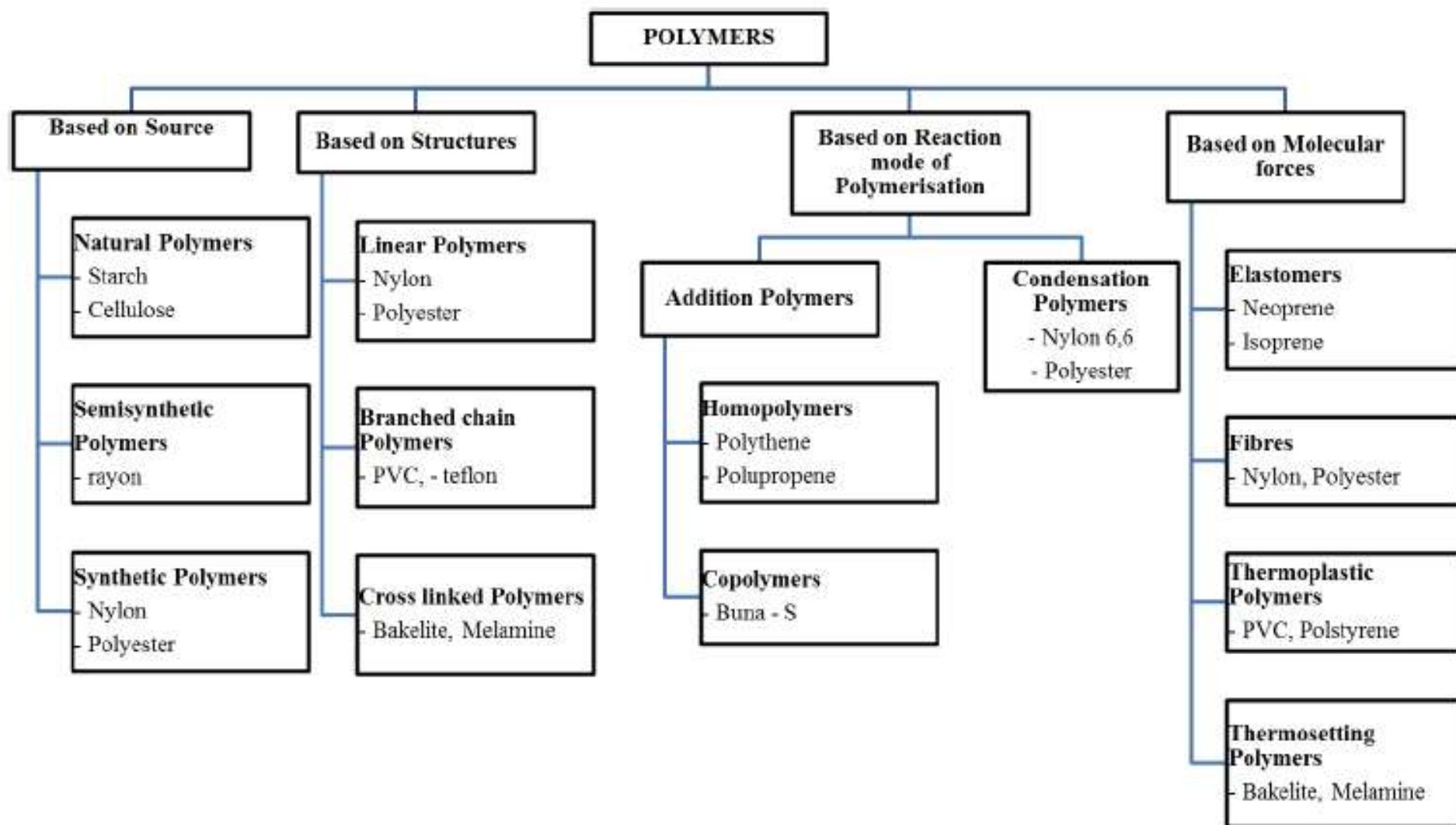


# Classification



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Presented by

Course Instructor: Dr Bhar Saha  
Dept. of Science & Mathematics  
IITG, Guwahati

## **Macromolecules**

A **macromolecule** is a very large molecule, such as polysaccharides, proteins and nucleic acids, commonly created by polymerization of smaller subunits (monomers). They are typically composed of thousands or more atoms. They can be natural like rubber, starch, glycogen, proteins & silk; or man-made like plastics & PVC.

Synthetic macromolecular compounds are characterized as:

1. **Elastomers:** possessing elasticity characteristic of rubber
2. **Fibers:** thin, threadlike and having tensile strength of fiber similar to cotton, wool
3. **Plastics:** molded or extruded as sheets/pipes
  - a. **Thermoplastic**
  - b. **Thermosetting**

Macromolecules are basically polymers formed by a process called polymerization: linking together many small molecules / subunits called monomers to form polymers.

There are two types of polymerization:

1. Chain reaction polymerization
2. Step reaction polymerization

They can also be classified as addition polymerization (addition of monomers)  
& condensation polymerization (loss of simple molecules like water)

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## Differences between step-growth polymerization and chain-growth polymerization

### Step growth

- Growth throughout matrix
- Rapid loss of monomer early in the reaction
- Similar steps repeated throughout reaction process
- Average molecular weight increases slowly at low conversion and high extents of reaction are required to obtain high chain length.
- Ends remain active (no termination)
- No initiator necessary

### Chain growth

- Growth by addition of monomer only at one end of chain
- Some monomer remains even at long reaction times
- Different steps operate at different stages of mechanism.
- Molar mass of backbone chain increases rapidly at early stage and remains approximately the same throughout the polymerization
- Chains not active after termination
- Initiator required

## Chain polymerization

### Radical polym.

The C=C is prefer the Polym. by R.P. and also can be used in the steric hindrance of the substituent



radical



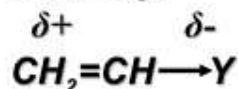
cationic



anionic

### Anionic polym.

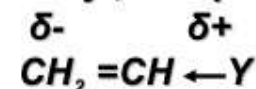
Electron withdrawing substituent decreasing the electron density on the double bond and facilitate the attack of anionic species such as cyano and carbonyl



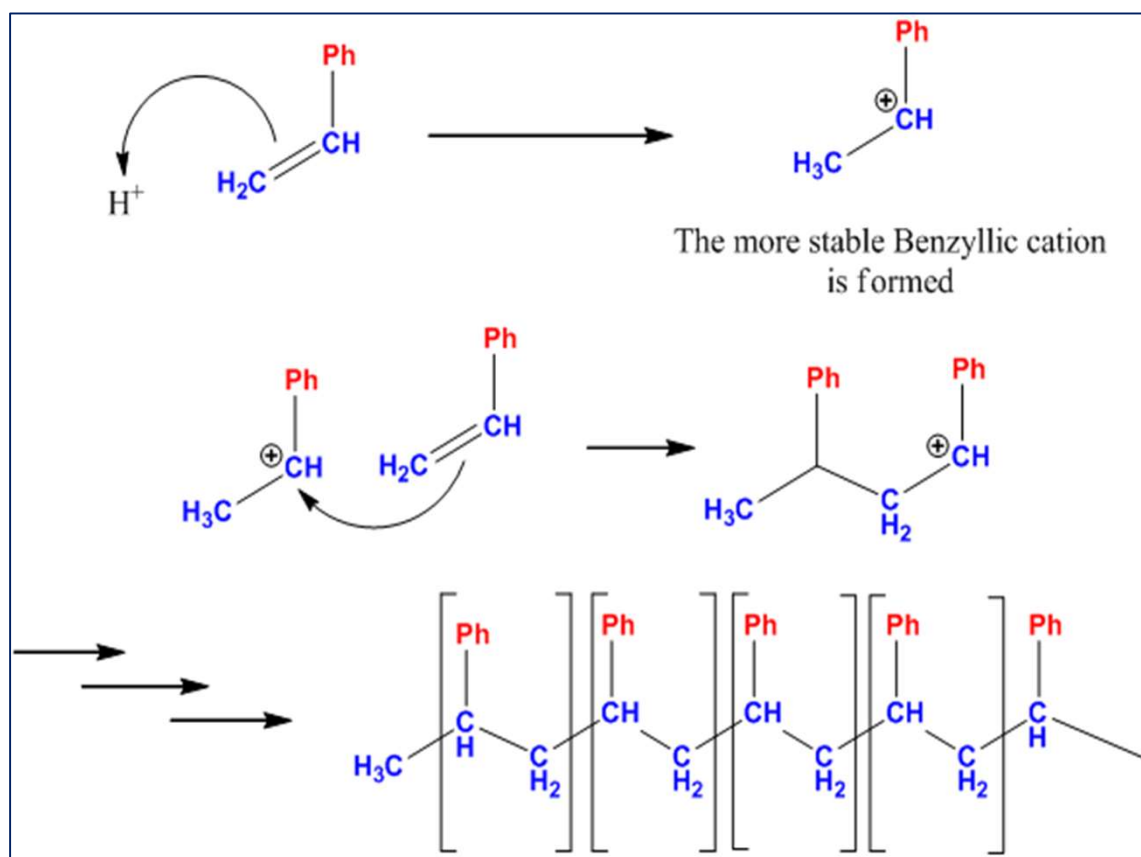
### Ionic polym.

