: In case of polyfunctional groups, monomer molecules are connected to each other by covalent bonds, resulting in the formation of a three-dimensional netwrork polymer. In such polymeric molecules the movement of individual molecules is prevented by strong cross-links.



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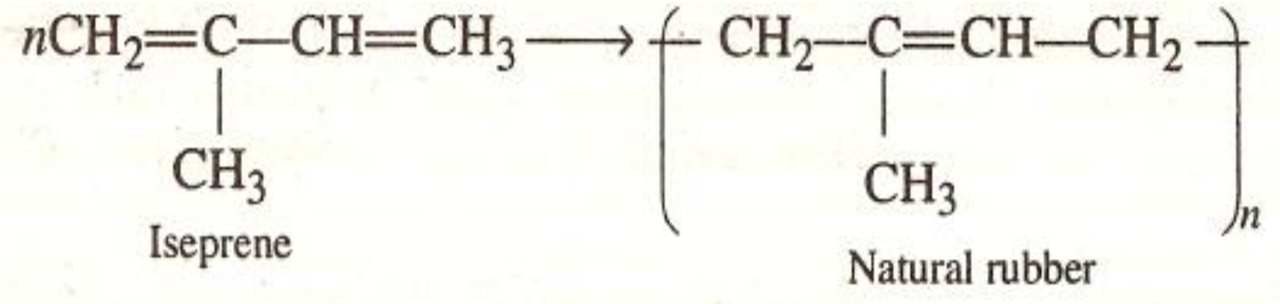
4. Based on Origin :

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.



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

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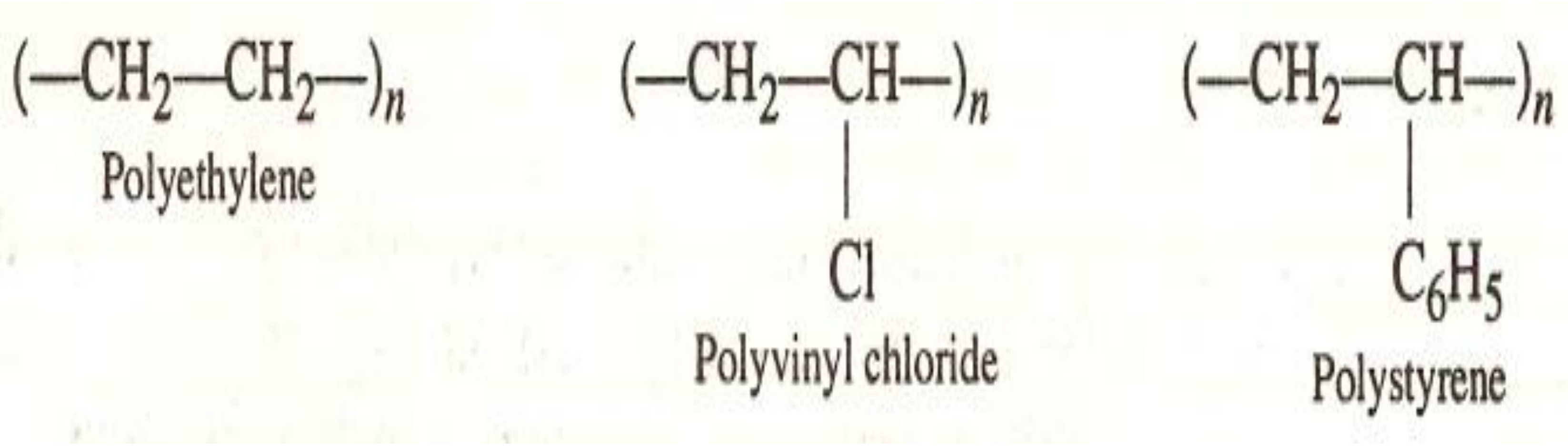
(ii) Synthetic Polymers: Synthetic polymers are man made polymers. Most of the synthetic polymers are long-chain organic molecules containing thousands of monomer units. Most common synthetic polymers are :



$(-CH_2-CH_2-)_n$

Polyethylene

$(-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-)_n$

Polyvinyl chloride

$(-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-)_n$

Polystyrene

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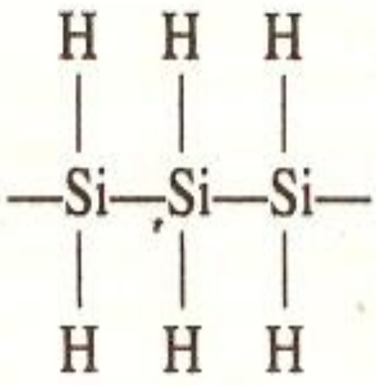
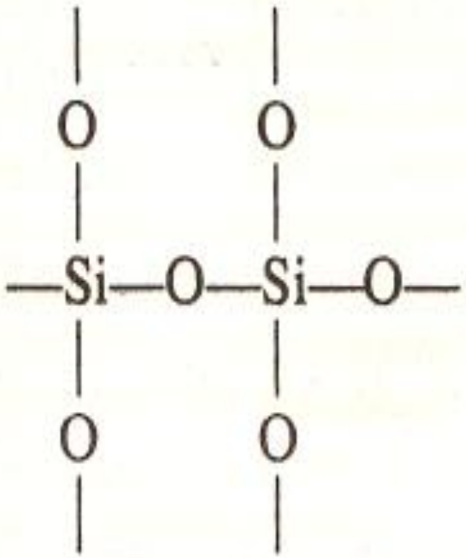
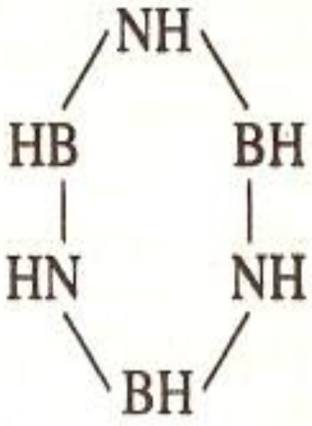
(iii) Inorganic Polymers: These are polymers containing no carbon atoms. The chains of these polymers are composed of different atoms joined by chemical bonds, while weaker inter-molecular forces act between the chains, *e.g.*,



Polysilanes



Silicon di-oxide



Borazole

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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.

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(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.

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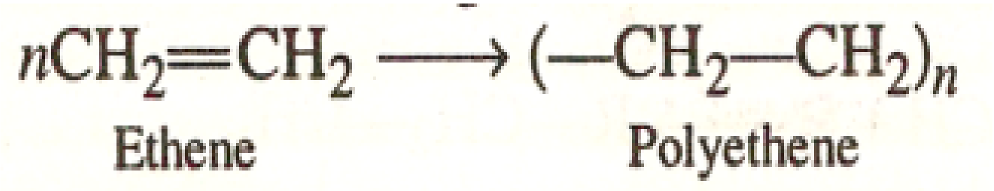
POLYMERIZATION : Polymerization is the process by which simple (monomer) molecules join together to form very large (polymer) molecules. Hence, the synthesis of large molecular weight polymers by the combination of monomer molecules is termed as polymerization. There are three different ways for doing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

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



$$nCH_2{=}CH_2 \longrightarrow (-CH_2-CH_2)_n$$

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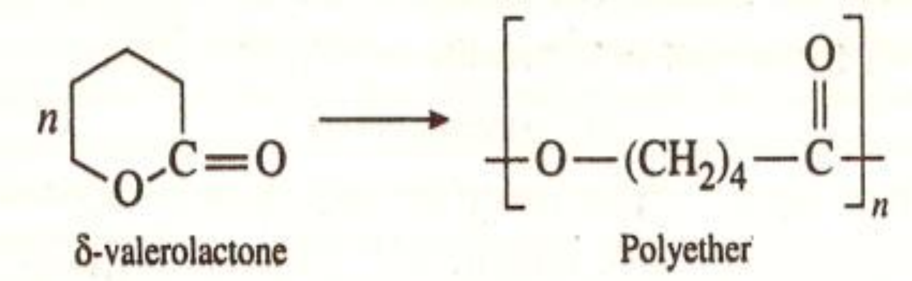
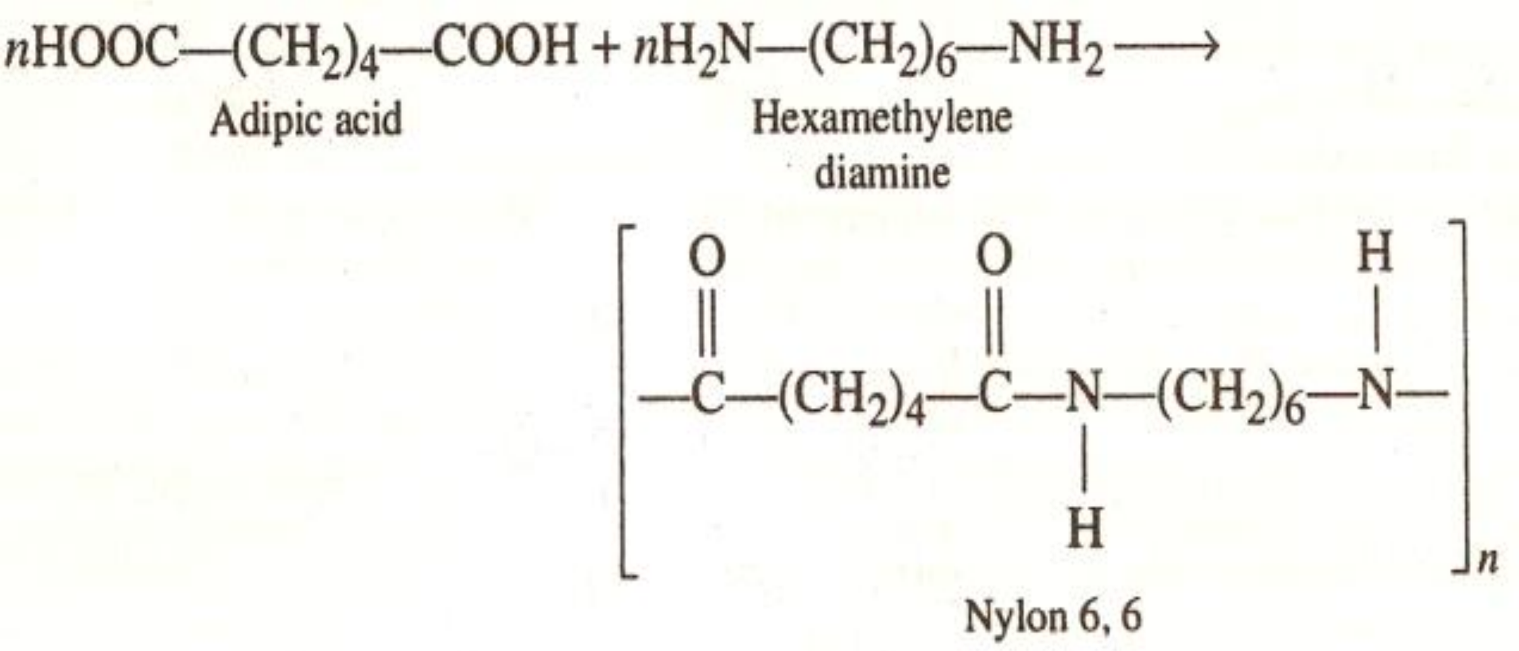
(b) By opening a ring e.g.



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



$$n\mathrm{HOOC}\text{—}(\mathrm{CH_2})_4\text{—}\mathrm{COOH} + n\mathrm{H_2N}\text{—}(\mathrm{CH_2})_6\text{—}\mathrm{NH_2} \longrightarrow \left[\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_4\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\text{—}(\mathrm{CH_2})_6\text{—}\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}\text{—} \right]_n$$

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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.

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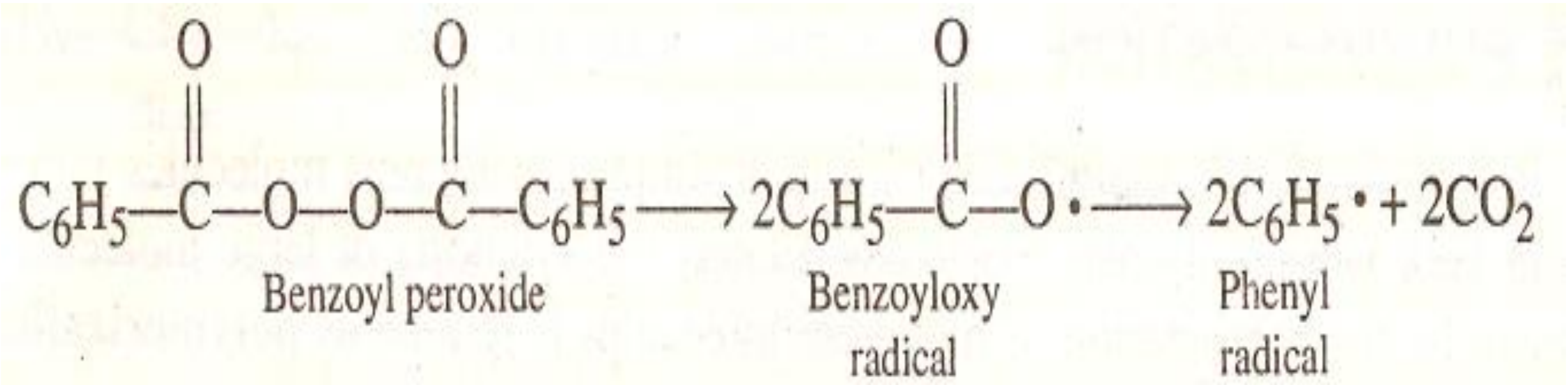
(a) Free radical polymerization :

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.



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

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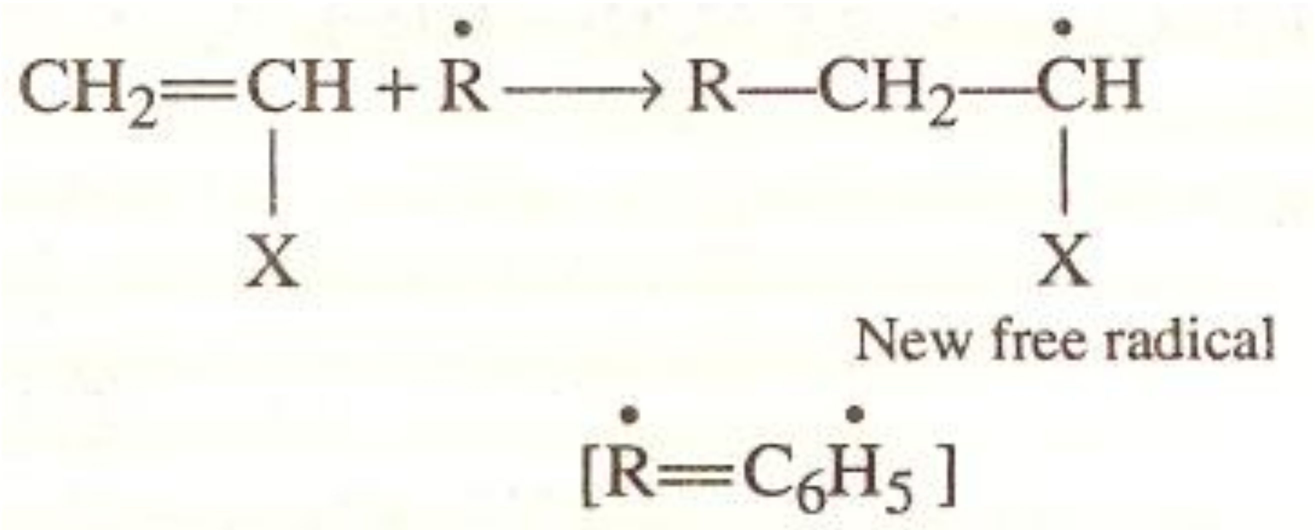
The radical so formed then adds to the monomer to form a new free radical, *e.g.,* it adds to vinyl monomer in the following way



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

New free radical

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

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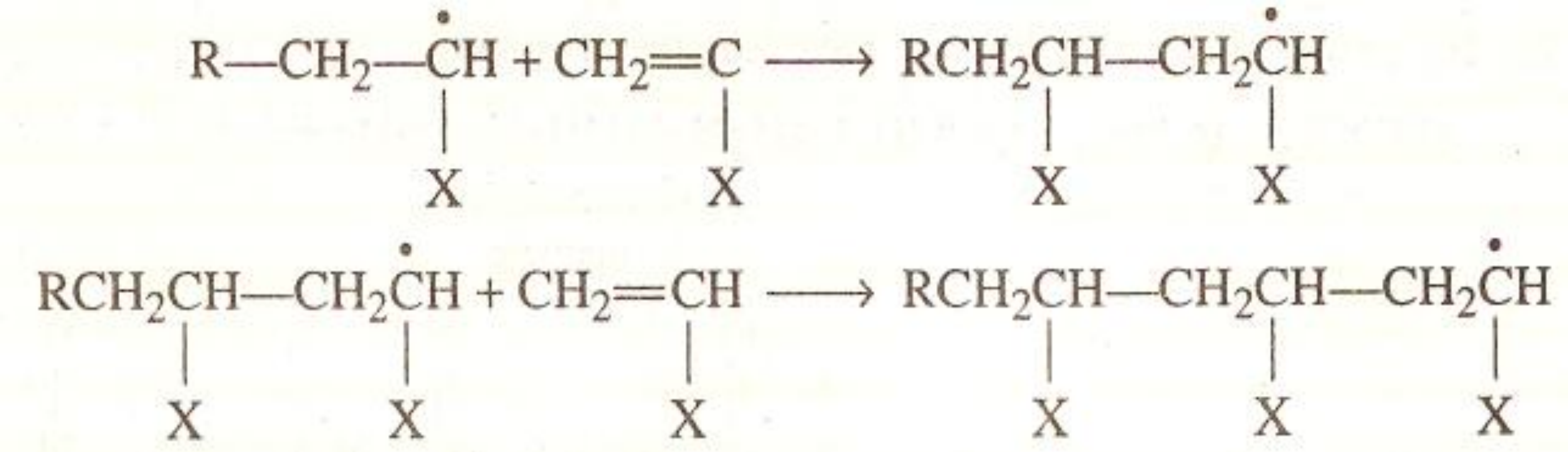
(ii) Propagation step: The new free radical now adds to another molecule of monomer to form another new free radical until a large free radical is formed .



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

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

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.

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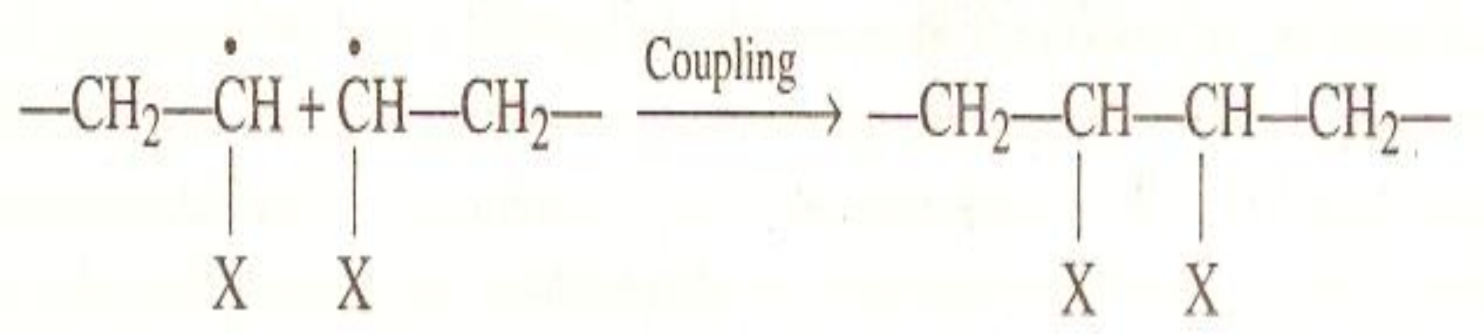
(iii) Termination step: Termination of chains usually occurs by radical coupling or disproportionation reactions.