#### Cationic polym.

Electron donating substituent increasing the electron density on the double bond and facilitate the attack of cationic species such as alkoxy, alkyl, alkenyl, and phenyl



**Chain reaction polymerization:** A series of reactions each of which consumes a reactive particle and produces another; each individual reaction depending upon the previous one. The reactive particles can be free radicals, cations, or anions. Example : polymerization of styrene, in which the chain-carrying particle is an ion, adding to a monomer to form a bigger chain.



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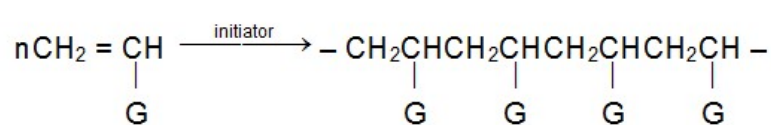
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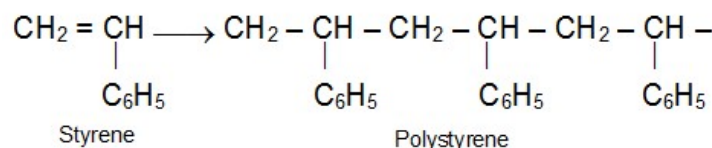
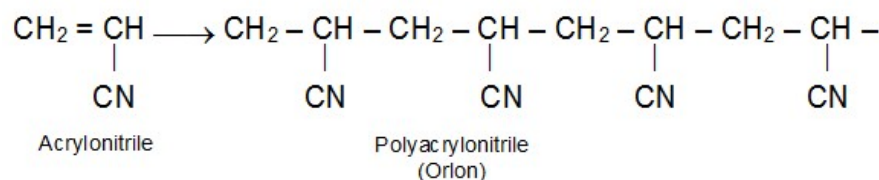
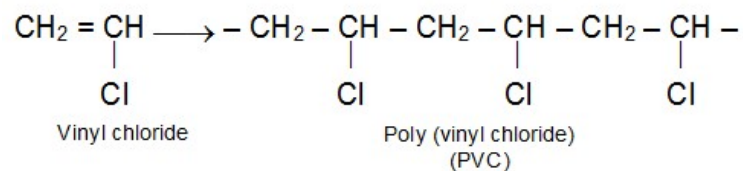
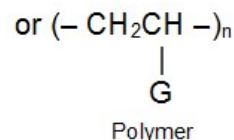
Free-radical vinyl polymerization:

*Free radicals are generated typically in the presence of small amounts of an initiator, such as a peroxide.*

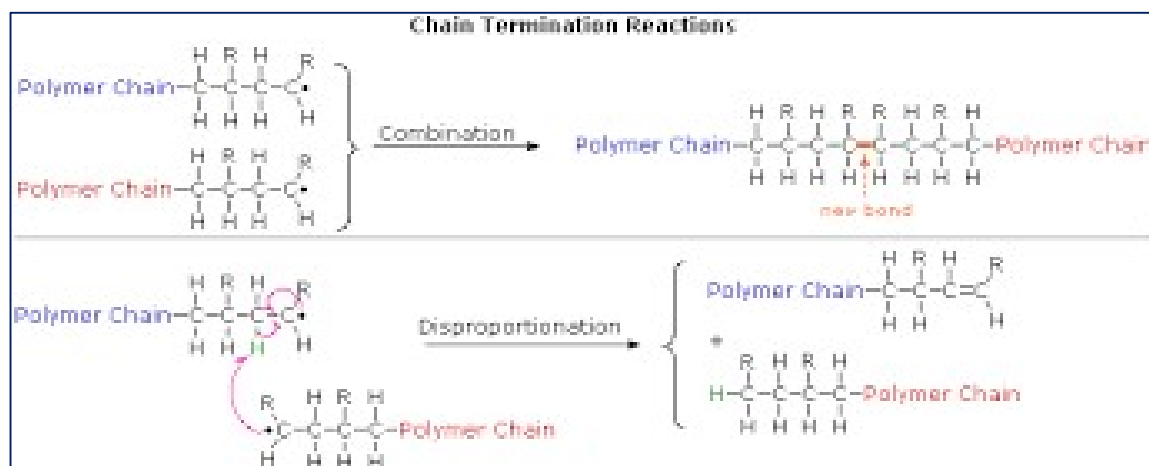
*Reaction takes place at the doubly-bonded carbons of the vinyl groups and is called vinyl polymerization.*



Vinyl monomer



Eventually, the reaction chain is terminated by steps that consume but do not form free radicals: **combination** or **disproportionation** of two free radicals.



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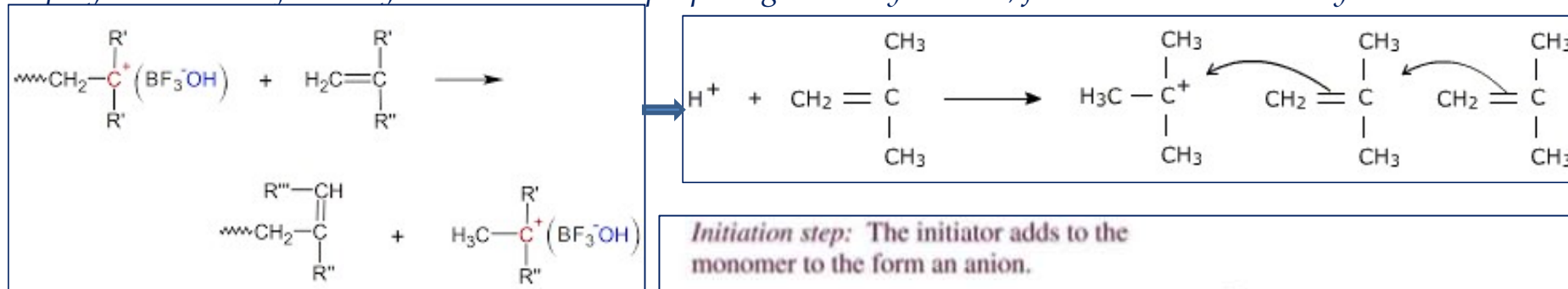
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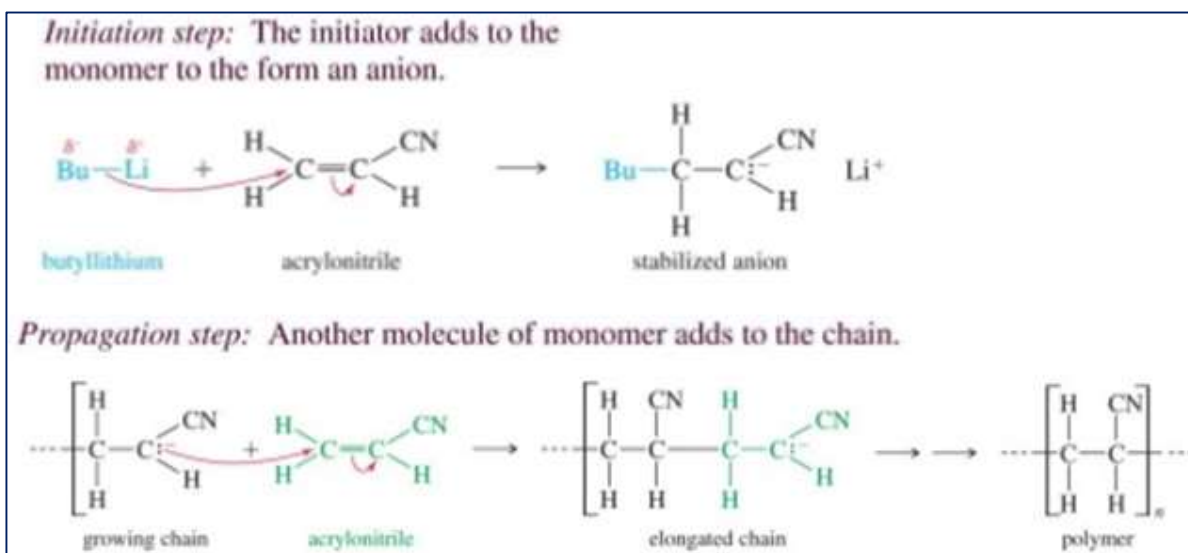
**Ionic polymerization:** Chain reaction polymerization can take place with ions instead of free radicals as the chain-carrying particles. It is of two types:

**Cationic polymerization:** Cations are the chain-carrying particles, initiated by acids like  $H_2SO_4$ ,  $AlCl_3$  or  $BF_3$ .