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



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

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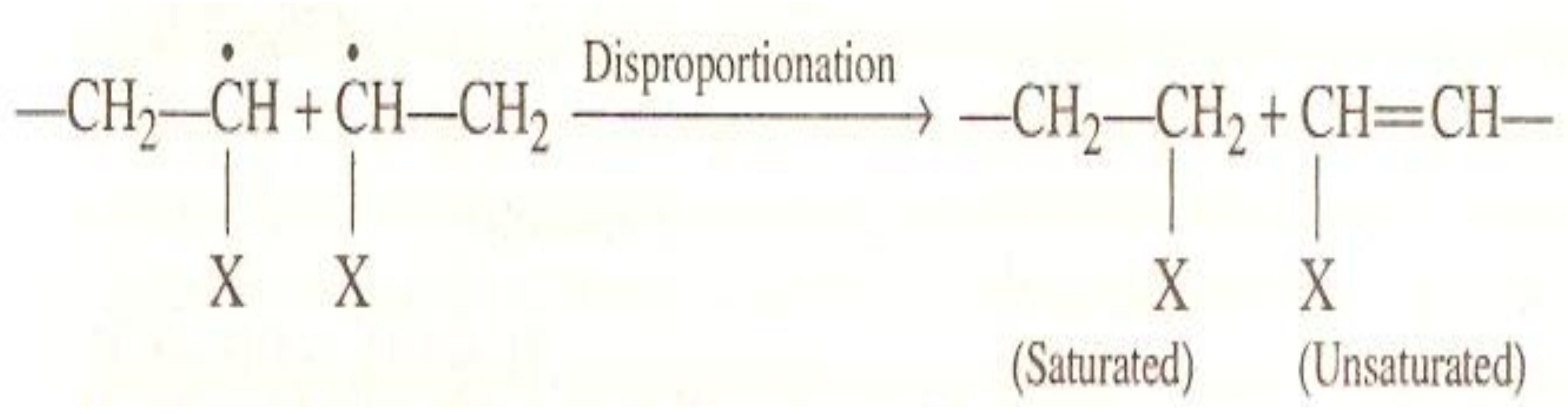
Disproportionation: In which a hydrogen atom of one radical centre is transferred to another radical centre. This results in the formation of two polymer molecules, **one saturated** and **other unsaturated,** *e.g.,*



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

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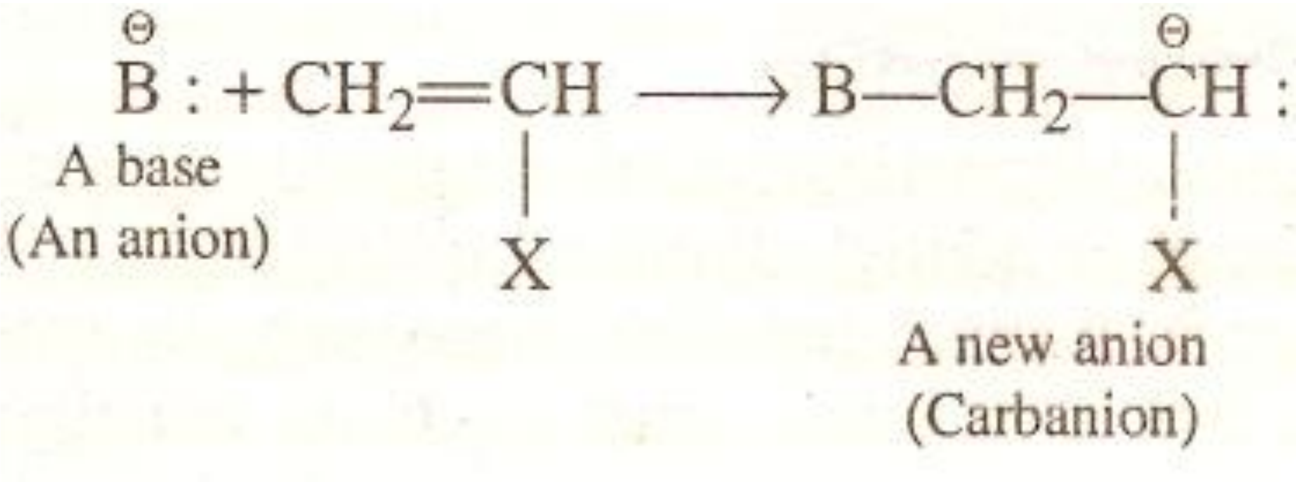
(b) Ionic Polymerization :

(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.



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

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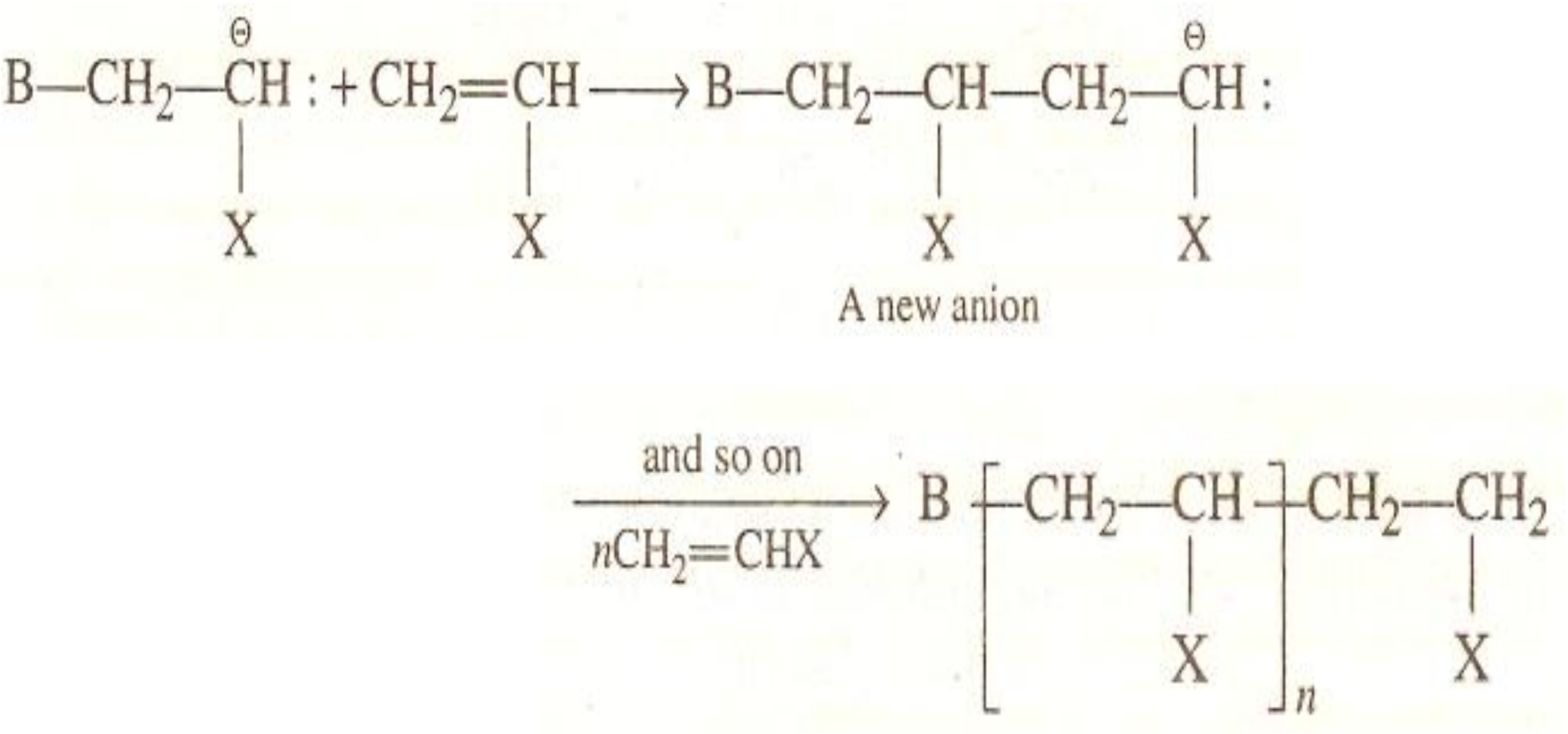
Propagation :



$$\mathrm{B{-}CH_2{-}\underset{X}{\overset{\ominus}{C}H}:+\,CH_2{=}\underset{X}{CH}\longrightarrow B{-}CH_2{-}\underset{X}{CH}{-}CH_2{-}\underset{X}{\overset{\ominus}{C}H}:}$$

A new anion

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

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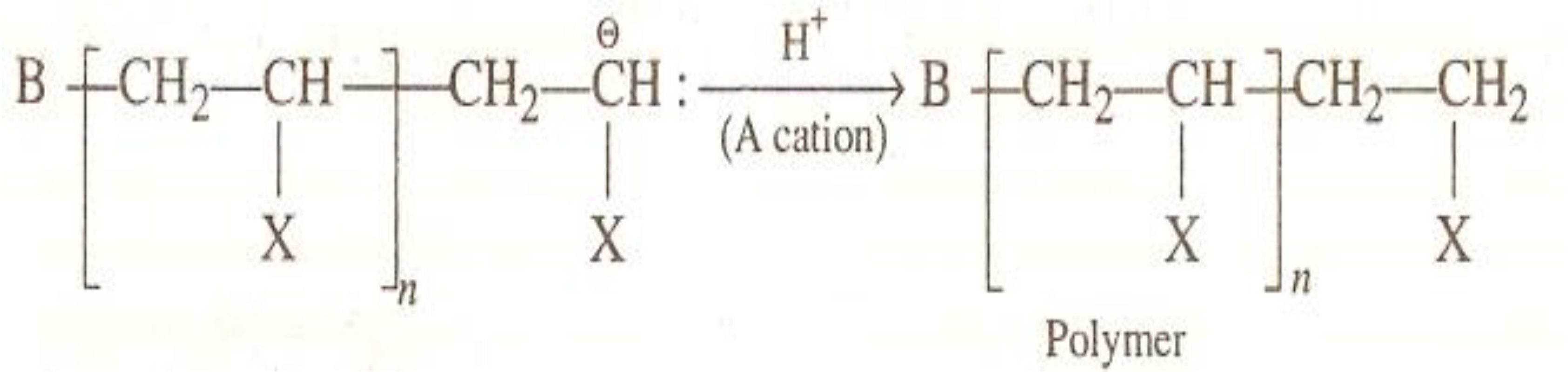
Termination: Termination occurs by a hydride transfer or by the action of reactive centres with solvent or with -nctional group of the monomer,



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

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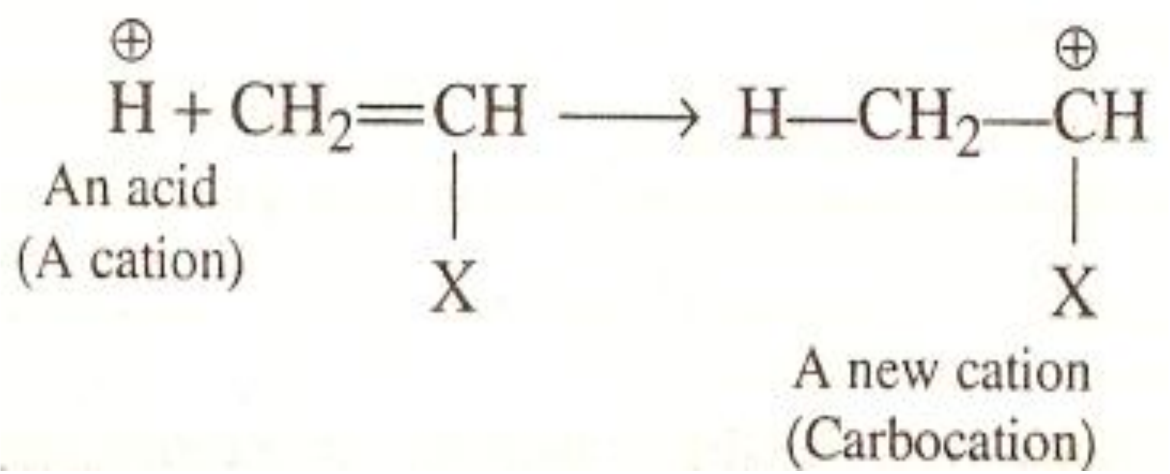
(ii) Cationic Polymerization: Cationic polymerization is initiated by acids and involves carbocationic centres. Monomers with electron-releasing substituents such as alkoxy or phenyl groups readily undergo this type of polymerization. The mechanism is as follows:

Initiation:



$$\overset{\oplus}{H} + CH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow H{-}CH_2{-}\underset{X}{\underset{|}{\overset{\oplus}{CH}}}$$

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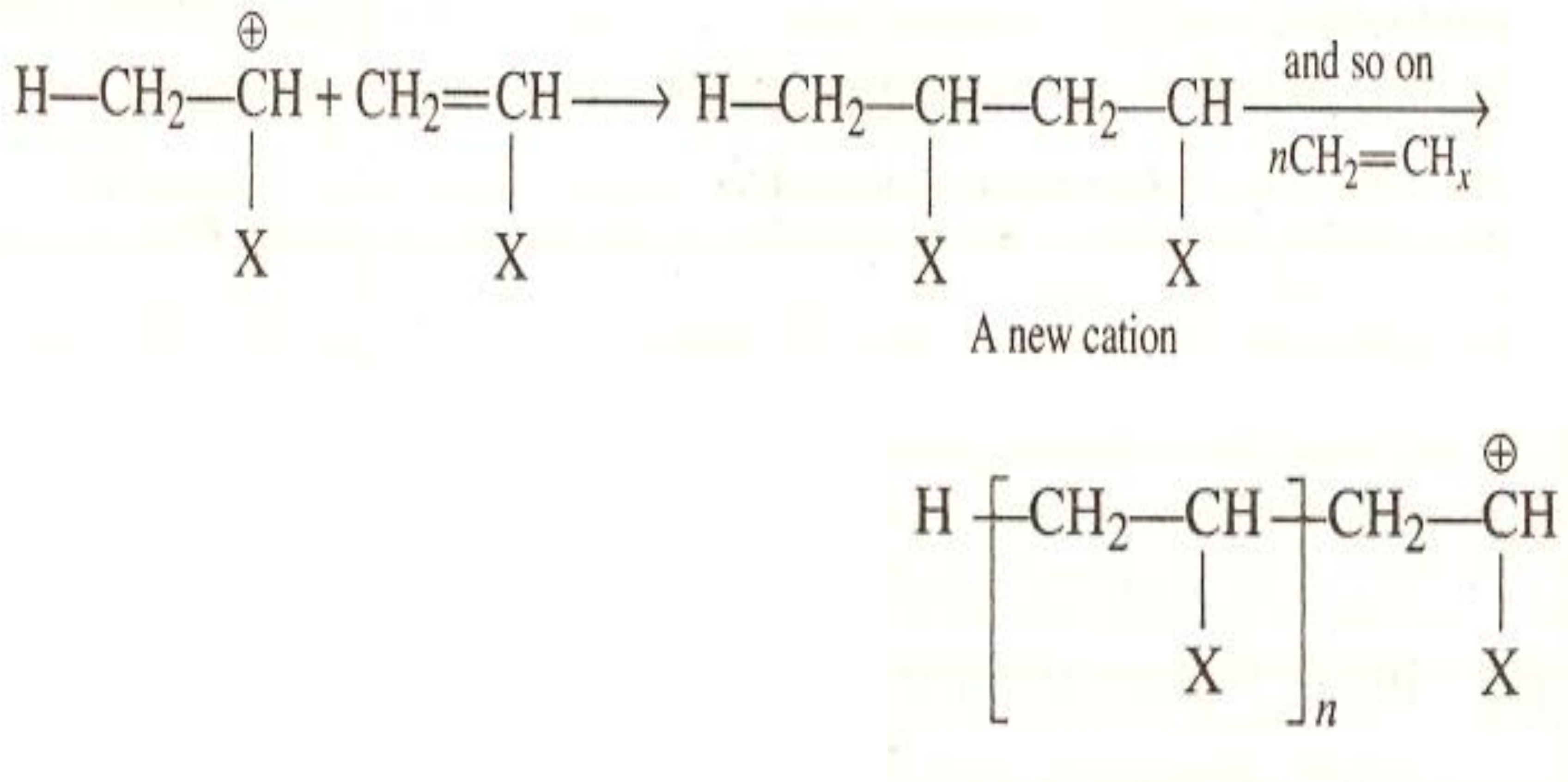
Propagation :



$$H-CH_2-\underset{\substack{|\\X}}{\overset{\oplus}{CH}} + CH_2=\underset{\substack{|\\X}}{CH} \longrightarrow H-CH_2-\underset{\substack{|\\X}}{CH}-CH_2-\underset{\substack{|\\X}}{CH} \xrightarrow[nCH_2=CH_x]{\text{and so on}}$$

A new cation

$$H\left[-CH_2-\underset{\substack{|\\X}}{CH}-\right]_n CH_2-\underset{\substack{|\\X}}{\overset{\oplus}{CH}}$$

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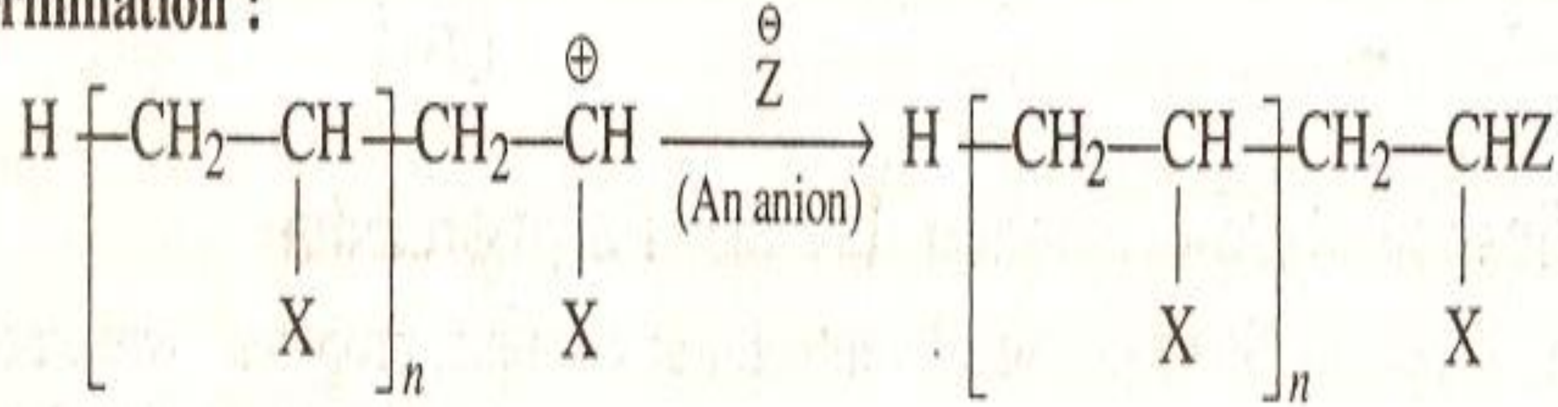
Termination :



$$\mathrm{H}\left[-\mathrm{CH_2}-\underset{\mathrm{X}}{\mathrm{CH}}-\right]_n\mathrm{CH_2}-\overset{\oplus}{\underset{\mathrm{X}}{\mathrm{CH}}}\xrightarrow[\text{(An anion)}]{\overset{\ominus}{\mathrm{Z}}}\mathrm{H}\left[-\mathrm{CH_2}-\underset{\mathrm{X}}{\mathrm{CH}}-\right]_n\mathrm{CH_2}-\underset{\mathrm{X}}{\mathrm{CHZ}}$$

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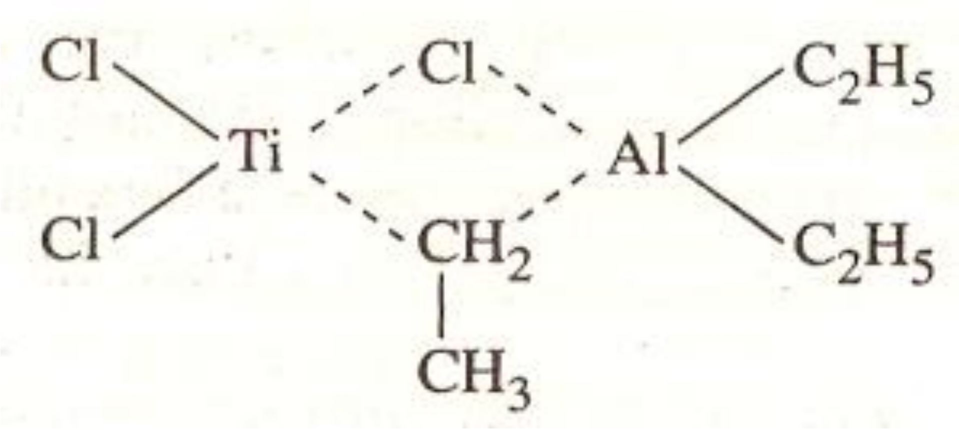
(c) Co-ordination Polymerization : Co-ordination addition polymerization are catalysed by a catalyst known as zeigler-Natta catalysts formed between triethyl aluminium Al$(C_2H_5)_3$ and titanium halide TiCI3. A co-ordination complex is formed between these two, in which the ethyl group is co-ordinated to titanium, this is an active catalyst and its structure is as :



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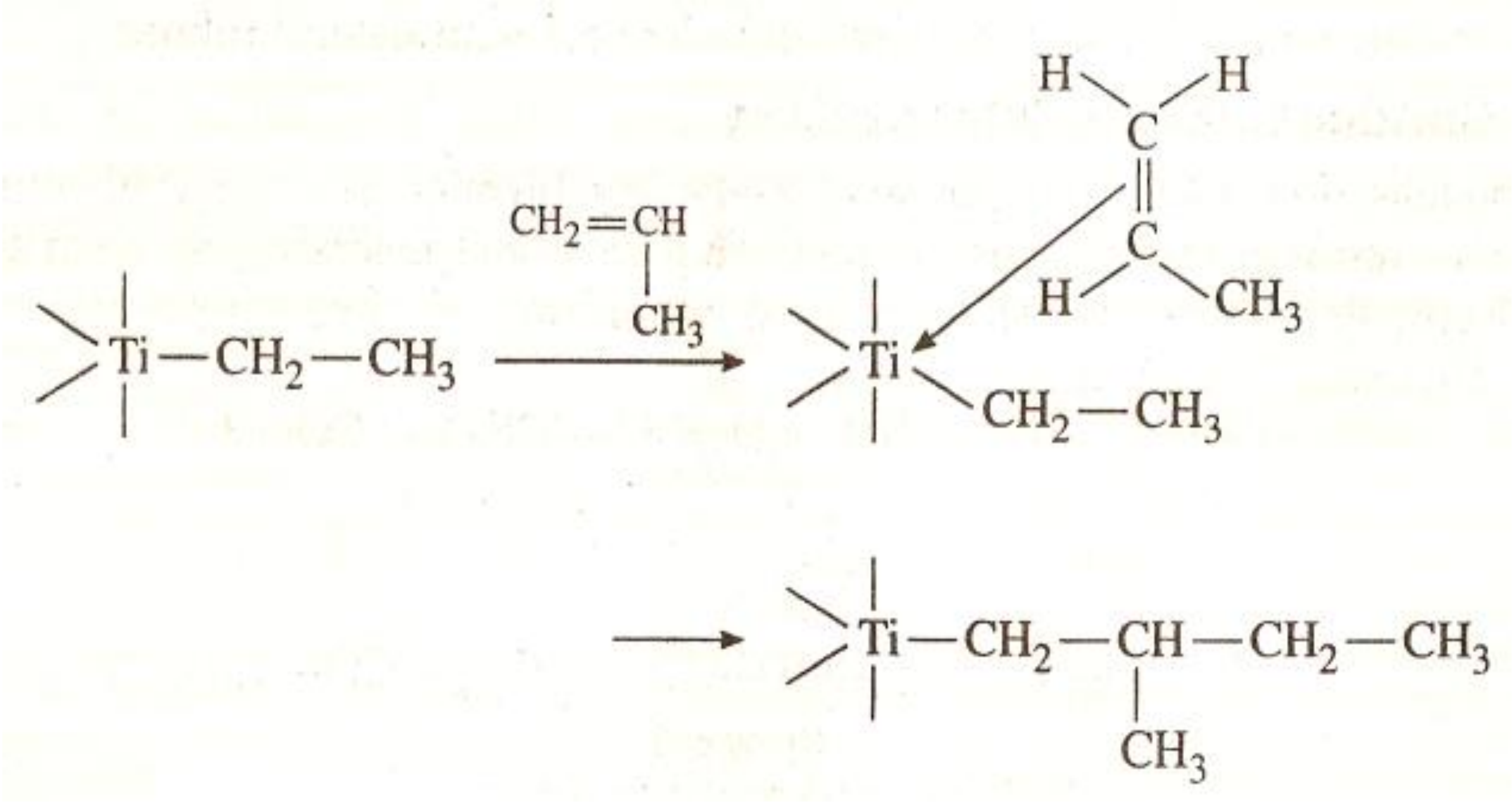
Initiation: In the initiation step, π-cloud of alkene overlaps with an empty orbital of titanium, then there is insertion of alkene molecules between the Ti-C bond.



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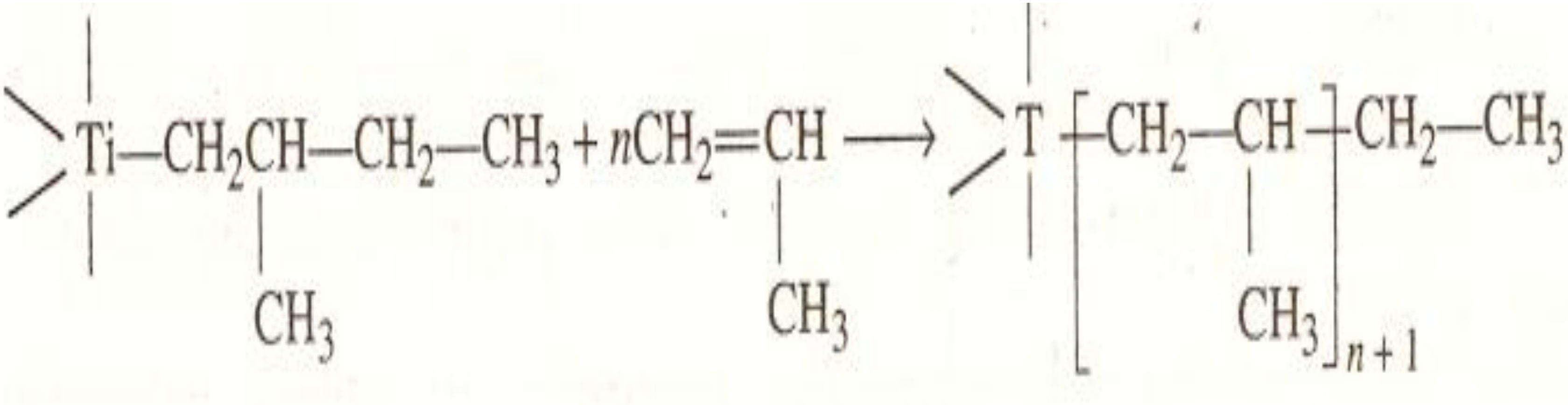
Propagation: As intermolecular rearrangement again generates a vacant site on titanium, each time one monomer molecule can be added in the same fashion.



$$\rangle\overset{|}{\underset{|}{\mathrm{Ti}}}-CH_2\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3+nCH_2{=}\underset{\underset{CH_3}{|}}{CH}\longrightarrow\rangle\overset{|}{\underset{|}{\mathrm{T}}}\left[-CH_2-\underset{\underset{CH_3}{|}}{CH}-\right]_{n+1}CH_2-CH_3$$

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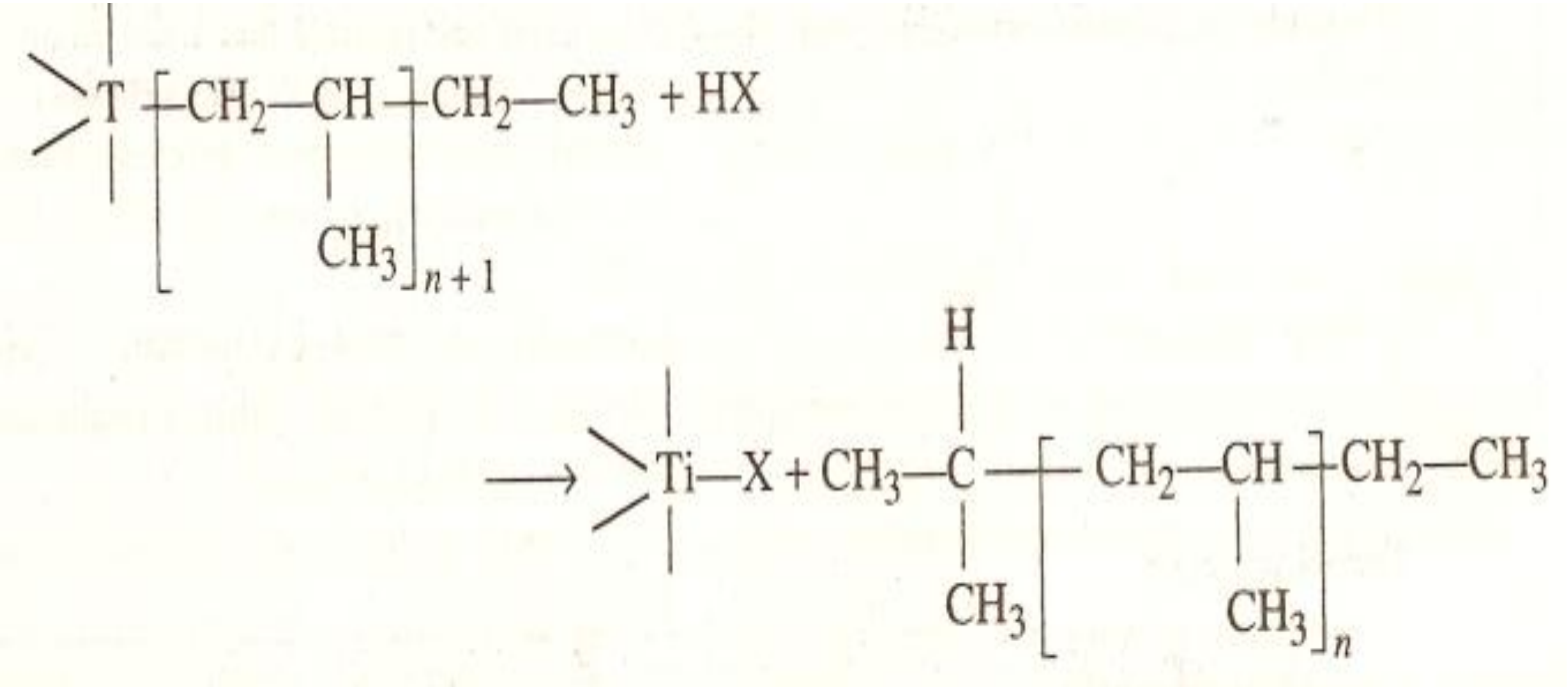
Termination: It can be done by the addition of molecules containing active hydrogen like HX.



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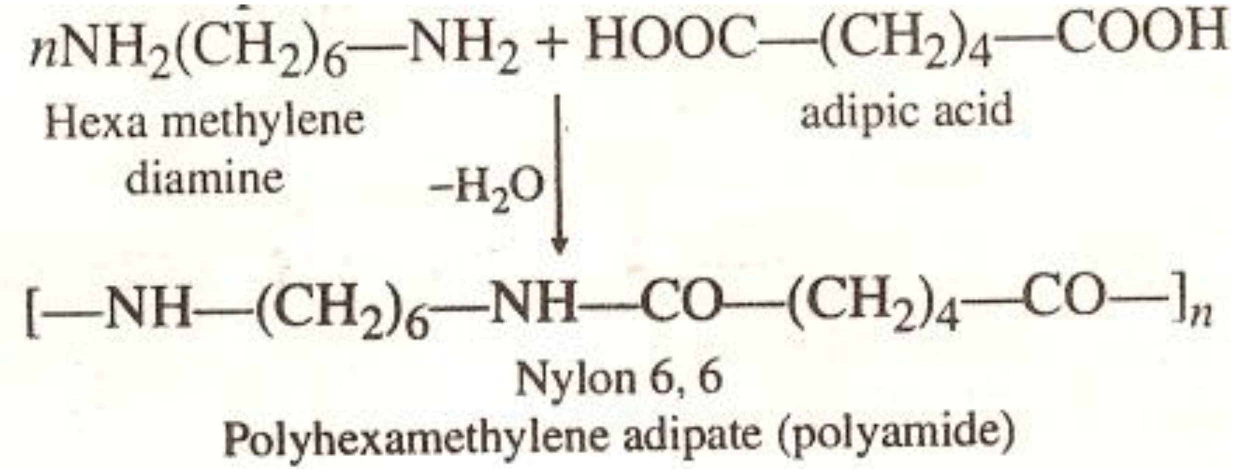
2. Condensation Polymerization :

Condensation polymerization involves the combination of several monomers to one another as a result of the migration of some mobile atom (generally hydrogen atom) from one molecule to another molecule with the elimination of some simple molecules (such as H_20, HCl etc.).

Example :



$$n\mathrm{NH_2(CH_2)_6{-}NH_2 + HOOC{-}(CH_2)_4{-}COOH}$$

Hexa methylene diamine

adipic acid

$$\Big\downarrow -\mathrm{H_2O}$$

$$\mathrm{[{-}NH{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO{-}]}_n$$

Nylon 6, 6

Polyhexamethylene adipate (polyamide)

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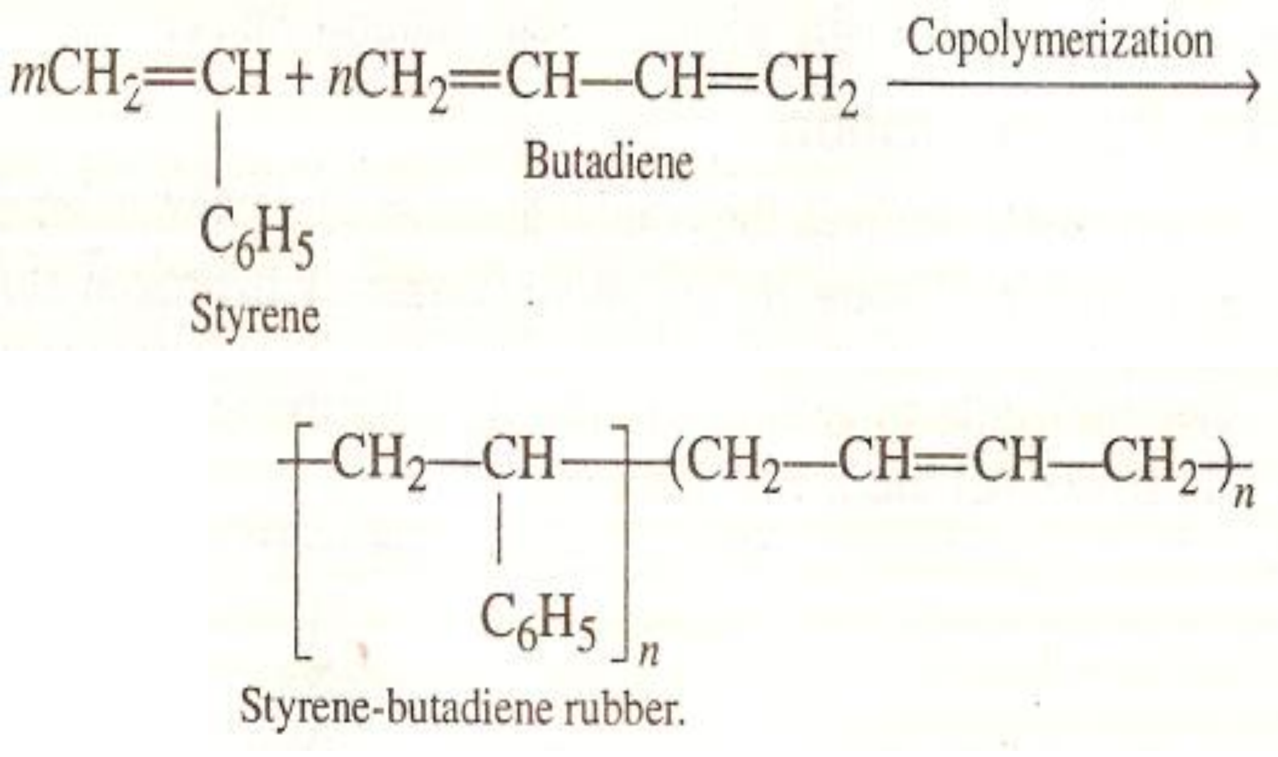
3. Copolymerization : Copolymerization has been used by nature in polypeptides which may contain as many as 20 different amino acids. Copolymerization is a polymerization of two or more monomeric species together.

Example :



$$m\,CH_2{=}\underset{\substack{|\\ C_6H_5}}{CH} + n\,CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\text{Copolymerization}} \left[CH_2{-}\underset{\substack{|\\ C_6H_5}}{CH}\right]_n \left(CH_2{-}CH{=}CH{-}CH_2\right)_n$$

Styrene

Butadiene

Styrene-butadiene rubber.

POLYMERS

Natural Rubbers :

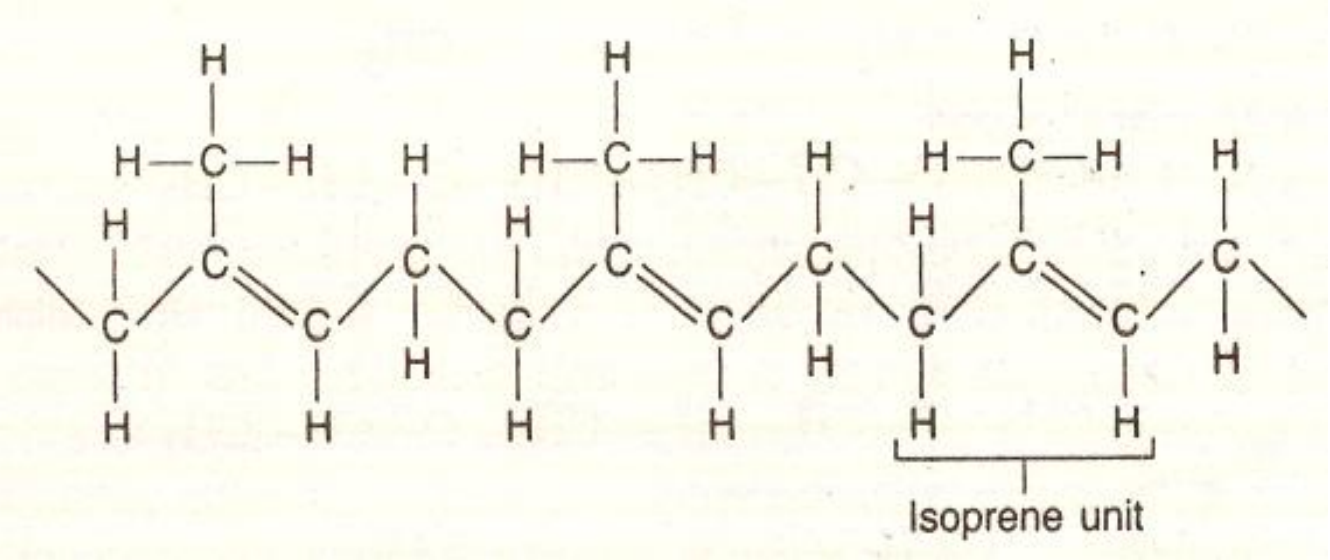
1. Caoutchouc or Hevea Rubber :

The main source from which the commercial natural rubber is obtained is the tree hevea braziliensis, The rubber is obtained from latex collected from the cuts made in the bark of the tree, The latex contains 25% to 40% of rubber hydrocarbon along with other impurities,such as fatty acids, proteins, resins, etc. The latex is treated with an acid such as acetic acid which coagulates the Crude rubber. The crude rubber is composed of 90-95% of rubber hydrocarbon, 2-4% of protein and 1 to 4% of resins. On destructive distillation, rubber gives isoprene as the main product which led to the suggestion that rubber is a polymer of isoprene, C_5H_8 and hence can be represented $(C_5H_8)_{n.}$

POLYMERS

2. **Gutta percha :** It is obtained from the mature leaves of dichopsis gutta and palagum gutta trees. Gutta percha may be recovered by solvent extraction, when insoluble resins and germs are separated. Alternatively, the mature leaves are ground carefully; treated with water at about 70°C for half an hour and then poured into cold-water when gutta percha floats on water surface and is removed.

Structure :



POLYMERS

Properties:

1. At room temperature, gutta percha is horny and tough, but it softens at about 100°C.
2. It is soluble in aliphatic hydrocarbons, but insoluble in aromatic and chlorinated hydrocarbons.
3. Structurally it is trans-poly-isoprene.

Uses:

1. In the manufacture of golf-ball covers.
2. In the manufacture of submarine cables.
3. In the manufacture of adhesives and tissues for surgical purpose.