Copolymerization of isobutylene with little isopropene gives butyl rubber, for automobile industry.



**Anionic polymerization:** Anions are the chain-carrying particles, initiated by bases like  $LiNH_2$ ,  $KNH_2$  or organometallic compounds such as *n*-butyllithium (*n*-BuLi).

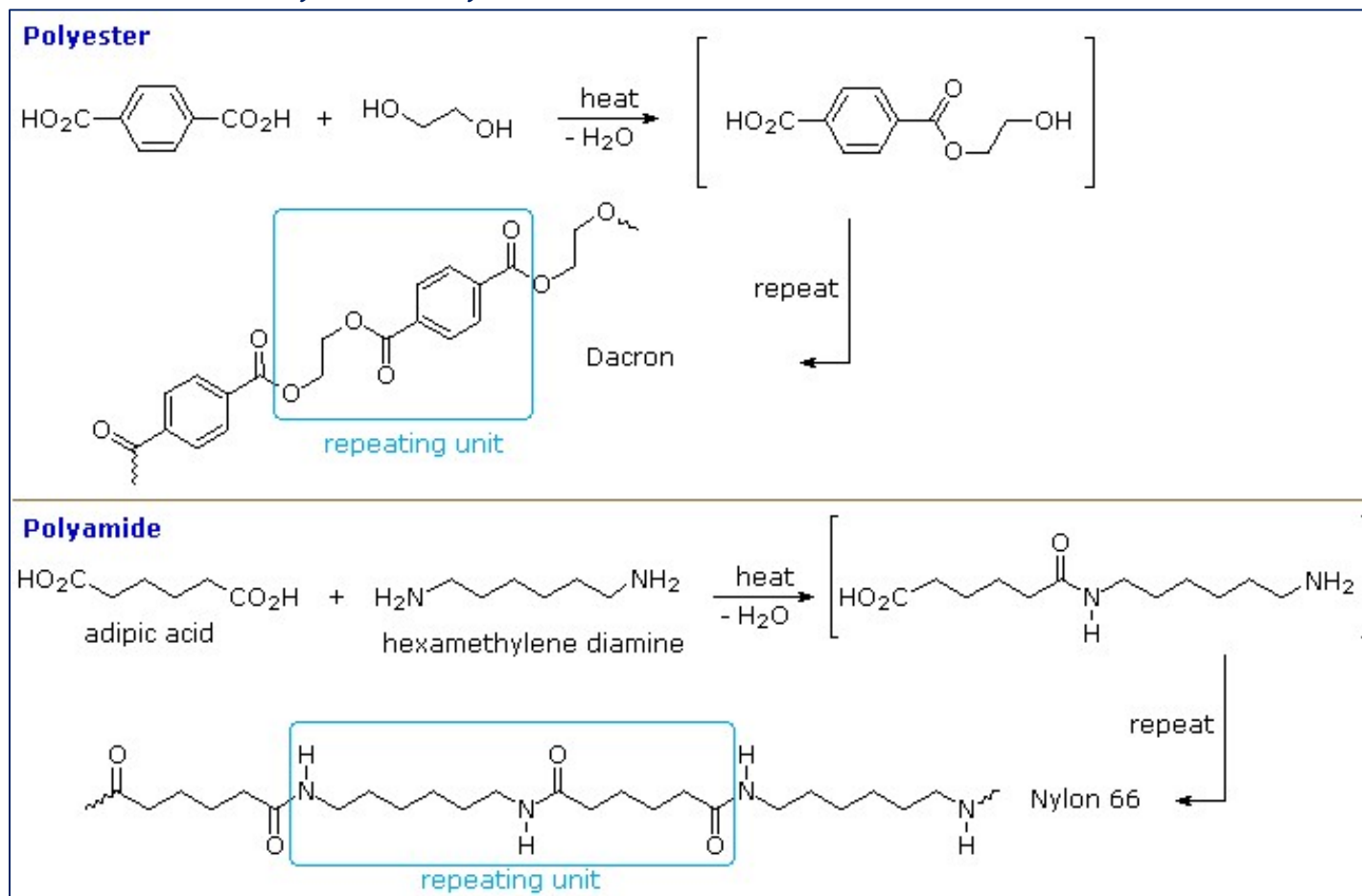


When conditions are carefully controlled, there are no termination steps or at least none that happen very fast. The reaction stops when all the monomer is consumed, but the reaction mixture contains what has been named “**living polymer**” molecules. When additional monomers like either styrene or butadiene are fed into it, they continue to grow. However, by addition of a compound that reacts with carbanions, like water can terminate the growth. The generation of living polymers is of immense practical importance; it provides the best route to block copolymers, and permits the introduction of a variety of terminal groups.

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**Step reaction polymerization:** A series of reactions each of which is essentially independent of the preceding one; a polymer is formed because the monomer happens to undergo reaction at more than one functional group. For example, a glycol reacts with a dicarboxylic acid to form an ester; but each moiety of the simple ester still contains a group that can react to generate another ester linkage and hence a larger molecule, which itself can react further.



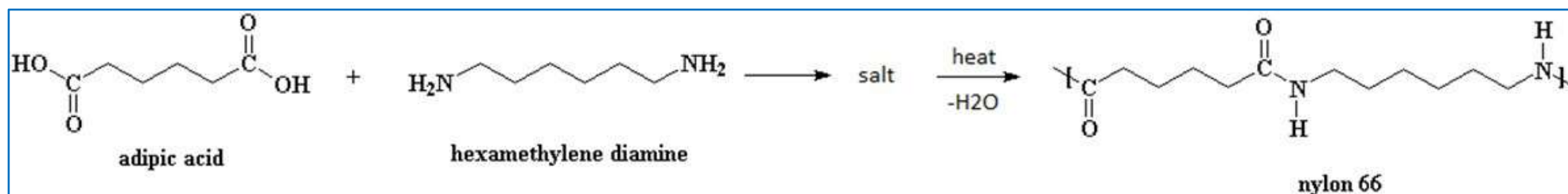
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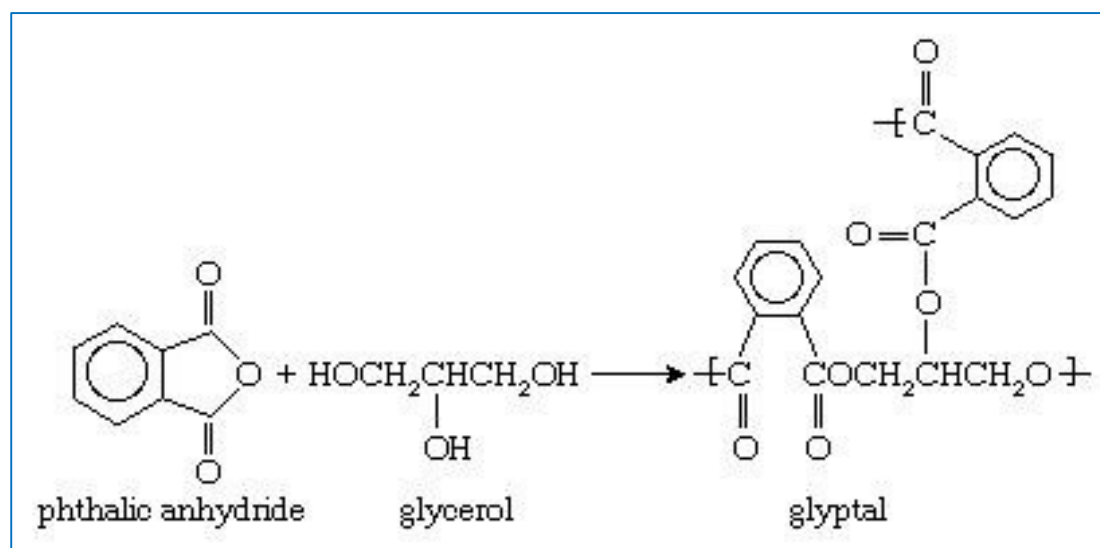
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**Step-reaction polymerization**: does not depend on chain-carrying free radicals or ions. Instead, the steps are essentially independent of each other; they involve more than one functional group in a monomer molecule. If each monomer molecule contains just two functional groups, growth can occur in only two directions, and a linear polymer is obtained, as in nylon 66 or Dacron.



But if reaction can occur at more than two positions in the monomer, a highly cross-linked space network polymer, as in Glyptal, an alkyd resin/ a polyester, is formed.



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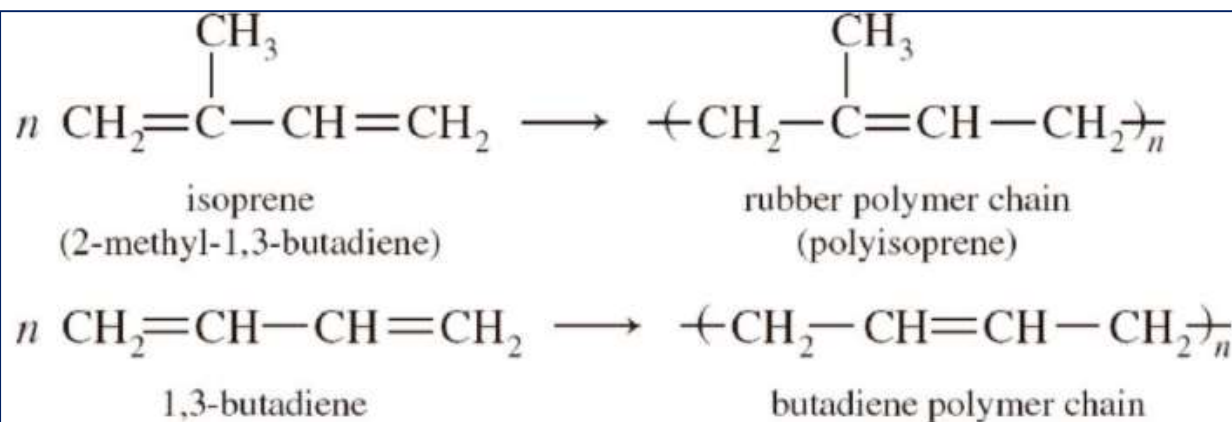
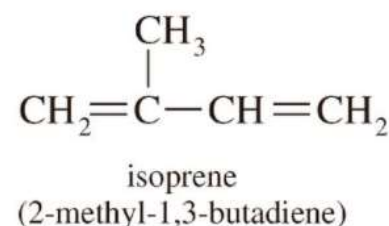
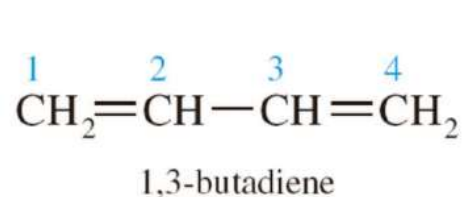
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## BASED ON ORIGIN OF SOURCE

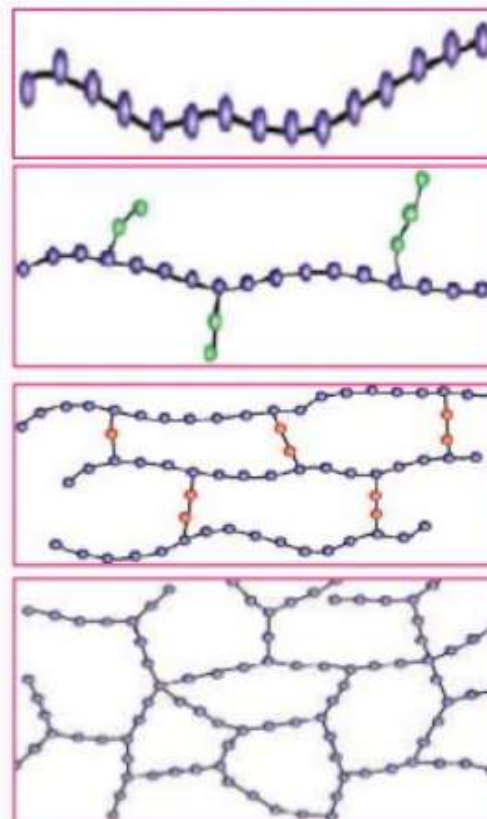
- **Natural Polymer :-** Polymers which are isolated from natural materials are called as Natural Polymers . E.g. : Cotton , silk , wool , rubber
- **Synthetic Polymer :-** Polymers which are synthesized from low molecular weight compounds are called as Synthetic Polymers . E.g. : Polyethylene , nylon , terylene.
- **Semisynthetic Polymers :-** These polymers are mostly derived from naturally occurring polymers by chemical modification . E.g. : Rayon

Natural rubber is a polymer of **isoprene** (2-methyl-1,3-butadiene) which is also a diene. Many synthetic elastomers or rubberlike materials are polymers of isoprene and of butadiene.



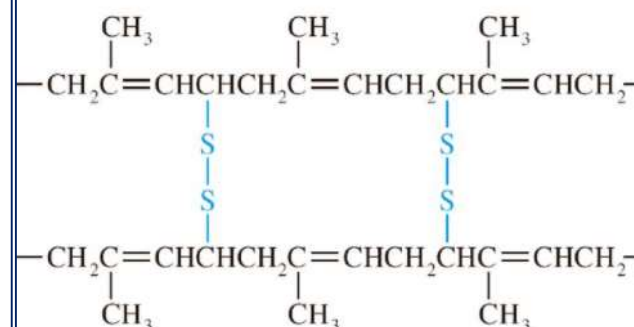
## BASED ON STRUCTURE

- **Linear Polymer** : Molecules form long chains without branches.
- **Branched Polymer** : Molecules having branch points that connect 3 or more segments .
- **Cross-Linked Polymer** : It includes interconnections between chains .
- **Network Polymer** : A cross linked polymer that includes numerous interconnections between chains .



The presence of double bonds at intervals along the chains of rubber and rubberlike synthetic polymers makes **vulcanization** possible.

Vulcanization is the cross-linking of polymer chains with sulfur atoms.



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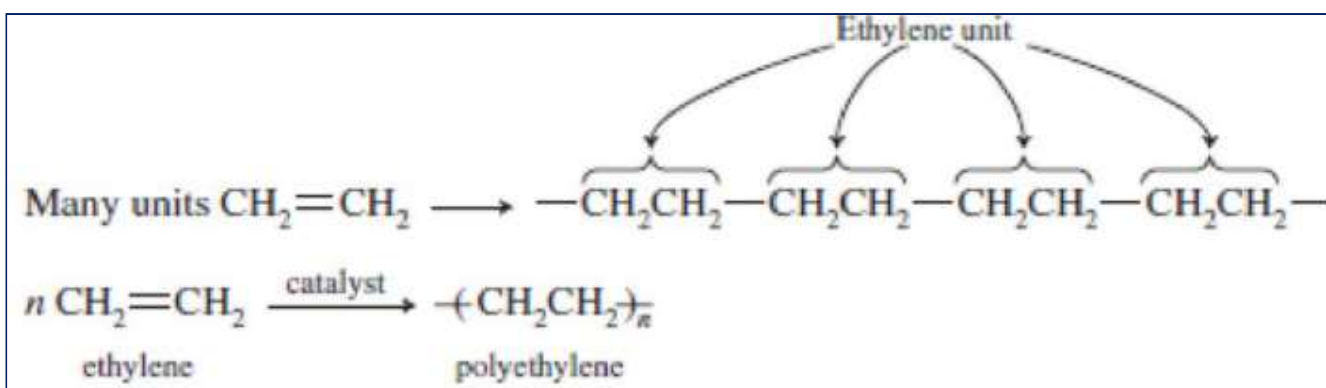
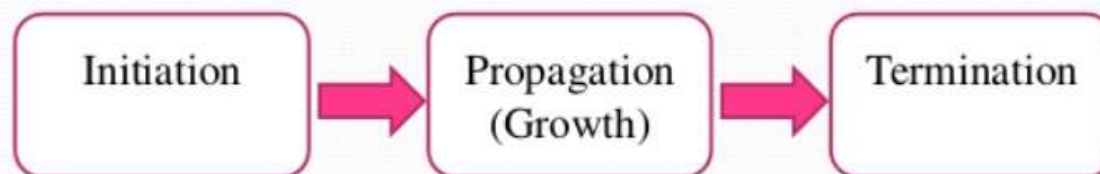
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## Based on reaction: Addition

An **addition polymer** is a polymer that is produced by successive *addition reactions*. Polyethylene is an example of an addition polymer.