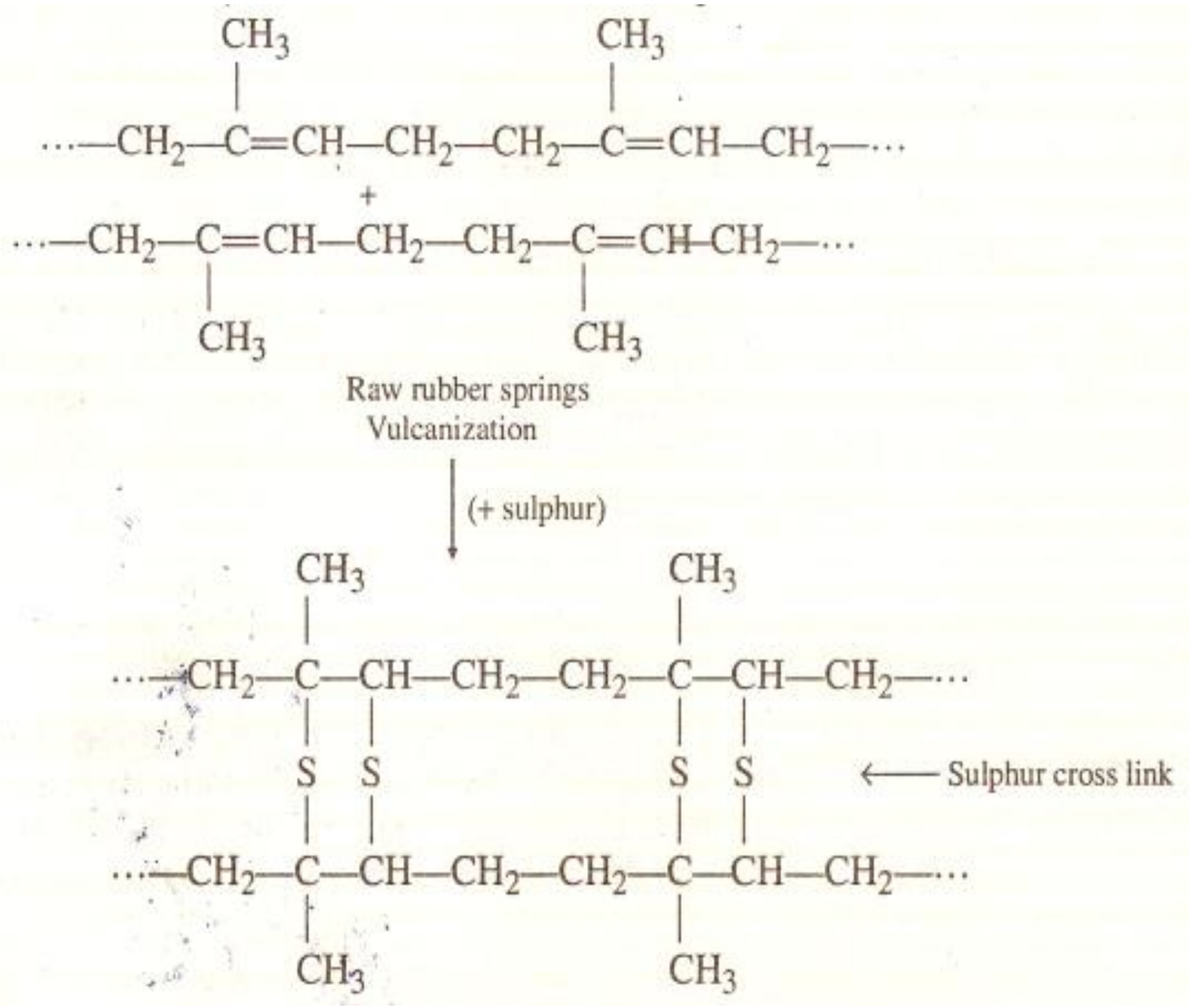
POLYMERS

Vulcanization of Rubber :

Raw rubber is of little use as such because it has very undesirable properties, e.g; it possesses elasticity only over a limited range of temperature, does not resume its original shape after being extended and becomes softer, more plastic and sticky on heating and brittle on cooling. The undesirable properties may be overcome by a process known as vulcanization.

Process : The process consists in heating the raw rubber with sulphur to 100-140°C. The added sulphur combines chemically at the double bonds of different rubber springs. Vulcanization thus serves to stiffen the material by a sort of anchoring and consequently, preventing intermolecular movement of rubber springs. The extent of stiffness of vulcanized rubber depends on the amount of sulphur added. The vulcanization can also be done by hydrogen sulphide and benzoyl chlorides.

POLYMERS


Raw rubber springs
Vulcanization
(+ sulphur)
Sulphur cross link

POLYMERS

Advantages of Vulcanization Vulcanized rubber :

(1) has good tensile strength and extensibility.

(2) has excellent resilence, *i.e.,* article made from it returns to the original shape,when the deforming load is removed;

(3) has higher resistance to oxidation .

(4) has much higher resistance to wear and tear as compared to raw rubber.

(5) is better electrical insulator, although it tends to absorb small amount of water.

Ebonite (raw rubber vulcanized with about 32% rubber) is better insulator.

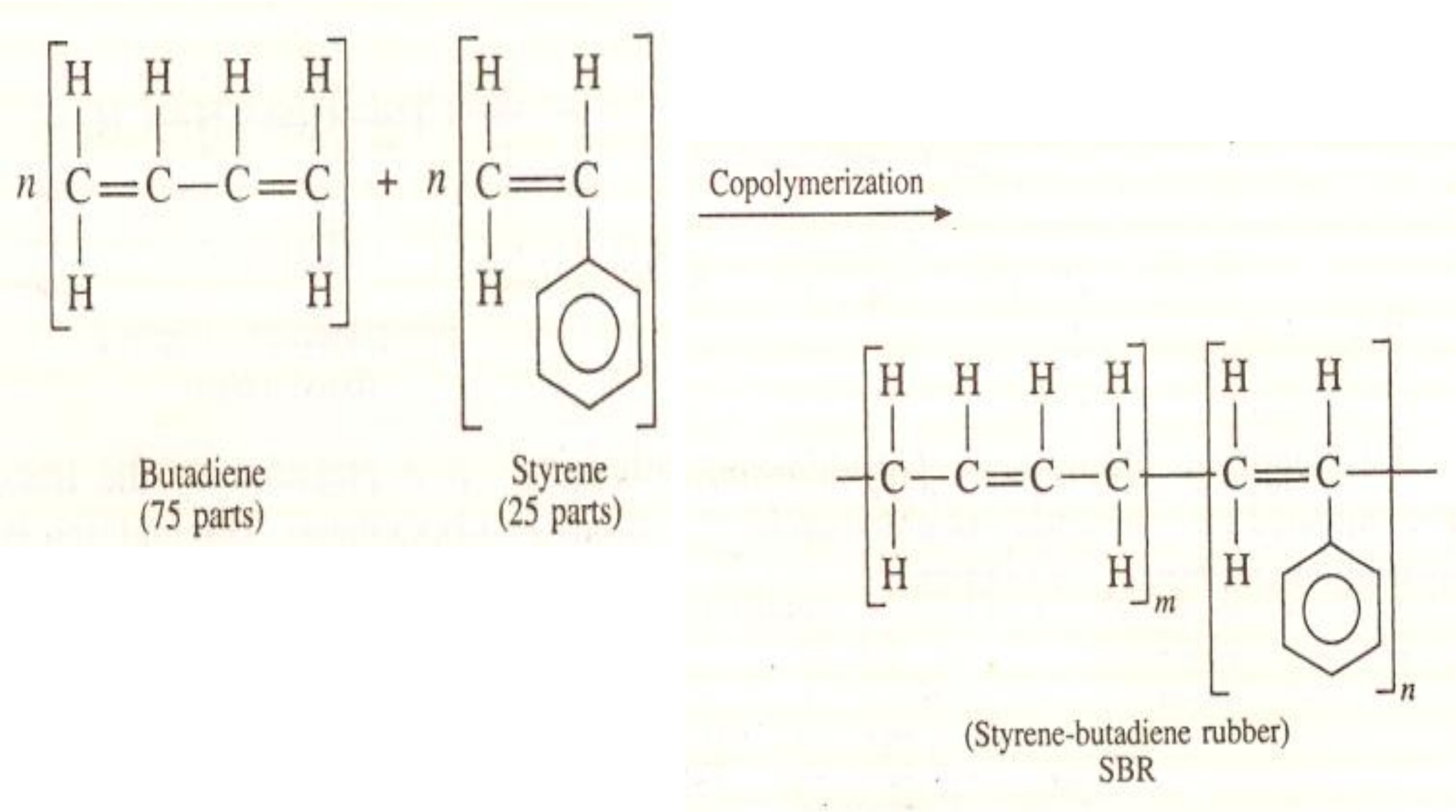
(6) is resistant to organic solvents (such as petrol, benzene, carbon tetrachloride), fats and oils. It swells in these liquids.

POLYMERS

Synthetic rubber : Synthetic rubber is the term used for that rubber like material which is obtained by means of synthesis (i.e., in the laboratory) and can compete with natural rubber in its many uses.

(a) Styrene Rubber or Buna-S : Buna-S is copolymer of 75% butadiene ($CH_2=CH-CH=CH_2$) and 25% styrene ($C_6H_5CH=CH_2$). The polymerization is carried out in an emulsion system at 50°C in the presence of peroxide catalyst. The polymer consists of the repeating units of mainly 1, 4-addition product of butadiene along with a small amount of I, 2-addition product.

POLYMERS


Butadiene
(75 parts)
Styrene
(25 parts)
Copolymerization
(Styrene-butadiene rubber)
SBR

POLYMERS

Properties: 1. Styrene rubber resembles natural rubber in processing characteristics well as quality of finished products.

2. It possesses high load-carrying capacity.

3. It gets readily oxidized, especially in presence of traces of ozone present in the atmosphere.

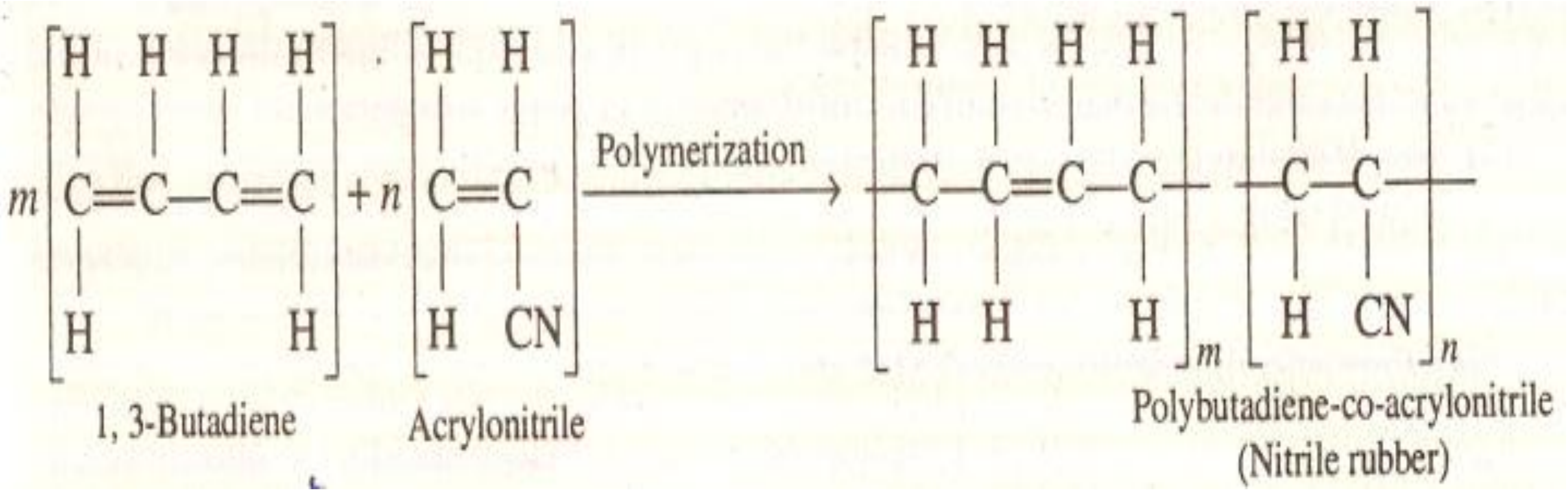
4. It can be vulcanized in the same way as natural rubber either by sulphur or sulphur monochloride (S_2Cl_2).

Uses: 1. It is mainly used for the manufacture of motor tyres.

2. Other uses of this elastomer are floor tiles, shoe sholes, gaskets, footwear components, wire and cable insulations, adhesives etc.

POLYMERS

(b) Nitrile Rubber or Buna-N: It is a copolymer of 75% butadiene and 25% acrylonitrile (CH_2=CHCN).



POLYMERS

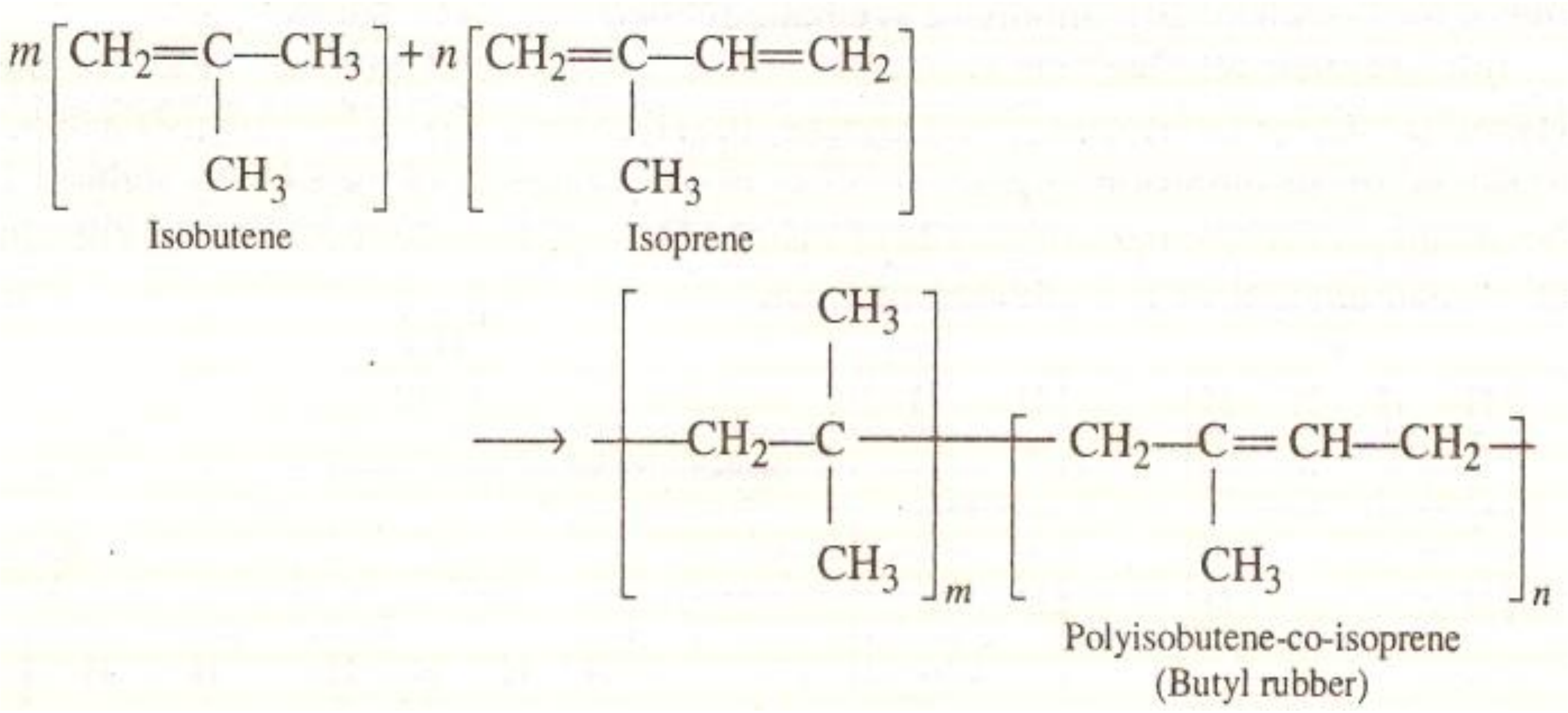
Properties:

1. It possesses excellent resistance to heat, sunlight, oils, acids and salts, but it is less resistant to alkalis than natural rubber, because of the presence of cyano groups (-CN).
2. As the proportion of acrylonitrile is increased, the resistance to acids, salts, oils, solvents, etc., increases.
3. Vulcanized-nitrile rubber is more resistant to heat and ageing than natural rubber and may be exposed to high temperatures.

Uses: For making conveyor belts, high altitude aircraft components, tank-linings, printing rollers, adhesives, oil-resistant foams and automobile parts, etc.

POLYMERS

(c) Butyl Rubber: It is a copolymer of 98% isobutene ($Me_2C=CH_2$) and nearly 2% butadiene or isoprene ($CH_2=CMe-CH=CH_2$); the latter is added to introduce the necessary ethylenic linkages for vulcanization.



$$m\left[CH_2=\underset{CH_3}{\underset{|}{C}}-CH_3\right] + n\left[CH_2=\underset{CH_3}{\underset{|}{C}}-CH=CH_2\right] \longrightarrow \left[-CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\right]_m\left[-CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_2-\right]_n$$

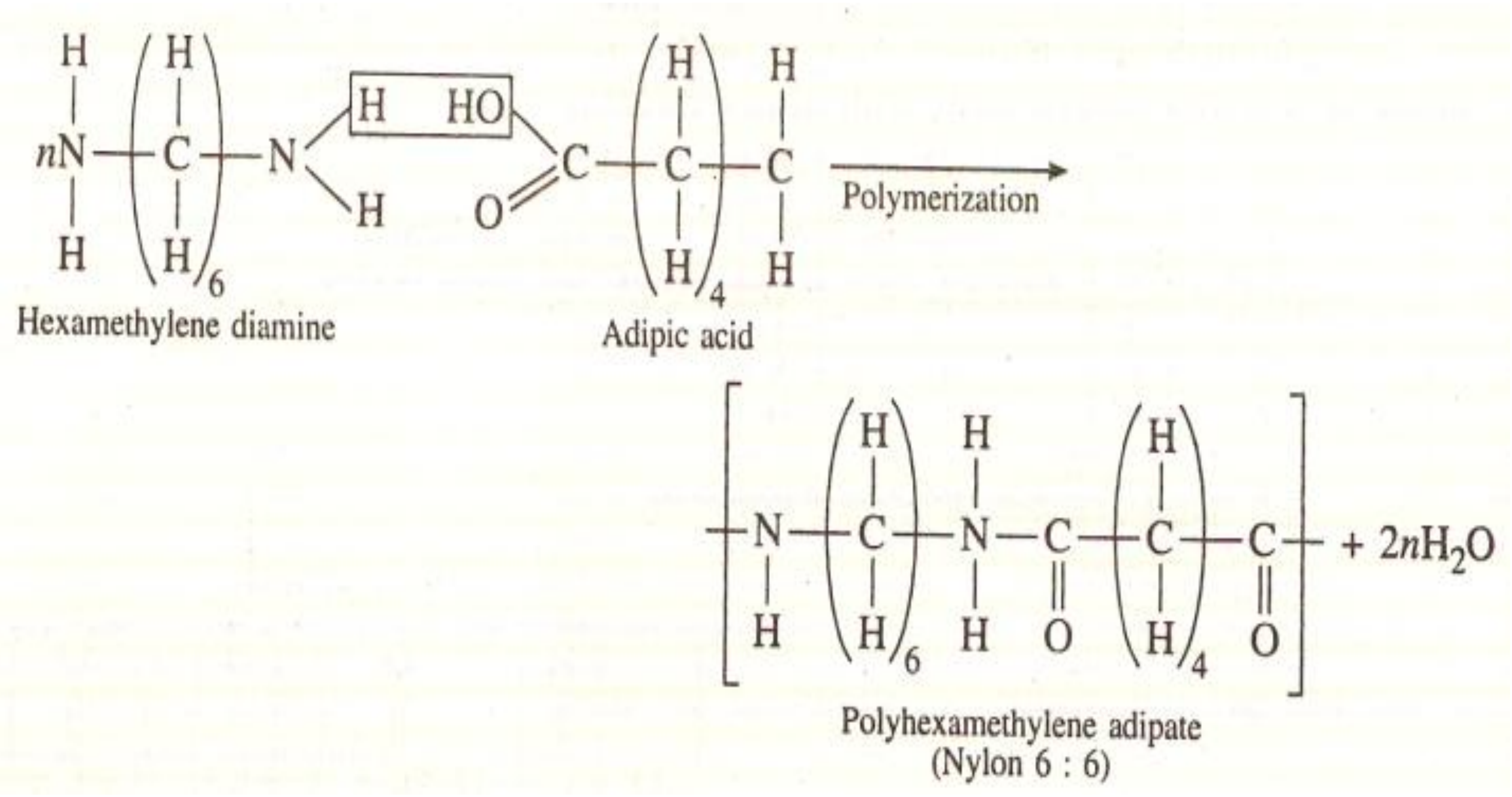
POLYMERS

POLYAMIDES :

Nylon is a generic term for synthetic polyamides capable of forming fibres. polyamides are synthetic polymers, which have recurring amide groups. Polyamides of commercial importance are Nylon 6; Nylon 6 : 6, Nylon 6 : 10 and Nylon 11.