- Additional Polymerization :
  - ✓ Same kind of monomers are straight forwardly added
  - ✓ It is rapid chain reaction having chemically activated mers
  - ✓ Each reaction sets up the condition for another to proceed
  - ✓ It consists of 3 stages :



Ethylene can form low-density polyethylene (LDPE) molecules in the 20,000–40,000 molar mass range and high-density polyethylene (HDPE) in the 100,000s molar-mass range.

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## Addition: Free Radical

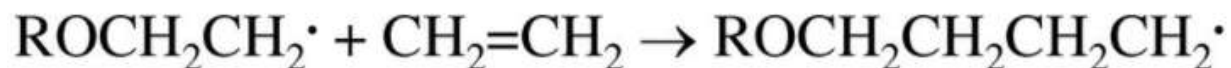
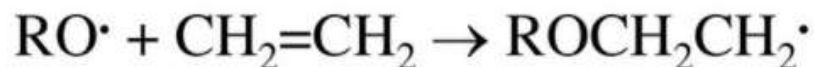
Free radical polymerization consist of three steps:

- Free-radical formation
- Propagation of the polymeric chain
- Termination

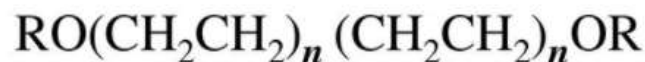
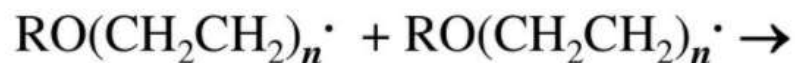
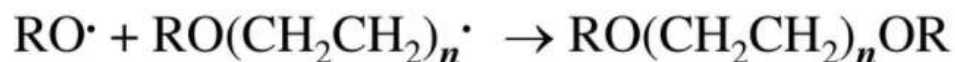
Step 1: Free-radical formation.



Step 2: Propagation of Polymeric chain



Step 3: Termination



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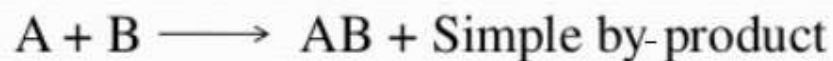
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## Based on reaction: Condensation

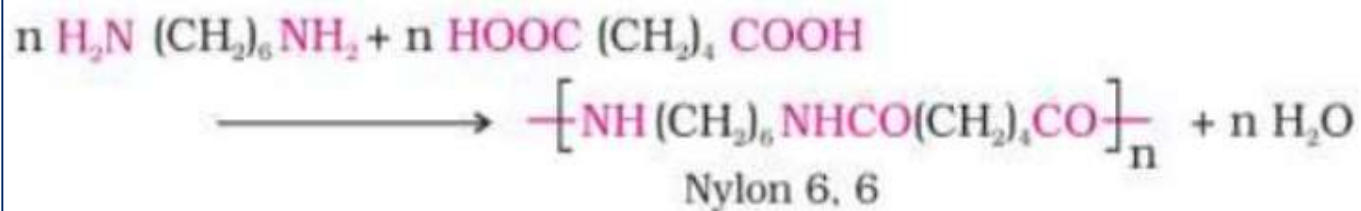
A **condensation polymer** is a polymer that is formed when monomers combine with the elimination of water or some other simple substance. This is a *condensation reaction*. Nylon is a condensation polymer.

- Condensation Polymerization :

- ✓ It involves a polymerization reaction between two monomers with the expulsion of a simple by product



- ✓ It involves individual chemical reaction between reactive mer
- ✓ By product is formed and condensed out
- ✓ This reaction is slower than additional polymerization
- ✓ Need reactive functional groups



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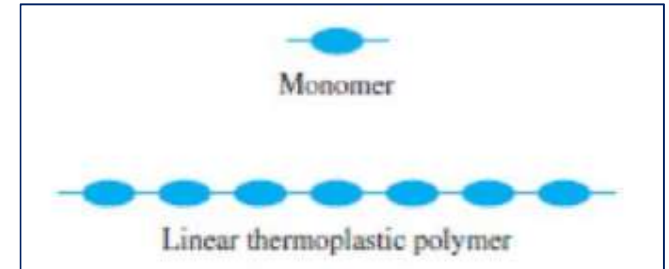
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# Thermoplastic and Thermosetting Polymers

Polymers can also be classified based on their thermal properties. There are **thermoplastic polymers** and **thermosetting polymers**

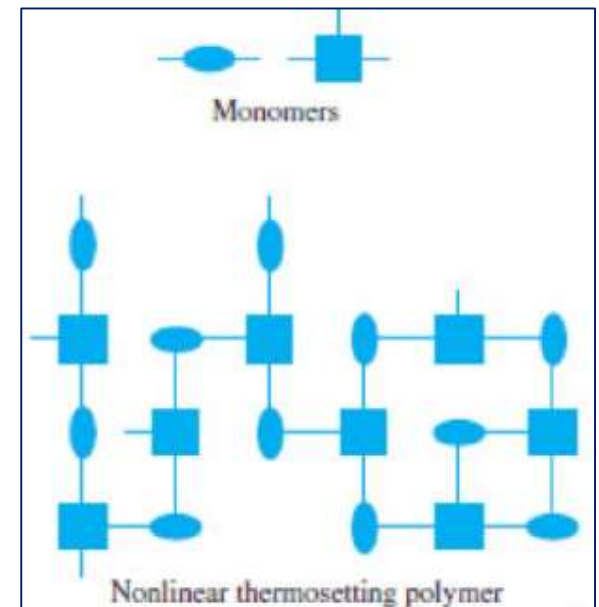
Thermoplastic polymers are formed when monomer molecules join end to end in a linear chain with little or no cross-linking between the chains.



Thermoplastic polymers soften when reheated. Polyethylene and polystyrene are examples.

Thermosetting polymers are macromolecules in which the polymeric chains are cross linked to form a network structure.

Thermosetting polymers are infusible solids and do not soften when reheated. Phenolics (polymers made from phenol) are an examples.



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## CHARACTERISTICS OF POLYMER

- Low density
- Low coefficient of friction
- Good corrosion resistance
- Good mould ability
- Poor tensile strength
- Low mechanical properties
- Poor temperature resistance

The double bonds in isoprene and butadiene polymers allow for *cis-trans* isomers.

Recall that *cis-trans* isomers are molecules that differ only in the spatial orientation of their atoms.