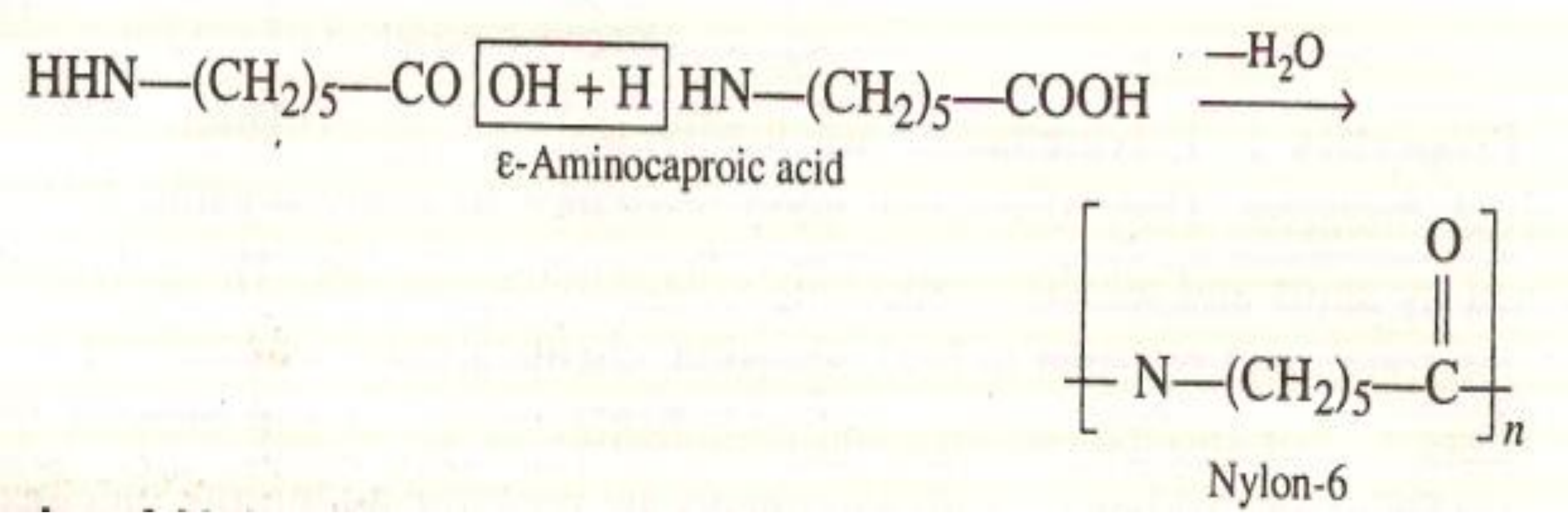
Nylon 6 : 6 It is prepared by the condensation of adipicacid and hexamethylene diamine in the absence of air. The amine and carboxyl groups condense to form amide linkage with the evolution of water.

POLYMERS


Hexamethylene diamine
Adipic acid
Polymerization
+ 2nH2O
Polyhexamethylene adipate
(Nylon 6 : 6)

POLYMERS

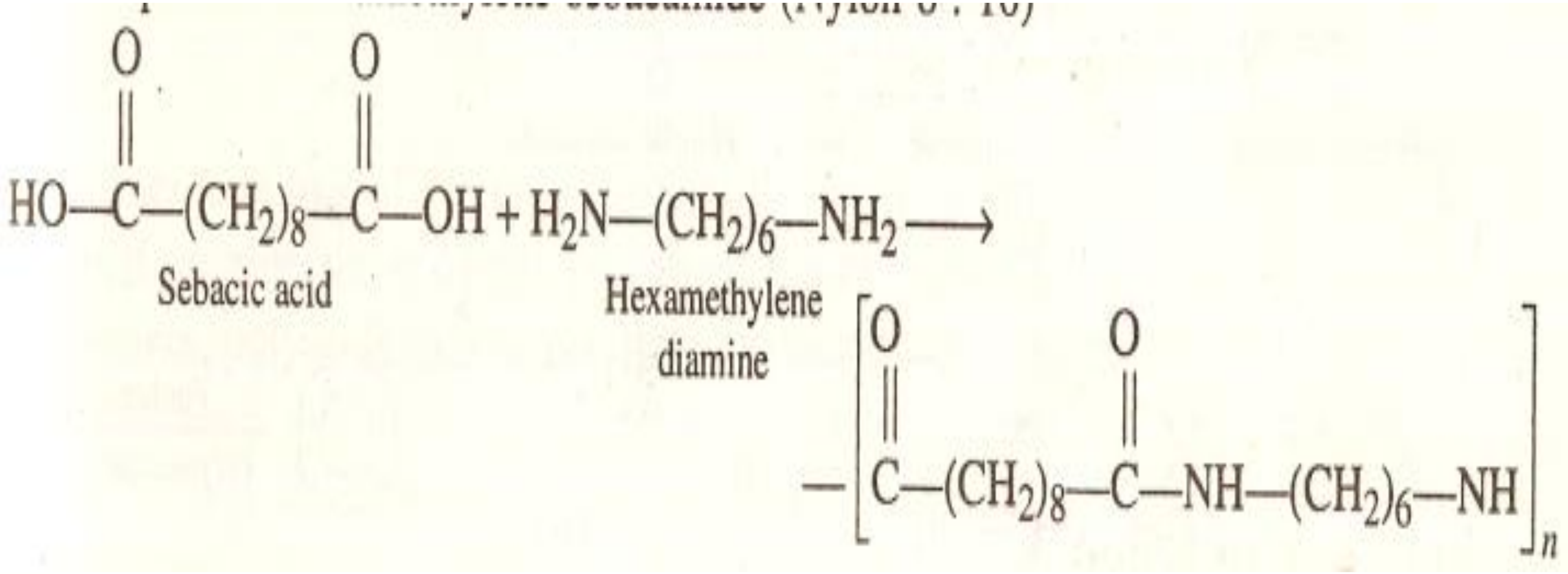
Nylon 6 : It is produced by the self condensation of ε-amino caproic acid.



$$HHN{-}(CH_2)_5{-}CO\boxed{OH + H}HN{-}(CH_2)_5{-}COOH \xrightarrow{-H_2O} \left[-N{-}(CH_2)_5{-}\overset{\overset{\displaystyle O}{\|}}{C}- \right]_n$$

POLYMERS

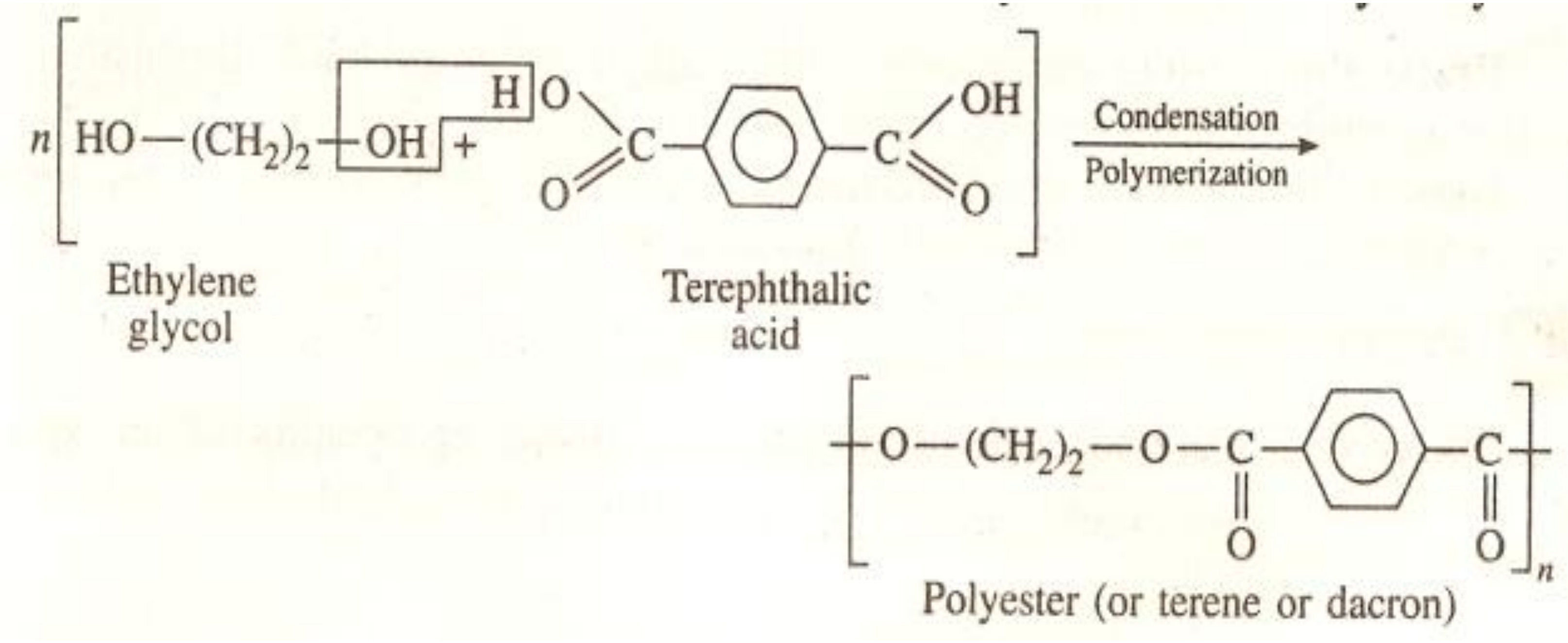
Nylon 6 : 10 It is prepared from reaction between hexamethylene diamine and sebacic acid to produced hexamethylene sebacamide (Nylon 6 : 10).



$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-OH + H_2N-(CH_2)_6-NH_2 \longrightarrow -\left[\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\right]_n$$

POLYMERS

Polyester : These are the condensation products of dicarboxylic acid with dihydroxy alcohols.



POLYMERS

Properties:

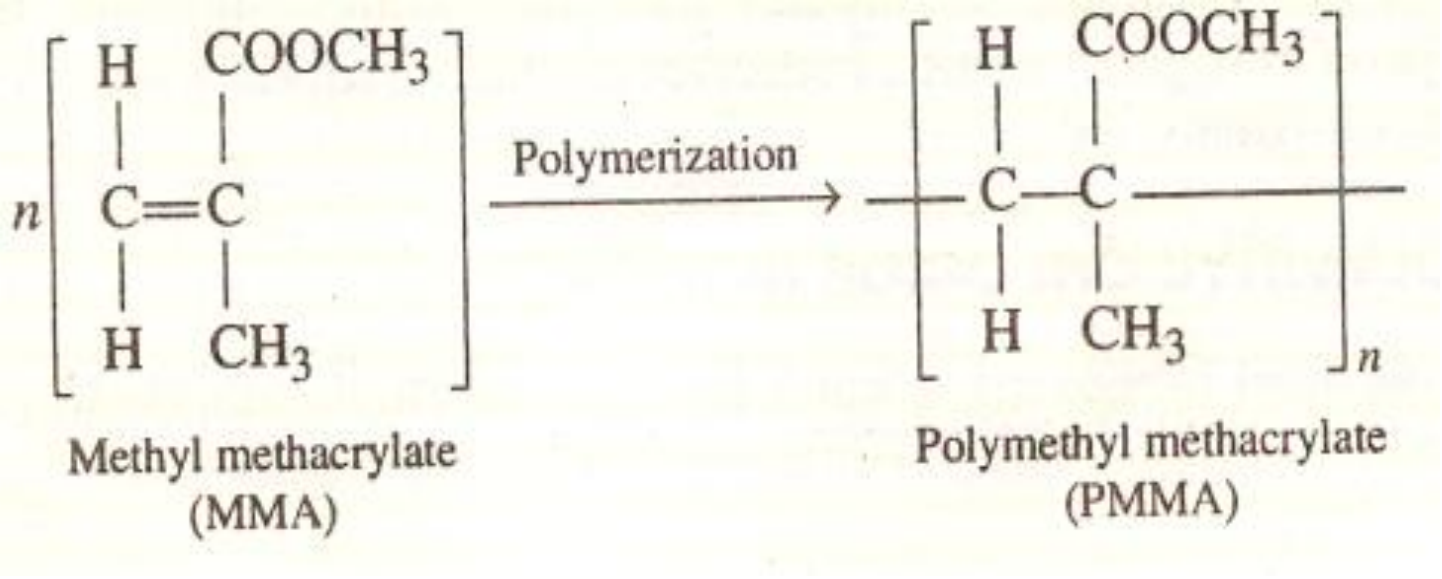
1. Because of its relative symmetrical structure and presence of numerous polar groups, the polyester is a good fibre-forming material and is converted into commercial fibres.
2. Such fibres have high stretch-resistance (due to high stiffness of polymer chains).
3. Polyethylene terephthalate (PET) is highly resistant to mineral and organic acids, but is less resistant to alkalis.

Uses : 1. It is mostly used for making synthetic fibres like terylene, dacron etc.

2. For blending with wool to provide better crease and wrinkle resistance.
3. As glass reinforcing material in safety he/ments, aircrafls ballery boxes, etc.

POLYMERS

Polymethyl Methacrylate (PMMA) or Lucite or Plexiglass : It is obtained by polymerization of methyl methacrylate (ester of methyl acrylic acid, $CH_2=C(CH_3)COOH$) in presence of acetyl peroxide or hydrogen peroxide. It is an acrylic polymer.



POLYMERS

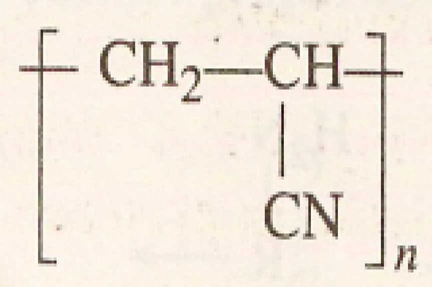
Properties:

1. Polymethyl methacrylate (PMMA) is hard, fairly rigid material with a high softening point of about 130-140°C, but it becomes rubber-like at a temperature above 65°C.
2. This relatively wide span of temperature from its rigid state to viscous consistency accounts for the outstanding shape-forming properties of polymethyl metha-crylate.
3. It has high optical-transparency, high resistance to sunlight and ability of transmitting light accurately, even in curved sections.

Uses: For making lenses, aircraft light fixtares, transparent models of compljcated machines, bone splints, artificial eyes, dentares, emulsions, paints, adhesives, automotive appliances, jewellery, wind screens, T. V. Screens, guards etc.

POLYMERS

POLYACRYLONITRILE (PAN) : It is also known as polyvinyl cyanide and obtained from acrylonitrile.



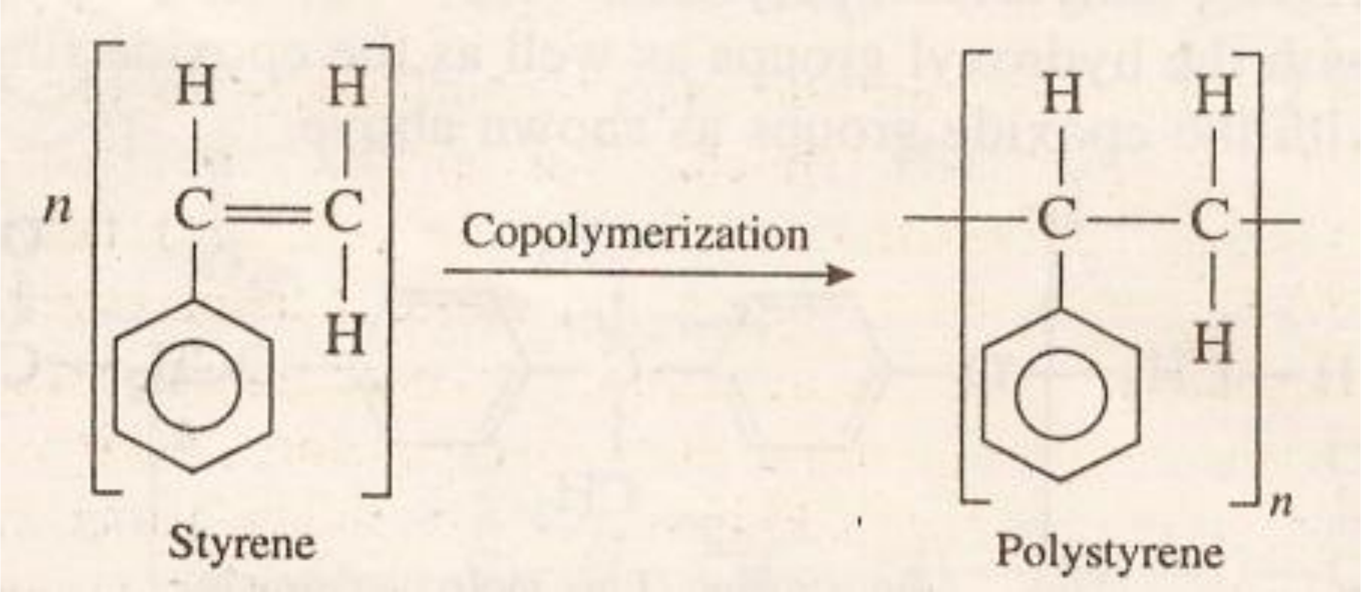
$$\left[-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}- \right]_n$$

Properties : It is quite hard, horny material of high melting point.

Uses : It is used for cloth, carpets and blankets.

POLYMERS

POLYSTYRENE : It is prepared by polymerization of styrene (dissolved in ethyl benzene) in presence of peroxide catalyst.



POLYMERS

Properties:

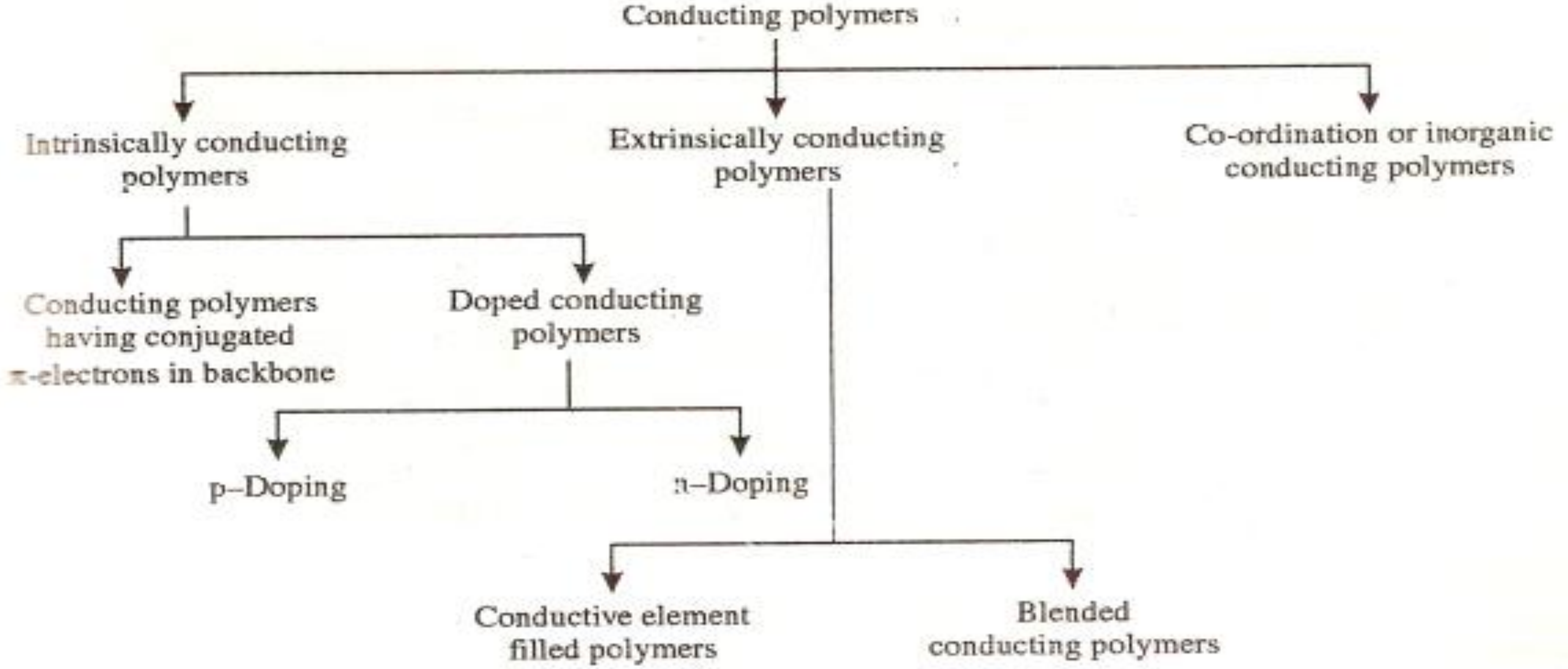
1. Polystyrene is a transparent, light, good light-stable, excellent moisture-resistant.
2. It can be nitrated by fuming nitricacid and sulphonated by conc. H_2S0_4. At about lOO°C, it yields water-soluble emulsion.
3. It is highly electric insulating, highly resistant to acids and good chemical-resistant.
4. It has the unique property of transmitting light through curved sections.