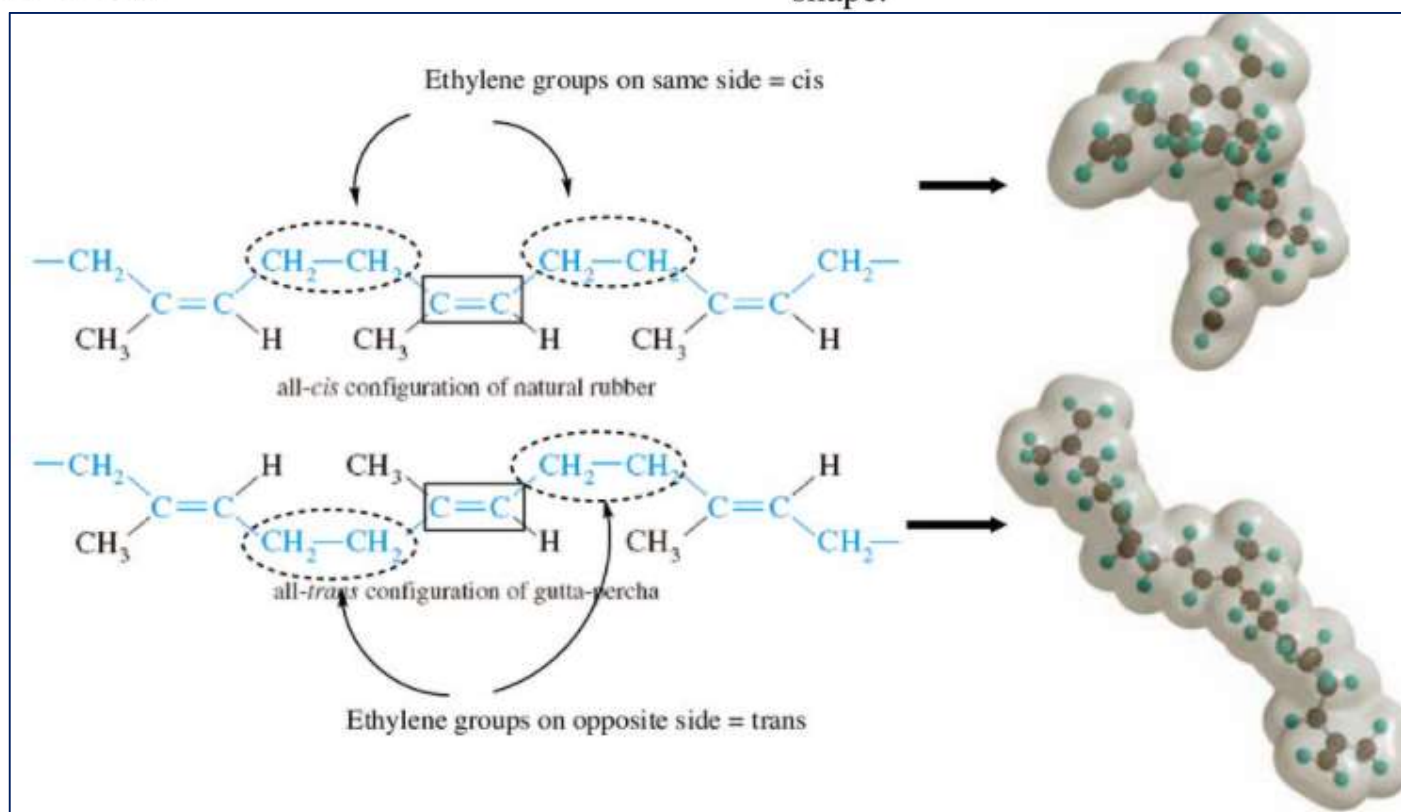
For example an isoprene polymer can have all-*cis*, all-*trans*, or a random distribution of *cis* and *trans* configurations about the double bonds.

Natural rubber is *cis*-polyisoprene with an all-*cis* configuration about the carbon-carbon double bonds.

The *cis* isomers give rubber molecules a “kinked” shape.

Gutta-percha, also obtained from plants, is a *trans*-polyisoprene with an all-*trans* configuration.

The *trans* isomers give gutta-percha molecules a linear shape.



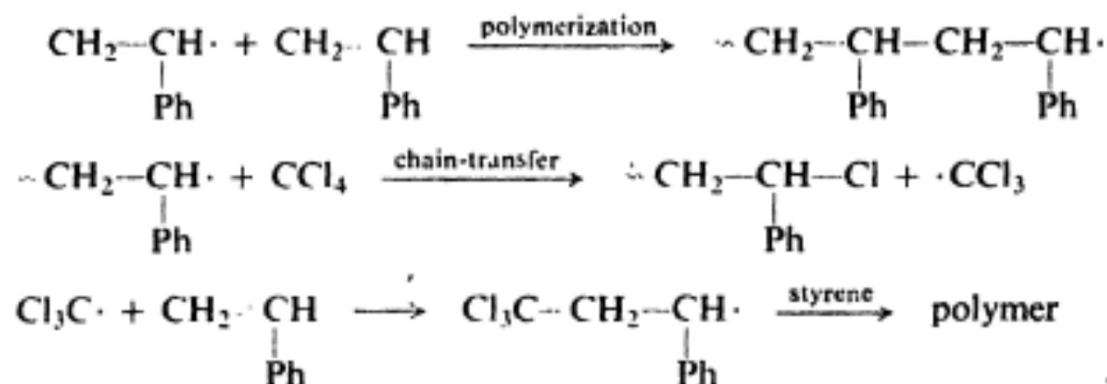
The *cis* natural rubber is a soft, elastic material, whereas the *trans*-gutta-percha is a tough, nonelastic, hornlike substance.

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Added compounds can modify the polymerization process drastically. Example, in presence of carbon tetrachloride, styrene undergoes polymerization at the same rate as it would have in its absence, but the polystyrene obtained has a lower average molecular weight; also, it contains small amounts of chlorine. This is an example of **chain-transfer**, where the termination of one polymerization chain occurs with the simultaneous initiation of another.



An added compound that reacts with the growing free radical to generate a new free radical which is not reactive enough to add to monomer i.e. a chain reaction is terminated but no new reaction is initiated, is an **inhibitor**. Amines, phenols, and quinones act as inhibitors.

● **Inhibitor**

When Y take part in chain opening reaction, polymer moves from one site to another. In this case, hydroquinone etc. are used as inhibitor.

● **Retarder**

When the reactivity of Y is low, controlling the MW of the monomer including these two materials, Mercaptan etc. are used as Retarder.

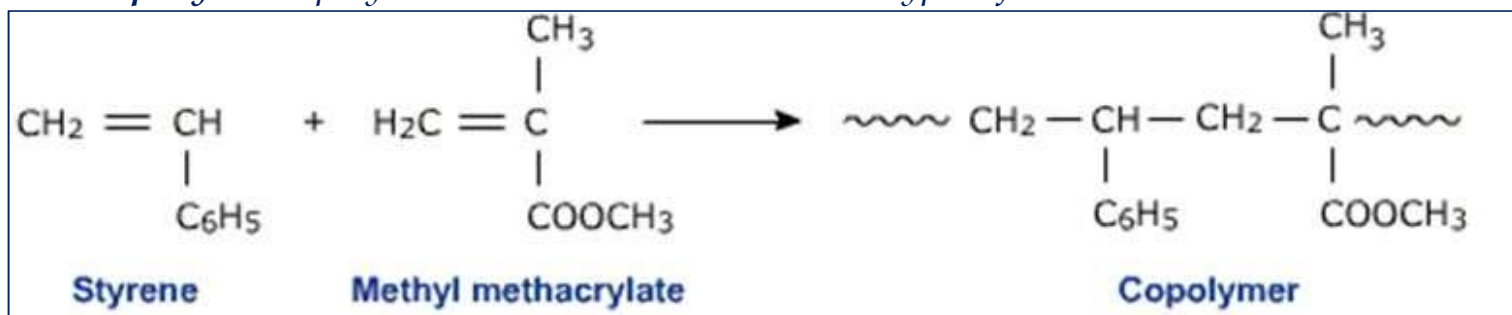
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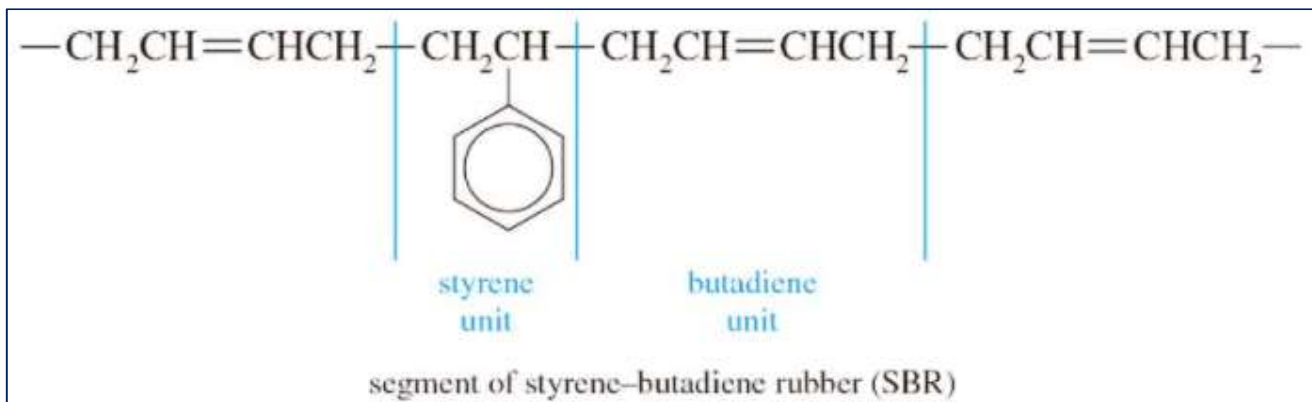
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# Copolymerization

Polymerisation of a single monomeric compound produces a **homopolymer**, a polymer comprising identical units. If a mixture of two or more monomers is allowed to undergo polymerization, there is obtained a **copolymer** a polymer that contains two or more types of monomeric units in the same molecule.