Uses: In moulding of articles like toys, combs, buttons, buckles, radio and television parts, refrigerator parts, battery cases, high frequency electric insulators, lenses, indoor lighting-panels, etc.

POLYMERS

CONDUCTING POLYMERS : Polymers which can conduct electricity are called conducting polymers. Ordinary polymers obtained by usual methods are nearly insulators. However, some specific polymers may act as conductors.

Classification: Conducting polymers may be classified as



POLYMERS

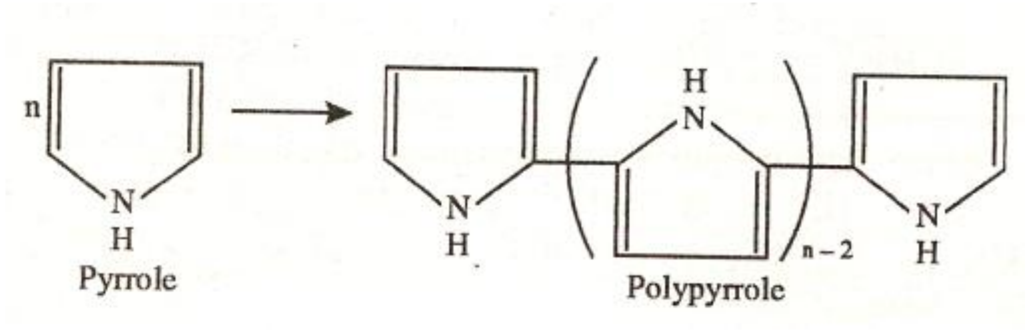
1. Intrinsically conducting polymers :

These types of polymers have a solid backbone made up of extensive conjugated system, which is responsible for conductance. They may be of two types:

(i) **Conducting polymers having conjugated π-electrons in the backbone :** These polymers essentially contain a conjugated π-electron backbone responsible for electrical charge. Under the influence of electrical field conjugated π -electrons of the polymer get excited, which can then be transported through the solid polymer. Fulther, overlapping of orbitals of conjugated π -electrons over the entire backbone results in the formation of valence bands as well as conduction bands, which extend over the complete polymer molecule. The presence of conjugated π -electrons in polymers increases its conductivity, *e.g.,*

POLYMERS

Polypyrrole



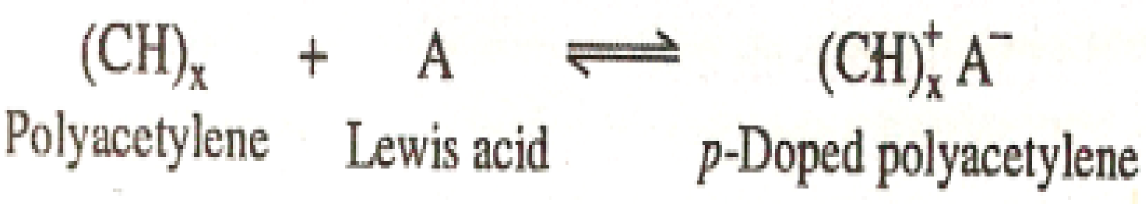
POLYMERS

(ii) Doped conducting polymers: The conducting polymers obtained by exposing the polymer to a charged transfer agent in either gas phase or in solution are called *doped conducting polymers.*

Doping is the process by which conductivity of the polymers may be increased by creating negative or positive charge on the polymer backbone by oxidation or reduction.

Doping may be of two types:

(A) p-Doping : It is done by oxidation process. In this process, the conducting polymer is treated with a Lewis acid.



$$(CH)_x + A \rightleftharpoons (CH)_x^+ A^-$$

POLYMERS

(B) n-Doping : It is done by reduction process. In this process, the conducting polymer is treated with a Lewis base.

$$(CH)_x + B \rightleftharpoons (CH)^-_x B^+$$

Polyacetylene   Lewis base   n-Doped polyacetylene

Advantages of intrinsically conducting polymers :

(i) Their conductivity

(ii) Their ability to store a charge.

(iii) Their ability to undergo ion exchange.

(iv) They can absorb visible light to give coloured products.

(v) They are transparent to X-rays.

POLYMERS

Limitations of intrinsically conducting polymers:

(i) Their conductivities are poorer than metals.

(ii) Their improcessability.

(iii) Their poor mechanical strength.

(iv) They are less stable at high temperatures.

(v) On storage they lead to loss in their conductivity.

POLYMERS

2. Extrinsically conducting polymers :

Those conducting polymers which owe their conductivity due to the presence of externally added ingredients in them are called *extrinsically conducting polymers.* They are of two types :

(i) Conductive element filled polymers : In this type, polymer acts as a binder to hold the conducting elements together in solid entity.

The minimum concentration of the conductive filler, which is added to let the polymer start conducting is called the *percolation threshold.*

Important characteristics of these polymers are : (a) They possess good bulk conductivity.

(b) They are cheaper.

(c) They are light in weight.

(d) They are mechanically durable and strong.

(e) They are easily processable in different forms, shapes and sizes.

POLYMERS

(ii) Blended conducting polymers: These types of polymers are obtained by blending a conventional polymer with a conducting polymer either physically or chemically. Such polymers can be easily processed and possess better physical, chemical and mechanical properties.

3. Coordination or inorganic conducting polymers :

These polymers contain charge transfer complexes and are obtained by combining metal atoms with polydentate ligands.

POLYMERS

Applications of conducting polymers: Conducting polymers are widely used :

1. In rechargable batteries.
2. In making analytical sensors for pH, O_2, SO_2, NH_3, glucose, etc.
3. In the preparation of ion exchangers.
4. In controlled release of drugs.
5. In optical filters.
6. In photo voltaic devices.
7. In telecommunication systems.
8. In micro-electronic devices.
9. In bio-medical applications.

BIODEGRADABLE POLYMERS

Biodegradation is the breakdown of polymer by microbial organisms (such as bacteria, fungi etc.) into smaller compounds. The microbial organisms degrade the polymer through metabolic or enzymatic processes. The biodegradability of a given polymeric material is defined by the chemical structure of the polymer. Photodegradation is often subsequently followed by microbial or biodegradation. Natural products which are susceptible to biological attack are: starch, cellulose etc. Biodegradation of any organic material under controlled aerobic and anaerobic conditions produce **compost**. The process is termed as **composting**. Hence, a plastic that undergoes degradation by microbial action during composting to yield CO_2, H_2O and inorganic compounds, leaving no toxic residue is termed as **compostable plastic.** Ideal conditions for micro organism growth are obtained during the composting process.

Environmental Degradable Polymers

A variety of natural, synthetic, and biosynthetic polymers are bio- and environmentally degradable. **A polymer based on the C-C backbone tends to be nonbiodegradable, whereas heteroatom-containing polymer backbones confer biodegradability**. Biodegradability can therefore be engineered into polymer by the judicious addition of chemical linkages such as anhydride, ester, or amide bonds, among others.

Many polymers that are claimed to be 'biodegradable' are in fact 'bioerodable', 'hydrobiodegradable' or 'photo-biodegradable'. These different polymer classes all come under the broader category of '*environmentally degradable polymers*'.

Thus the classes of biodegradable plastics considered, in terms of the degradation mechanism, are:

1. Biodegradable
2. Compostable
3. Hydro-biodegradable
4. Photo-biodegradable
5. Bioerodable

Biodegradable: American society of Testing and Materials (ASTM) defines 'biodegradable' as: "*capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standardized tests, in a specified period of time, reflecting available disposal condition.*"

In simple words, biodegradation is the degradation caused by biological activity, particularly by enzyme action leading to significant changes in the material's chemical structure. In essence, biodegradable plastics should break down cleanly, in a defined time period, to simple molecules found in the environment such as carbon dioxide and water.

Compostable: Compostable plastics are a subset of biodegradable plastics. Compostable biodegradable plastics must biodegrade and disintegrate in a compost system during the composting process (typically around 12 weeks at temperatures over 50°C). The compost must meet quality criteria such as heavy metal content, ecotoxicity, and no obvious distinguishable residues caused by the breakdown of the polymers.

Hydro-biodegradable and Photo-biodegradable: Two closely linked mechanisms of degradation that are frequently confused with biodegradation are Hydro-degradation (degradation via hydrolysis) and Photo-degradation (degradation via photolysis). Since both mechanisms are often subsequently followed by microbial degradation, confusion of definition frequently occurs. Hydro-biodegradable and photo-biodegradable polymers are broken down in a **two-step** process - an initial hydrolysis or photo-degradation stage, followed by further biodegradation. Single degradation phase 'water- soluble' and 'photodegradable' polymer also exist.

Bio-erodable: Many polymers that claimed to be 'biodegradable' are in fact 'bioerodable' and degrade without the action of micro-organisms - at least initially in the first step. This is also known as abiotic disintegration, and may include process such as dissolution in water, 'oxidative embrittlement' (heat ageing) or 'photolytic embrittlement' (UV ageing).

Some Biodegradable Polymers:

- Starch based products including thermoplastic starch.
- Polyester blends and Polyvinyl alcohol (PVOH) blends.
- Naturally produced polyesters including polyhydroxybutyrate (PHB).
- Renewable resource polyesters such as polylactic acid (PLA).
- Synthetic aliphatic polyesters including polycaprolactone (PCL) and polybutylene succinate (PBS).
- Aliphatic-aromatic (AAC) copolyesters.
- Hydro-biodegradable polyester such as modified PET.
- Water soluble polymer such as polyvinyl alcohol and ethylene vinyl alcohol.
- Photo-biodegradable plastics.
- Controlled degradation additive masterbatches.

Biopolymers and Bioplastics

Biopolymers are polymers which are present in, or created by, living organisms. These include polymers from renewable resources that can be polymerized to create bioplastics.Carbohydrates and proteins, for example, are biopolymers. Many biopolymers are already being produced commercially on large scales, although they usually are not used for the production of plastics.

Bioplastics are plastics manufactured using biopolymers, and are biodegradable.These are also called green plastics. Green plastics are the focus of an emerging industry focused on making convenient living consistent with environmental stability.

Biopolymers and bioplastics are the main components in creating a sustainable plastics industry. These products reduce the dependence on non-renewable fossil fuels, and are easily biodegradable. Also, being biodegradable make bioplastics more acceptable for long term use by society.

Biopolymers

Types of Biopolymers: There are two main types of biopolymers:

(i) those that come from living organisms; and
(ii) those which need to be polymerized but come from renewable resources.

Both types are used in the production of bioplastics.

(i) Biopolymers From Living Organisms

These biopolymers are present in, or created by, living organisms. These include carbohydrates, and proteins. These can be used in the production of plastic for commercial purposes. Examples are listed in the table below.

Biopolymer	Source	Remarks
Cellulose	In plants cellulose is synthesized from glucose. It is the main component of plant cell walls Examples include wood, cotton, corn, wheat, and others	• Cellulose is the most plentiful carbohydrate in the world; 40 percent of all organic matter is cellulose • It has β glucose as the repeat unit. • Cellulose is insoluble in most of the solvents and hence it is converted to its derivatives to make it process able.
Soy protein	Soy protein and zein (from corn) are abundant plant proteins.	• They are used for making adhesives and coatings for paper and cardboard.
Starch	Starch is found in corn (maize), potatoes, wheat, tapioca (cassava), and some other plants.	• Starch is also made up of glucose units and is stored in plant tissues. It is not found in animal tissues. • It has β glucose as the repeat unit • Annual world production of starch is well over 70 billion pounds, with much of it being used for non-food purposes, like making paper, cardboard, textile sizing, and adhesives.
Polyesters	Polyesters are produced by bacteria, and can be made commercially on large scales through fermentation processes. Commercially produced mainly from cow's skimmed milk	• These polyesters are created through naturally occurring chemical reactions that are carried out by certain types of bacteria. • They are now being used in biomedical applications
Casein		• Casein is used in adhesives, binders, protective coatings, and other products

(ii) Polymerizable Molecules

These molecules come from renewable natural resources, and can be polymerized to be used in the manufacture of biodegradable plastics.Some of these are listed in the table below:

Biopolymer	Natural Source	Remarks
Lactic Acid	Beets, corn, potatoes, and others	• Produced through fermentation of sugar feedstocks, such as beets, and by converting starch in corn, potatoes, or other starch sources. • It is polymerized to produce polylactic acid — a polymer that is used to produce plastic.
Triglycerides	Vegetable oils mainly from soybean, flax, and rapeseed.	• Triglycerides are another promising raw material for producing plastics.

14.12 ORGANOMETALLICS

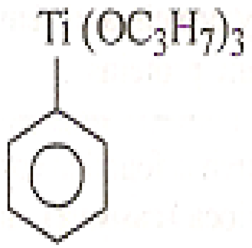
An organometallic compound is generally a compound which possesses a metal-carbon bond. Organometallic chemistry can be viewed as a bridge between organic and inorganic chemistry. The importance of organometallic compounds lies in the fact that these are excellent catalysts which play a major role in the production of pharmaceuticals agrichemicals, flavours and semiconductors etc. Organometallic chemistry is rapidly growing field of chemistry. The discovery of Grinard reagents in 1900 not gave versatile intermediates for a variety of organic preparations.

It may be noted that not all the compounds containing carbon and a metal atom are organometallic. The term 'organometallic' is reserved to the compounds which contain atleast one Metal-Carbon bond. An alkoxide such as $(C_3H_7O_4)$ Ti is not considered as organometallic compound because here the organic group is bonded to Ti through oxygen and not through carbon. Whereas the compound $C_6H_5Ti\ (OC_3H_7)_3$ is an organometallic compound because in this compound Ti is bonded to carbon of the organic group

$$(C_6H_5 - Ti)$$

$$Ti - (OC_3H_7)_4$$

Not an organometallic compound



Organometallic (Ti — C bond)

The common examples of organometallic compounds are those $Pb(C_2H_5)_4$ (tetraethyl lead), $(C_5H_5)_2$ Fe (ferrocene), $K[PtCl_3\ (C_2H_4)]$ (Zeise salt) etc.

Despite the rigorous definition, the boderline that distinguishes organometallic chemistry from other branches is unclear. For example metal cyanides (M–CN) and metal carbides (CaC_2, Al_4C_3 etc.) contain Metal–Carbon bond but are *not* considered organometallics because their properties are closely related to those of many other compounds of inorganic chemistry. On the other hand, $Ni(CO)_4$ (nickel tetracarbonyl) and other complexes having the ligand CD are considered organometallic because of the resemblence of their properties to organometallics.

Organometallics are also known as organo-inorganics, metallo-organics and metalorganics. Organometallic compounds are named by prefixing the metal with organo-, e.g. organopalladium compounds, organophosphorus compounds, organomagnesium compounds.

Reactivity

Organometallics are very reactive compounds and hence are kept in solutions in organic solvents (especially with H_2O, O_2 etc)

The organometallic compounds form electron rich or anionic carbon atoms i.e. carbanians during their reactions. This means, they will function as bases or nucleophiles. Thus it is reasonable to write the general formula of these compounds as R^-M^+.

$CH_3 \rightarrow Cl$	$CH_3 — Li$
alkyl halide	**Organometallic alkyl lithium**
Methyl group has lower electron density and hence is an electrophile	The methyl group has higher electron density and hence is a nucleophile

The alkyl group in alkyl halides acts as electrophile whereas the alkyl group in organometallics acts as nucleophile. In otherwords organolithium and organomagnesium compounds are strong bases since the negative charge is on carbon.

It is the carbonionic nature of organometallics that is responsible for their usefulness as synthetic reagents.

CLASSIFICATION

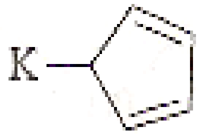
The organometallic compounds can be classified on the basis of the nature of metal-carbon bond.

(1) Ionic compounds of electropositive metals:

The organosodium and organopotassium compounds are essentially ionic organometallic compounds. In these type of compounds the bonding between the metal and the carbon is ionic. The carbon of the organic group (hydrocarbon) carry a negative charge which is strongly attracted by the positively charged metal ion by electrostatic forces of attraction.

These organometallic compounds are formed by the most electropositive metals of group IA and IIA. The formation of these compounds is favoured if the negative charge on the carbon atom is stabilized i.e it is delocalized over several carbon atoms.

Example: $K^+C_5H_5^-$ (potassium cyclopentadienyl). The negative charge is stabilized due to delocalization over the five carbon atoms of cyclopentadienyl ring.



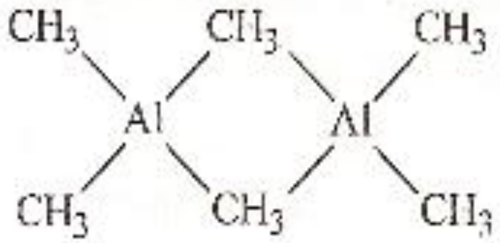
Other examples include $Na^+C_6H_5^-$, $Na^+C_4H_9^-$ etc. These compounds contain a very reactive C_5H_5 group. These compounds are referred to as metal cyclopentadienides. These organometallic compounds show behaviour typical of ionic compounds and are insoluble in organic or non-polar solvents. The reactivity of these compounds depend upon the stability of the anion. However, there are certain metal cyclopentadienides which have substantial amount of covalent character present.

(2) Covalent organometallic compounds:

These compounds have organic past bonded to the metal atom by a normal sigma covalent bond. These compounds are very common and are generally formed by Zn, Cd, Hg and representative elements of group III, IV and V. The covalent organometallic compounds are generally metal-alkyl compounds. Examples are $Pb(C_2H_5)_2$, $(C_6H_5)_2Zn$, $(CH_3)_2Cd$, C_4H_9Li etc. The polarity of the covalent bond between metal and alkyl groups depends upon the difference in electronegativity between metal atom and carbon atom.

(3) Electron deficient organometallic compounds:

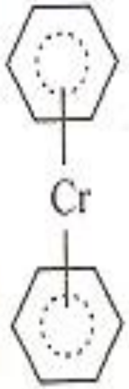
These type of compounds include the compounds having bridging alkyl groups. For example, dimeric trialkyl aluminium which have bridging alkyl groups.



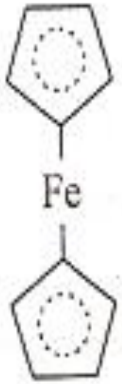
Dimeric dialkyl aluminium

(4) Organometallics involving π bonds:

These constitute an important class of organometallics having metal-ligand bond between a metal and the π orbitals of organic ligands such as alkenes, benzene ring etc. Ferrocene was the first of many π complexes which came to be known as metallocenes. In these complexes the metal ion is sandwitched between two parallel carbocyclic rings became known as "sandwich" compounds. Example,



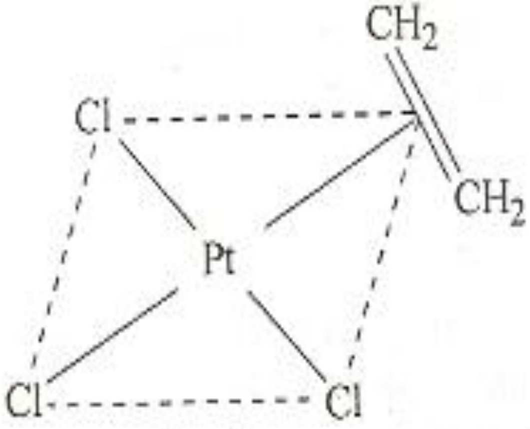
$(C_6H_5)_2$ Cr



$(C_5H_5)_2$ Fe

common example of ligands forming such type of organometallic compounds are :

Complexes of alkenes are well known for transition metals like Pt(II), Pd(II), Cu(II), Ag(I), Hg(II) etc. The first compound of alkene with the metal ion was reported by Zeise (a Danish Chemist) and is known as Zeise salt. $K[PtCl_3.(C_2H_4)]$



Zeise salt
(π complex)

(5) Carbene/Carbyne complexes:

The chemistry of metal-carbon single bond dates back to 19th century (e.g. Grignard's reagent) Transition metal compounds containing metal carbon double bond or triple bond have come to be understood more recently.

$$\text{M—CR}_3, \quad \text{M}=\text{CR}_2, \qquad \text{M}\equiv\text{CR}$$

Metal Carbones Metal Carbynes

If these occurs multiple bonding between metal and carbon, the bond strength would be increased. It has been observed that in carbene compounds, the metal-carbon bond is shorter than metal-alkyl sigma bond but larger than metal-carbon double bond. Thus metal carbenes are generally stable organometallics. The first carbene complex $(CO)_5$ W[:CRX] was synthesized by Noble Laureate in 1964 by E.O. Fisher.

Metal Carbynes have triple bonds. For example $(CO)_4M\ (\equiv CR)X$. The chemistry of alkyne complexes is more complicated than that of alkene complexes.

(6) Transition-metal Organometallic Compounds:

A large number of organometallics are based on transition metals. Examples include organometallics containing iron, nickel, chromium, platinum and rhodium.

A transition-metal complex consists of a transition-metal to which are attached groups called *ligands*. Essentially, anything attached to a metal is a ligand. A ligand can be an element (O_2, N_2), a compound (NO), or an ion (CN^-); it can be inorganic as in the examples just cited or it can be an organic ligand. Ligands differ in the number of electrons that they share with the transition metal to which they are attached. Carbon monoxide is a frequently encountered ligand in transition-metal complexes and contributes two electrons; it is best through of in terms of the Lewis structure $:\bar{C}\equiv\overset{+}{O}:$ in which carbon is the reactive site. An example of a carbonyl complex of a transition metal is nickel

(ii) Hexacarbonyl chromium (0), $Cr(CO)_6$

Atomic number of Cr = 24

Cr(0) = 24

Six CO groups (6 × 2) = 12

EAN = 36

Thus, EAN rule is obeyed.

(iii) Pentacarbonyl iron (0), $Fe(CO)_8$

Atomic number of Fe = 26

Fe(0) = 26

Five CO groups (5 × 2) = 10

EAN = 36

Thus, EAN rule is obeyed.

(iv) **Pentacarbonyl manganate (—I) ion, $[Mn(CO)_5]^-$**

Atomic number of Mn = 25

Mn(–1) = 26

Five CO groups (5 × 2) = 10

EAN = 36

Thus, $[Mn(CO)_5]^-$ obeys EAN rule.

General Methods of Synthesis of Organometallics

(1) By reductive substitution of alkyl halides: (Preparation of metal alkyls)

The first reported organometallic compounds were prepared by the reductive substitution of alkyl halides. The following equations illustrate these reactions for the commonly used metals lithium and magnesium (R may be hydrogen or alkyl groups in any combination).

$R_3C\text{-}X + 2Li \rightarrow R_3C\text{-}Li + LiX$	An Alkyl Lithium Reagent
$R_3C\text{-}X + Mg \rightarrow R_3C\text{-}MgX$	A Grignard Reagent

The alkyl magnesium halides described in the second reaction are called *Grignard Reagents* after the French chemist, Victor Grignard, who discovered them. The solvent used in this reaction is anhydrous diethyl ether. Typical solvents are normally anhydrous diethyl ether but pentane or hexane can also be used.

The other metals react in a similar manner, but the two shown here are the most widely used.

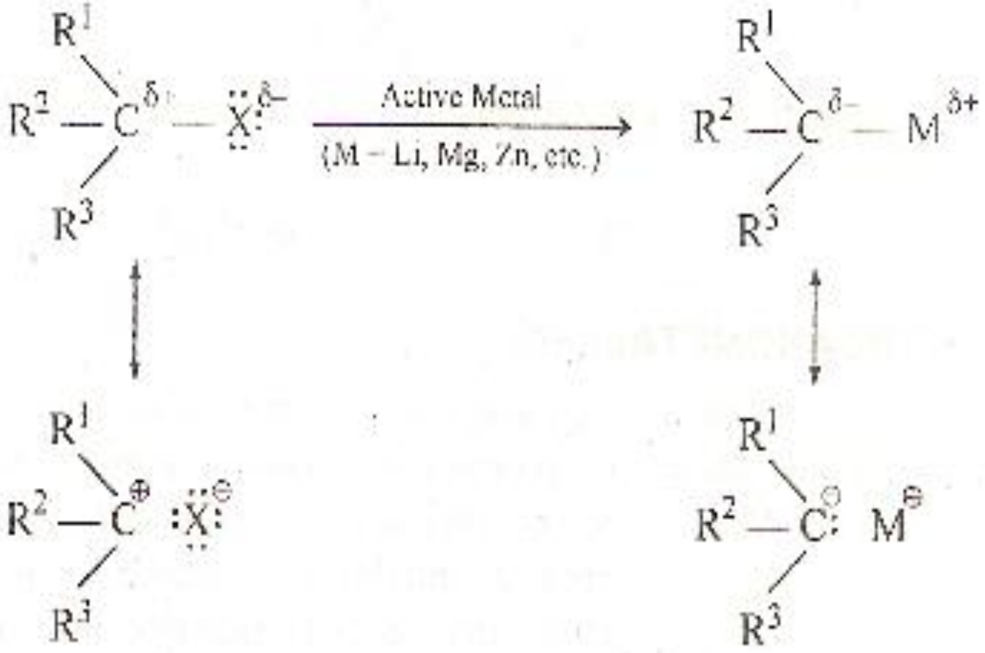
$R\text{-}X + Zn \rightarrow R\text{-}Zn\text{-}X$	An Alkyl Zinc Reagent	1849 E. Frankland
$R\text{-}X + Mg \rightarrow R\text{-}Mg\text{-}X$	A Grignard Reagent	1900 V. Grignard
$R\text{-}X + 2Li \rightarrow R\text{-}Li + LiX$	An Alkyl Lithium Reagent	1930 K. Ziegler

Reactions of organolithium and Grignard reagents reflect the nucleophilic (and basic) character of the functional carbon in these compounds

% Ionic Character of H_3C – Metal

$$(CH_3)_2Hg < (CH_3)_2Cd < (CH_3)_2Zn < (CH_3)_2Mg < CH_3Li$$

These reactions are obviously substitution reactions, *but they cannot be classified as nucleophilic substitutions*, as were the earlier reactions of alkyl halides. Because the functional carbon atom has been reduced, the polarity of the resulting functional group is inverted (an originally electrophilic carbon becomes nucleophilic). This change, shown below, makes alkyl lithium and Grignard reagents unique and useful reactants in synthesis.



(2) Metal Exchange Reactions:

Alternative methods of preparing a wide variety of organometallic compounds generally involve an exchange reaction in which a given metal is either moved to a new location or replaced by a new metal, which may include B, Al, Ti, V, Fe, Ni, Cu, Mo, Ru, Pd, Sn, Pt, Hg & Pb. Some of these reactions are:

Type I: $R{-}M + R'{-}H \rightleftharpoons R{-}H + R'{-}M$

Examples:

$$R—C \equiv R—C + C_2H_5MgBr \longrightarrow R—C \equiv R—MgBr + C_2H_6$$

Type 2: $R–M + M \rightleftharpoons R–M' + M$

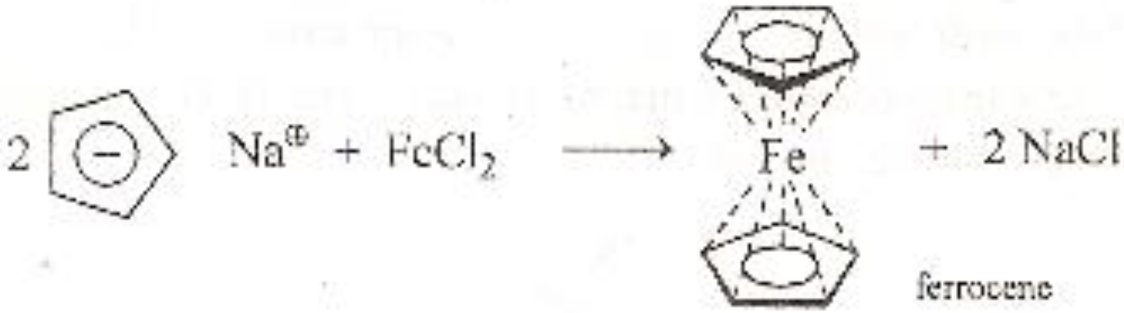
R-M is often a dialkylmercury compound.

Examples:

$$3(C_6H_5)_2Hg + 2Al \rightarrow 2(C_6H_5)_3Al + 3Hg$$

$$(C_2H_5)_2Hg + Mg \rightarrow 2(C_2H_5)_2Mg + Hg$$

Type 3: $R–M + M'X \rightleftharpoons R–M' + MX$



(3) Syntheses of metal carbonyls:

Metal carbonyls can beprepared in a variety of ways:

- For Ni and Fe, binary metal carbonyls can be made by the direction interaction with the metal

$$Ni + 4CO \xrightarrow{25°C} Ni(CO_4)$$

- In other cases, a reduction of a metal precursor in the presence of CO (or using CO as the reductant) is used

$$W(CH_3)_6 + 9CO \rightarrow W(CO)_6 + 3(CH_3)_2CO$$

APPLICATIONS OF ORGANOMETALLICS

Catalysis by organometallic compounds: The catalyst is defined as a substance, which alters the rate of reaction without undergoing any change in mass and composition. Generally, catalyst is used to speed up an otherwise slow reaction. Many important chemicals are produced commercially by reactions which are catalyzed by organometallic compounds and this is one of the important factor for studying organometallic chemistry. Some of the reactions catalyzed by organometallics are given below:

(1) **Alkene Hydrogenation** (Wilkinson's Catalysis) Although the reaction of hydrogen gas with ethylene is thermodynamically favourable, it does *not* take place at room temperature and pressure.

$$H_2C = CH_2 + H_2 \rightarrow H_3C - CH_3$$

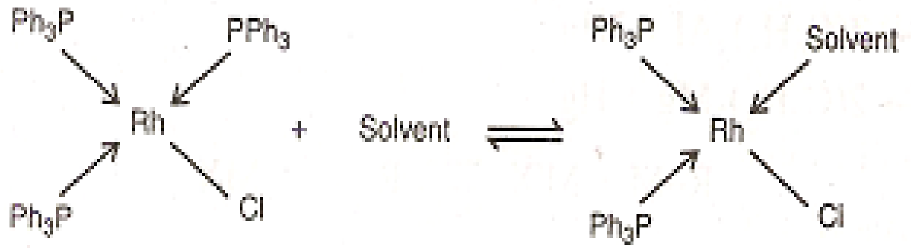
However, in the presence of the organometallic complex chlorotris (tri-phenylphosphine) rhodium(I), $(Ph_3P)_3$ RhCl, which is known as wilkinson's Catalyst, the reaction is very fact.

Wilkinson's catalyst is most widely used for homogeneous hydrogenation. This catalyst was discovered by Sir Geoffrey Wilkinson. It is a complex of a transition metal rhodium called tris (triphenylphosphine) chloro rhodium (I) having the formula $RhCl\ (PPh_3)_3$ where Ph stands for phenyl group.

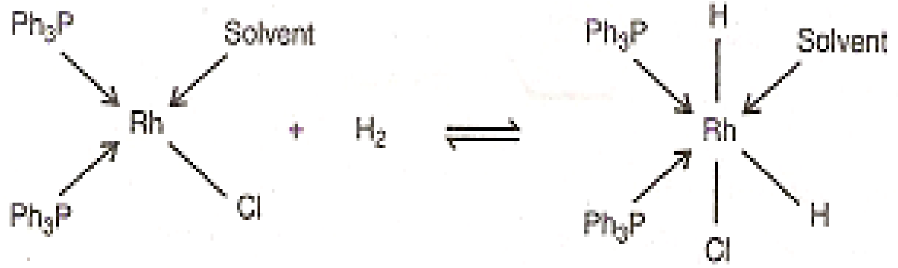
The phosphorus atom of phosphines has an unshared electron pair. It is through this electron pair, that triphenylphosphine is bonded to rhodium.

Rhodium can exhibit variable oxidation state of I and III and hence forms unstable intermediate with the reactant molecules. The mechanism can be explained as follows–

- It is believed that in solution the complex RhCl $(PPh_3)_3$ exchanges one of its PPh_3 for a solvent molecule, reversibly.

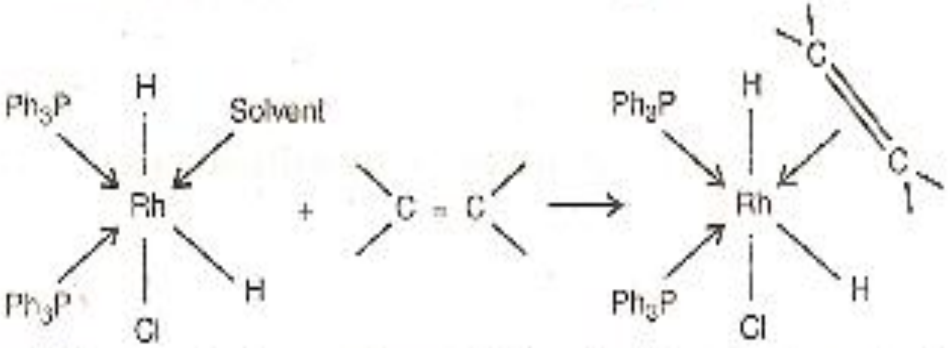


- The reactants, alkene and molecular hydrogen are brought close to the catalyst. The catalyst reacts with the hydrogen to form dihydrido complex RhH_2 Cl $(PPh_3)_2$. The H–H bond breaks and each hydrogen attach seperately to the rhodium.



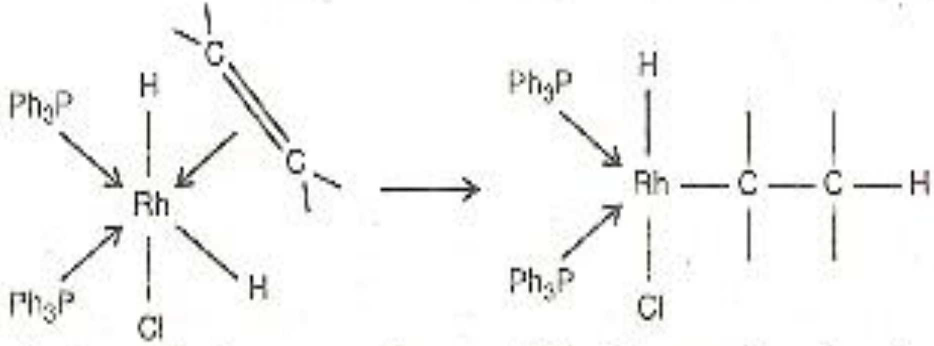
Thus in this step rhodium changes its oxidation state from (I) to (III).

- In the next step, alkene reacts with the catalyst by replacing a solvent molecule. The bond between the alkene and the metal atom rhodium is formed by the overlap of an empty orbital of the metal with the π cloud of alkene resulting in π complex.



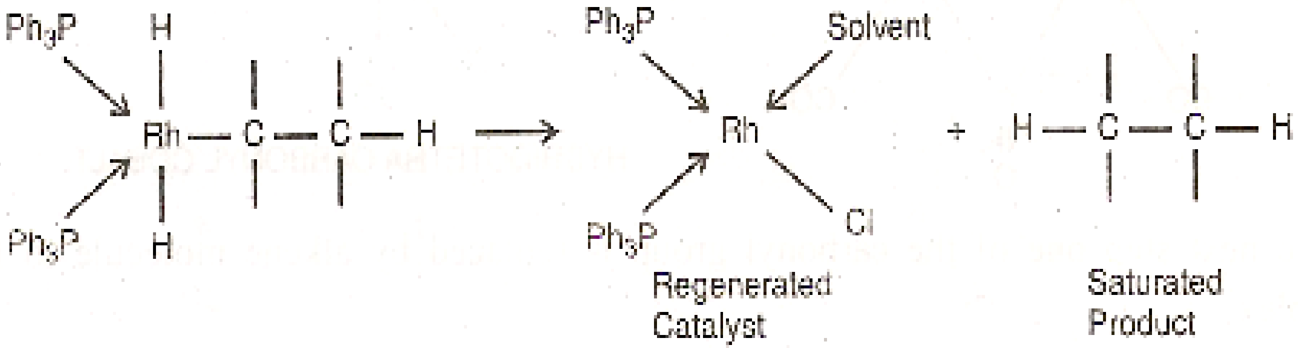
At this point both the reactants are bounded to rhodium and are in close proximity to react.

- A hydrogen atom migrates from the metal atom to one of the carbon atom of alkene whereas the other carbon attaches itself to the metal by a σ bond forming metal alkyl.



- The migration of alkene in between the metal hydrogen bond as in the above case is often referred to as insertion. Insertion can be defined as a process in which any atom or group is inserted between two other atoms initially bound together.

- Now, the second hydrogen migrates from the metal to carbon, which is still bonded to the metal atom, forming the hydrogenated product. The product detaches itself from the metal atom regenerating the catalyst. The rhodium atom regains its oxidation state of (I).



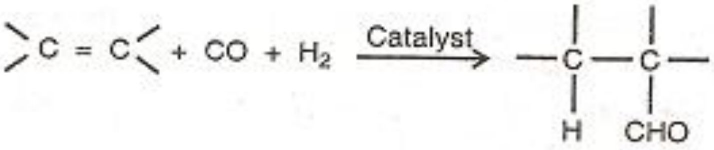
Evidence in Favour of the Above Mechanism

The most significant evidence comes from the fact that the above mentioned intermediates have been detected in solution and in some cases, isolated. Their structures have been well established by using spectroscopic techniques and have found to be in close agreement with the postulated structures.

Metal catalyst makes a significant contribution in industrial applications of catalysts. For example, the alcohols which form the backbone of aliphatic organic synthesis, can be obtained by the oxo process from alkenes, by using metal carbonyl, as catalyst.

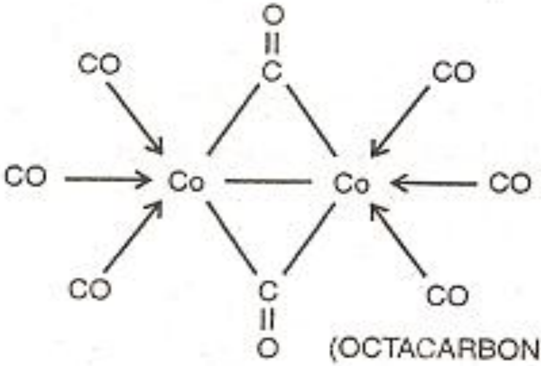
(2) Hydroformylation Oxo Process:

In presence of a metal catalyst, alkenes react with carbon monoxide and hydrogen to yield aldehydes. The aldehydes are again catalytically reduced to form alcohols.