Styrene, polymerized alone gives a good insulator that is used for radios, television sets, and automobiles. Copolymerization with butadiene (30%) adds toughness; with acrylonitrile (20-30%) increases resistance to impact and to hydrocarbons; with maleic anhydride yields a material that, on hydrolysis, is water-soluble, and is used as a dispersant and sizing agent. The copolymer in which butadiene predominates (75% butadiene, 25% styrene) is an elastomer.



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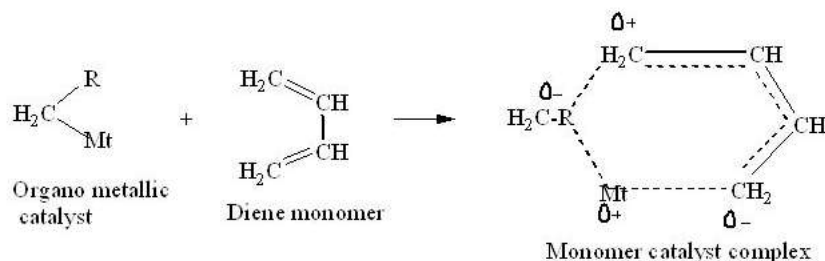
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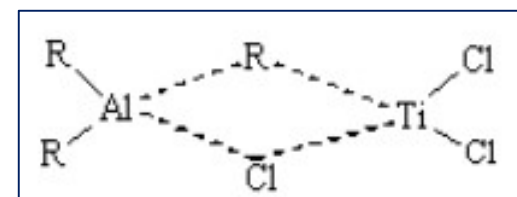


# Coordination polymerization

- Polymerization reactions especially of olefins and dienes catalysed by organometallic compounds is known as coordination polymerization.
- The first step in polymerization is the formation of a monomer – catalyst complex between the organometallic compound and the monomer.



When catalyst and co-catalyst components are mixed, there occurs a chemisorption of the aluminium alkyl (electro positive in nature) on the Titanium Chloride solid surface, resulting in the formation of an electron deficient bridge complex as



- Here Mt indicates metals like Ti, Mo, Cr, Ni.
- In the formation of monomer – catalyst complex, a coordination bond is involved in between a carbon atom of the monomer and the metal of the catalyst. Hence the polymerization effected by such catalyst systems is called coordination polymerization.
- It comprises of two components as against single component organo metallic component and other consisting of halides of IV-VIII group elements having transition valences.
- The co-catalysts are organo-metallic compound such as alkyls, aryls and hydrides of I-IV metals.
- The commonly used catalysts and co-catalysts are Titanium chlorides (both tri and tetrachlorides) and triethyl aluminium i.e.  $\text{Al}(\text{C}_2\text{H}_5)_3$ , diethyl aluminium chloride  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ .

The monomer is attracted towards Ti-C bond (C from alkyl group R) in the active centre. When it forms a  $\pi$ -complex with Titanium ion. The rate of reaction is influenced by the electrons present in the active centre.

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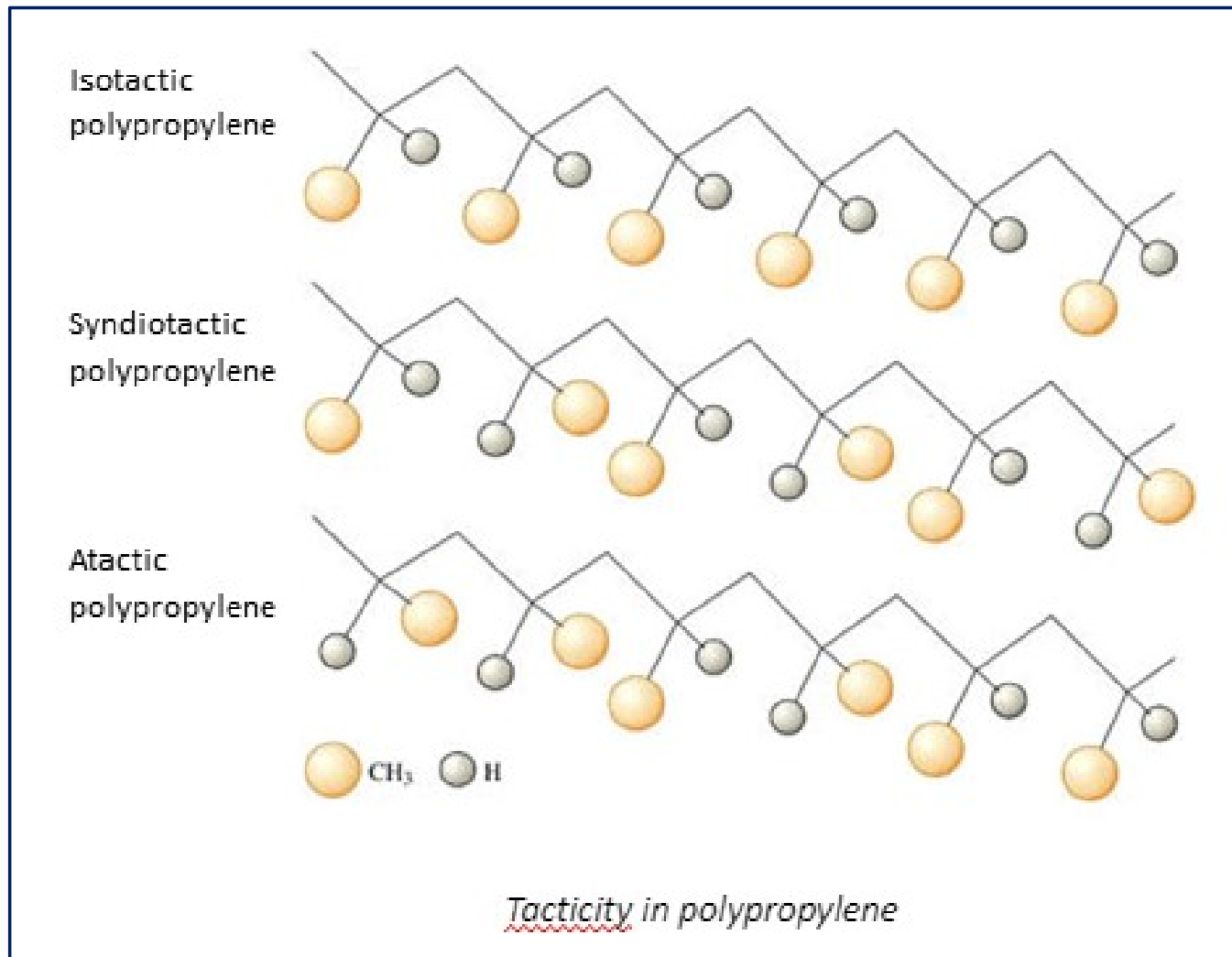
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**Coordination polymerization:** is a form of addition polymerization where the monomer adds to a growing polymer via an organometallic active centre. Addition polymerization which takes place in the presence of heterogeneous **Ziegler-Natta** catalysts gives linear, stereo-regular polymers such as high density polyethylene. Ziegler-Natta catalysts are complexes of transition metal halides with organometallic compounds : typically, triethylaluminum-titanium trichloride. These react to form the active catalyst: a titanium complex holding an ethyl group. Polymerization with Ziegler-Natta catalysts has two important advantages over free-radical polymerization: (a) it gives **linear** polymer molecules; and (b) it permits **stereochemical control**. Coordination catalysts also permit stereochemical control about the carbon-carbon double bond.