An aldehyde

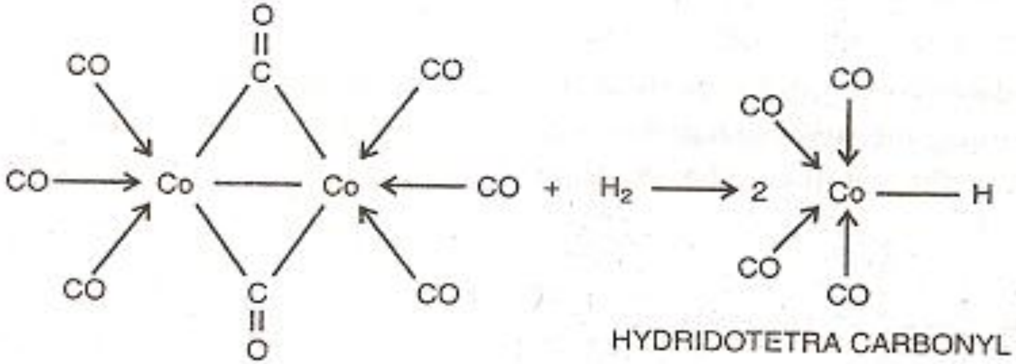
The catalyst employed in the above process is octacarbonyldicobalt, $Co_2(CO)_8$, **This process is the first industrial application of catalysis by a transition metal complex.**



(OCTACARBONYLDICOBALT)

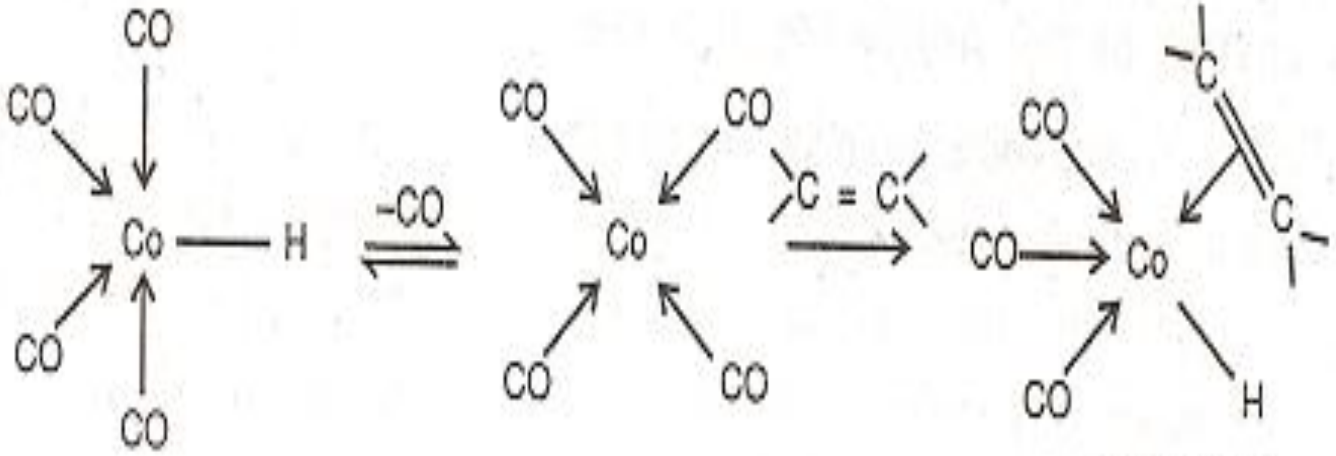
The mechanism of oxo process is believed to be as follows:

- The octacarbonyldicobalt reacts with hydrogen to form the hydrido complex $CoH(CO)_4$ which is the active catalyst. This catalyst is soluble in hydrocarbons, so oxo process can be grouped under homogeneous catalysis.



HYDRIDOTETRA CARBONYL COBALT

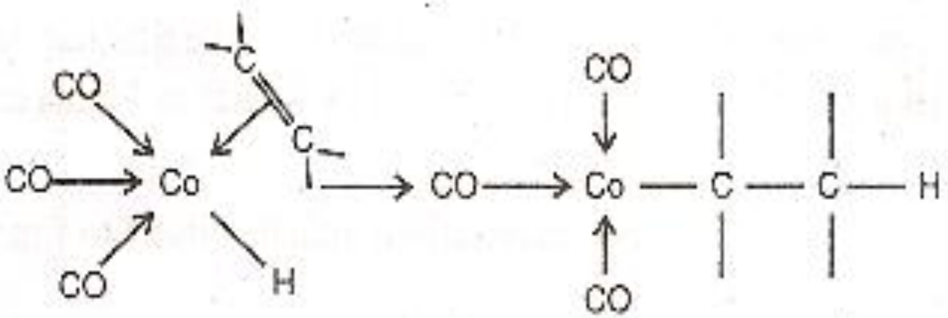
- In the next step one of the carbonyl group is replaced by alkene molecule to form a π-complex.



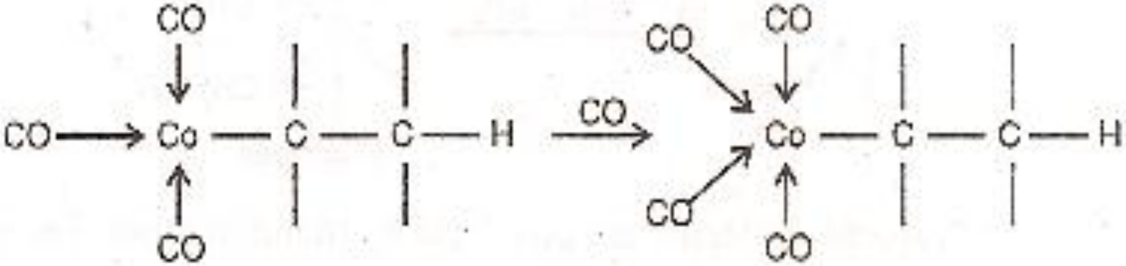
π Complex

Thus all the three reactants, viz CO, H_2 and alkene are in close proximity.

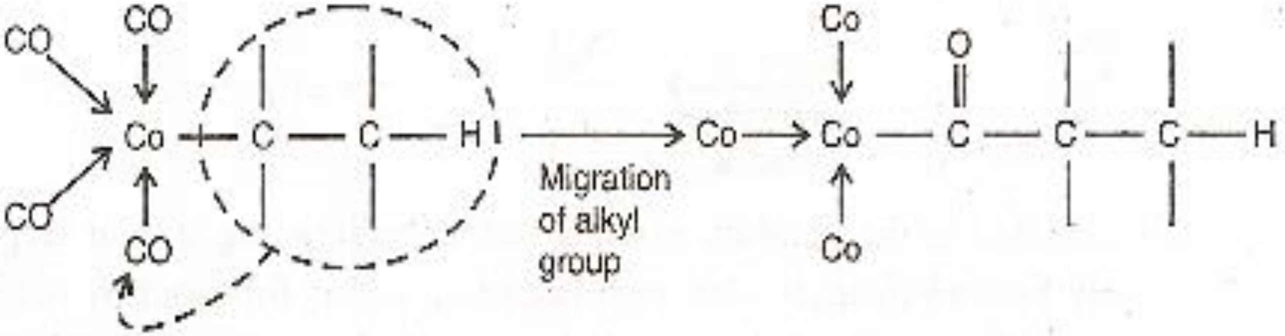
- The hydrogen migrates from Co to one of the carbon atom of alkene and the other carbon atom of alkene attaches itself to cobalt forming metal alkyl. In other words the alkene is inserted inbetween cobalt and hydrogen atom.



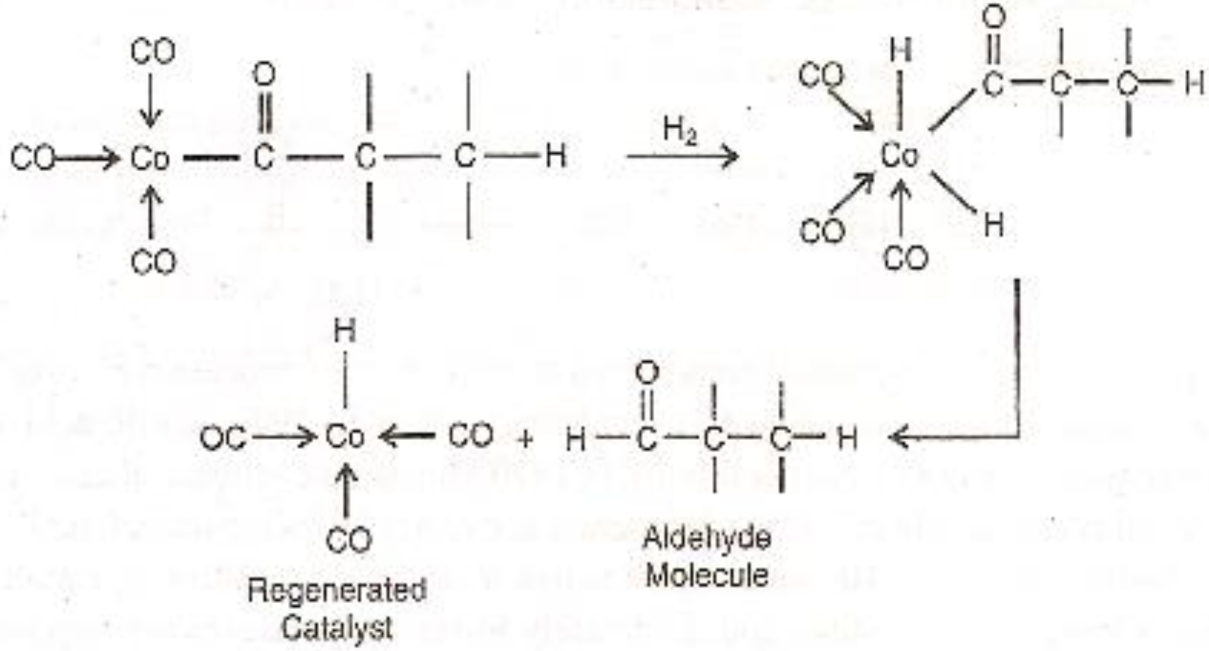
One molecule of CO is further added to the metal alkyl,



- The newly formed alkyl group then migrates to the carbonyl group, forming carbon-carbon bond.



- At this stage hydrogen is absorbed to form dihydrido complex. One of these hydrogens migrates to carbon of the C = O group and aldehyde molecule is formed which detaches itself from the metal complex, which becomes ready for fresh action.

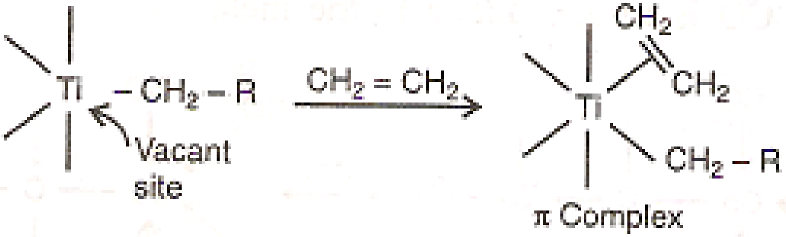


(3) Polymerization

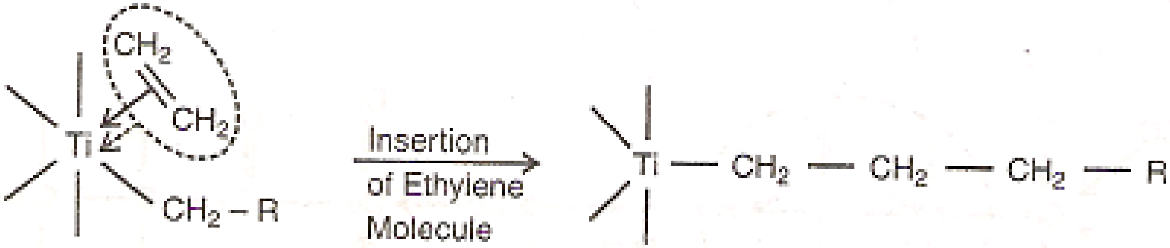
The catalyst which has revolutionised the field of polymer chemistry also belongs to metal salts i.e. the **Ziegler Natta catalyst**. This catalyst was discovered by Karl Ziegler and Giulio Natta who jointly received Nobel prize in 1963 for developing this catalyst. This catalyst exhibits remarkable power to control organic reactions.

Ziegler Natta catalyst comprises of a transition metal salt like titanium trichloride in combination with a metal alkyl like triethyl aluminium. These two react to form a complex having an ethyl group in situ.

The alkene which has to undergo polymerisation, attaches itself to titanium by π bond forming π complex.



Now the alkyl and the alkene molecule are both held by titanium atom. The ethylene unit inserts itself between the titanium and the alkyl group.

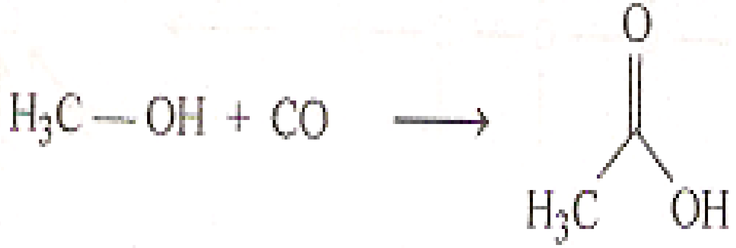


Thus, the chain attached to the titanium extends further undergoing similar steps. The bonding site which held ethylene becomes vacant with each insertion, and is followed by the formation of π complex with the next monomer unit. Thus the alkyl group keeps on growing with each cycle. The chain terminates finally by the insertion of hydrogen atom between titanium atom and the alkyl chain.

Ziegler Natta catalyst thus gives linear polymer molecules a great degree of stereochemical control.

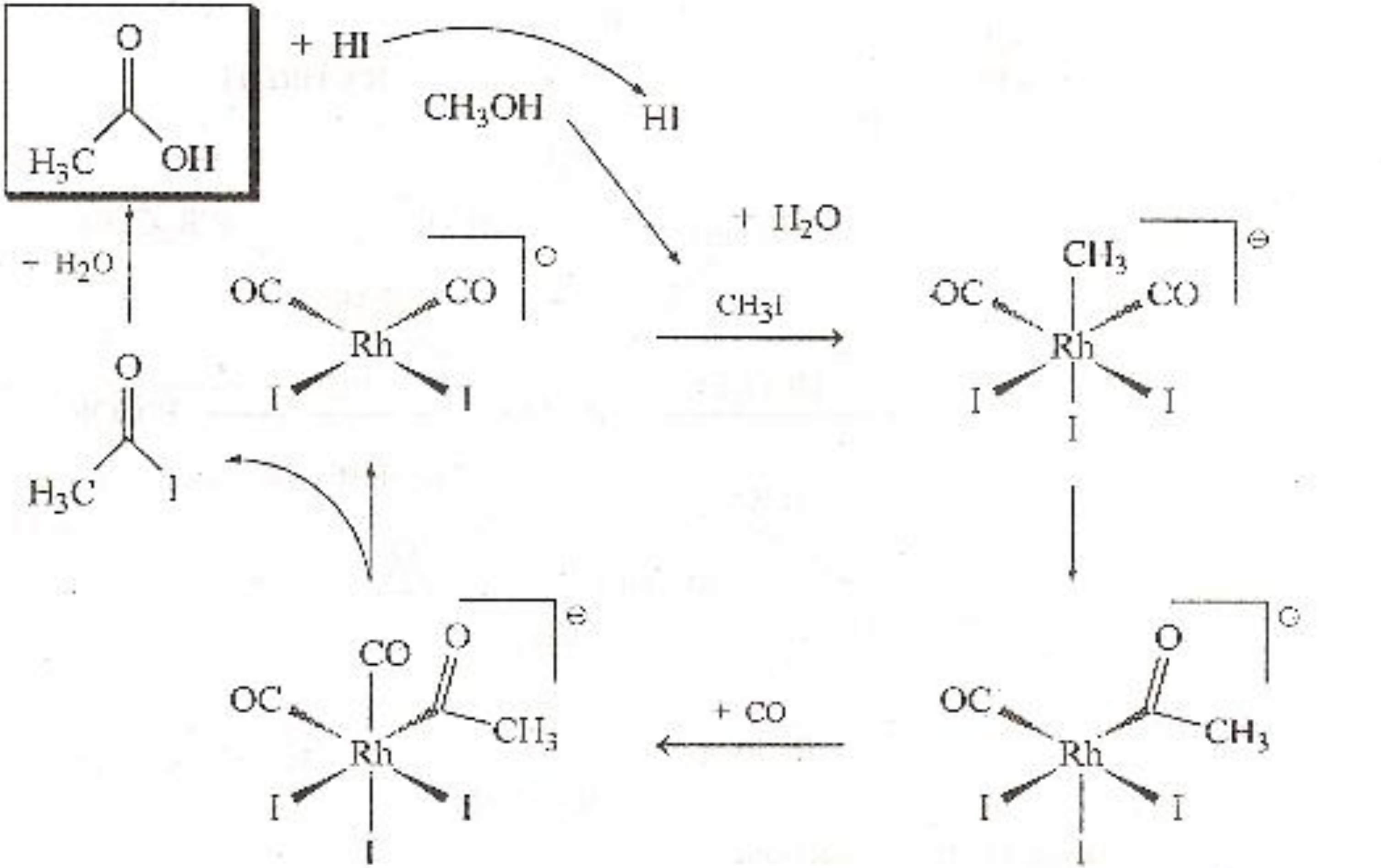
(4) Monsanto Acetic Acid Process (Manufacture of Acetic Acid):

The carbonylation of methanol produces acetic acid:



This is the second largest industrial homogeneous carbonlyation process with over 7 billion pounds of acetic acid produced each year using this technology. Prior to 1970, acetic acid was made using cobalt catalysts requiring rather severe conditions. In 1970 Monsanto commercialized a rhodiumcarbonyl iodide catalyst that is commonly called the *Mansanto Acetic Acid Process* (developed in the late 60's by James Roth. Rhodium is 10^3 to 10^4 times more active than the corresponding cobalt catalyst, which means that much lower CO pressures and moderately lower temperatures are required. Most importantly, the rhodium catlyst gives extremely high selectivities to acetic acid:

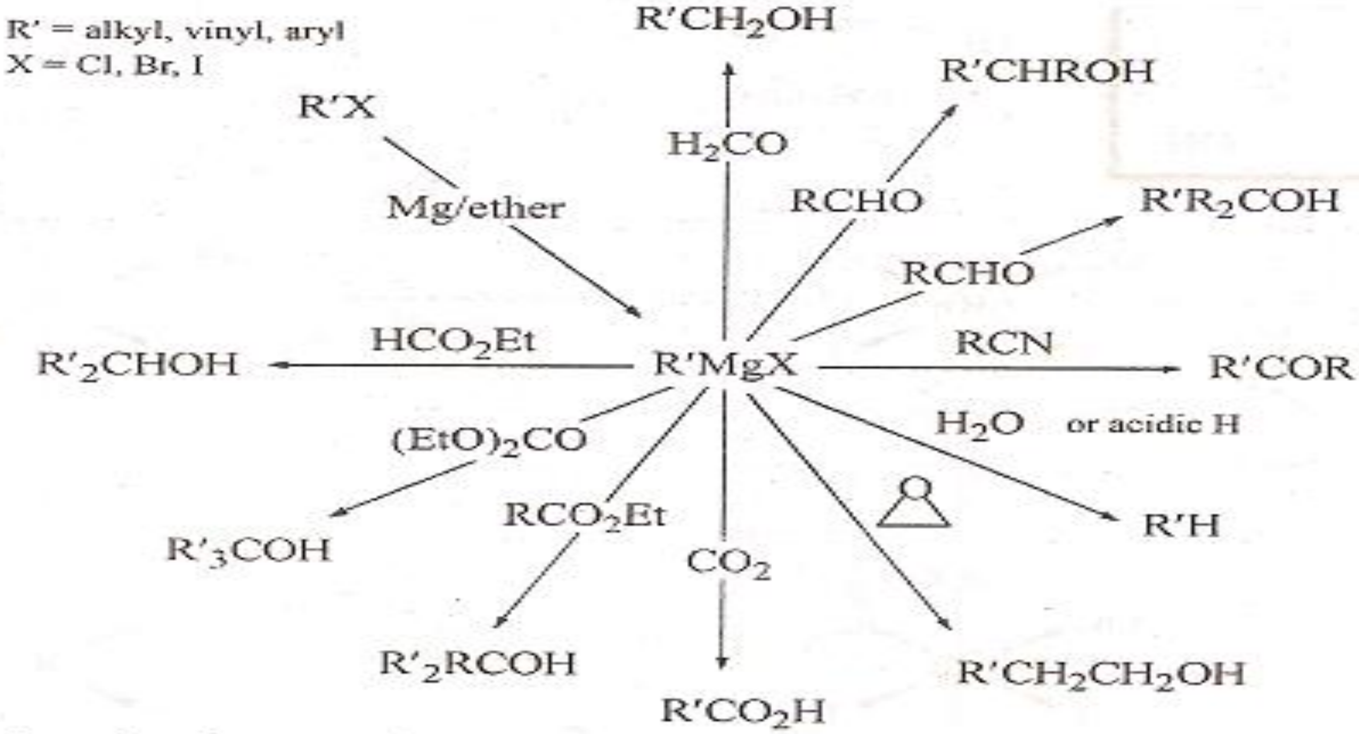
The mechanism has been extensively studied by Forster and coworkers at Monsanto and is shown below



This catalytic reaction is an unusual dual cycle system involving HI as one catalyst and $[RhI_2(CO)_2]$ as the transition metal component. HI catalyzes the conversion of MeOH to MeI and H_2O at the beginning of the Rh-catalyzed carbonylation reaction, followed by regeneration of HI at the end of the Rh-cycle by hydrolysis of the acyl-iodide. The Rh catalyst carbonylates the MeI to produce the acyl-iodide.

(5) Synthesis of organic compounds using Grignad Reactions:

Insert Organometallic compounds are very useful as catalysts or reagents in the **synthesis** of organic compounds, such as pharmaceutical products. One of the major advantages of organometallic compounds, as compared with organic or inorganic compounds, is their high reactivity. Reactions that cannot be carried out with the usual types of organic reagent can sometimes be easily carried out using one of a wide variety of available organometallics



Typical work-up for these reactions:

1. Dilute aqueous acid or
2. Aqueous ammonium chloride