Coordination type polymers are also **stereoregular** and can be **atactic** (methyl groups distributed at random), **isotactic** (methyl groups on one side of an extended chain), or **syndiotactic** (with methyl groups alternating regularly from side to side) . This tacticity is responsible for crystallinity in amorphous (powder-like) polymers. From these differences in polymerization type, the variation between low-density polyethylene (LDPE) and high-density polyethylene (HDPE) is introduced.



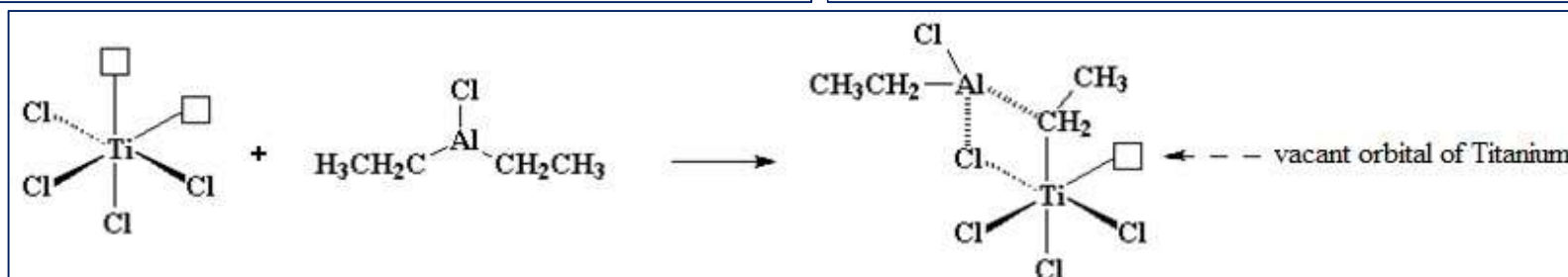
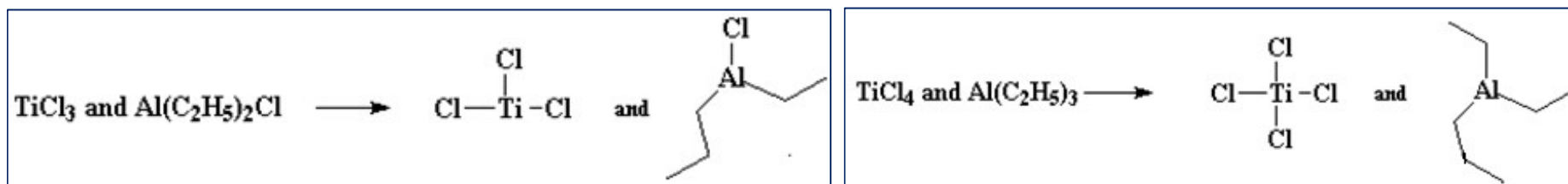
- Atactic PP is an amorphous some what rubbery in nature.
- Commercial polymer is usually 90-95% isotactic and rest is blocks of atactic and syndiotactic structures.

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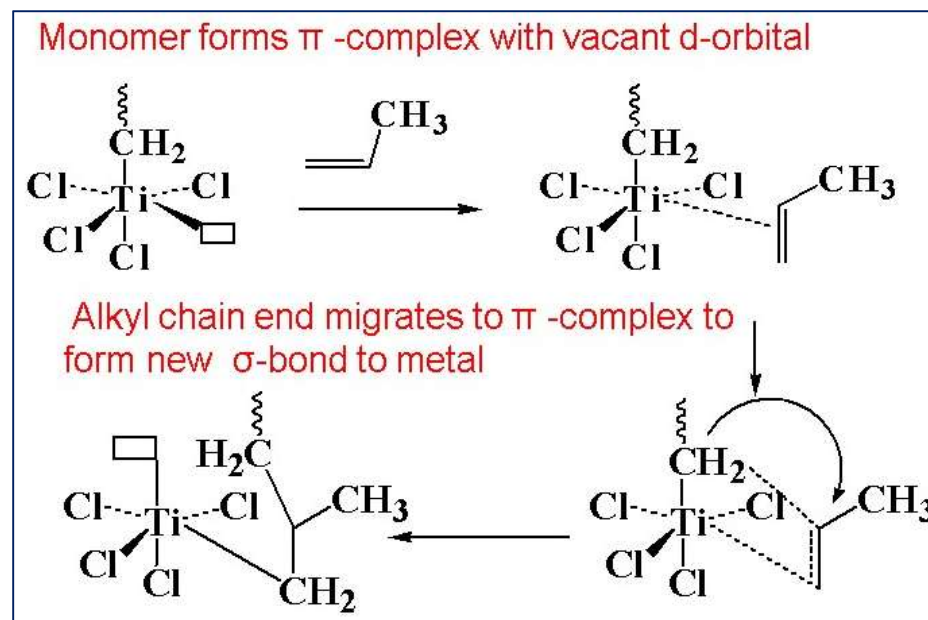
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Given below are two sets of Ziegler-Natta catalyst/co-catalyst systems, each having 4 Cl atoms.



There are two electrons in the  $\pi$ -system of a carbon-carbon double bond of a monomer like propylene. Those electrons can be used to fill the empty orbital of titanium.



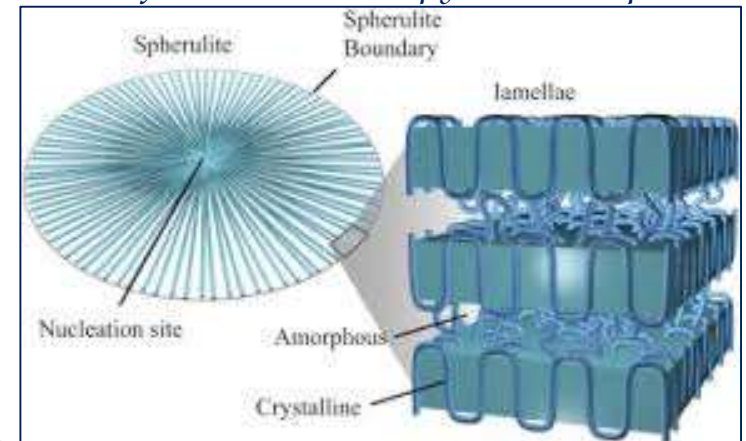
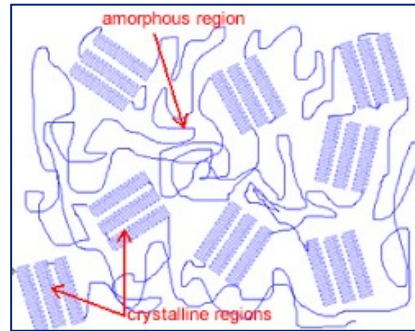
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## Structure and properties of macromolecules:

**Crystallinity**- a high polymer does not exist entirely in crystalline form. As solidification begins, the viscosity of the material rises and the polymer molecules find it difficult to move and arrange their long chains in the regular pattern needed for crystal formation. Chains become entangled; a change in shape of a chain must involve rotation about single bonds, and this becomes difficult because of hindrance to the swinging about of pendant groups. Polymers, then, form solids made up of regions of crystallinity, called **crystallites**, embedded in amorphous material. The degree of crystallinity of a polymer is the extent to which it is composed of crystallites. A huge aggregate of crystallites is called a **spherulite**. The regularity and close fittingness of the molecules in a crystal allow strong intermolecular forces like hydrogen bonding, dipole- dipole attractions, van der Waals forces which result in a favourable enthalpy. Fibers require great tensile (pulling) strength in the direction of the fiber.



An elastomer can be stretched to eight times its original length and regain its original shape yet again. In an elastomer, entropy beats enthalpy as intermolecular forces are weak. The long chains of an elastomer are connected by occasional cross-linking. Polymers are basically linear and branched or space-network polymers (resins).

Linear polymers are more crystalline, like polyenes. On heating, they soften and become **thermoplastic** polymers. Space-network polymers on heating, become harder, and become **thermosetting** polymers.

Course Code: SC202

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*Sample Problem:*

Draw a three-unit portion of polypropylene.

