Classification of Polymers

- Polymer contains repeating units
- Macromolecules contain no repeating units, examples are DNA, proteins, etc
- A polymer is a macromolecule……………………but a macromolecule may not be a polymer

- Many + Parts
- The repeating structural units are derived from some simple and reactive molecules known as **monomers** and are linked to each other by covalent bonds
- The word, polymer, implies that polymers are constructed from pieces (monomers) that can be easily connected into long chains (polymer)
- This process of formation of polymers from respective monomers is called **polymerization**
- The transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon 6, 6 are examples of two different types of polymerisation reactions

- The **functionality of a monomer** is the number of sites it has for bonding to other monomers under the given conditions of the polymerization reaction
- Thus, a bifunctional monomer, i.e., monomer with functionality two, can link to two other molecules under suitable conditions
- A polyfunctional monomer is one that can react with more than two molecules under the conditions of the polymerization reactions

- The number of repeating units (n) in the chain so formed is called the '***degree of polymerization***' (DP = n)
- Polymers with a high degree of polymerization are called '***high polymers***' and those with low degree of polymerization are called ***oligopolymers*** (short chain polymers or oligomers)
- Polymers do not exhibit strength for $n < 30$ and that the optimum strength of most of the polymers is obtained at n around 600
- The useful range of n is from 200 to 2000

- The following are some of the common classifications of polymers:

- [1] by Source
- [2] by Backbone of the chain
- [3] by Structure
- [4] by Compostion
- [5] by Mode of Polymerization
- [6] by Molecular force

Classification Based on Source:

- [1] ***Natural Polymers***: These polymers are found in plants and animals. Examples are proteins, cellulose, starch, resins and rubber
- [2] ***Semi-synthetic Polymers***: Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the usual examples of this sub category
- [3] ***Synthetic Polymers***: A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna - S) are examples of man-made polymers

➢ Classification Based on Backbone of the polymer chain:

- ***Organic and Inorganic Polymers:*** A polymer whose backbone chain is essentially made of carbon atoms is termed as organic polymer
- The atoms attached to the side valencies of the backbone carbon atoms are, however, usually those of hydrogen, oxygen, nitrogen, etc.
- The majority of synthetic polymers are organic
- On the other hand, generally chain backbone contains no carbon atom is called ***inorganic polymers***
- Glass and silicone rubber are examples of it

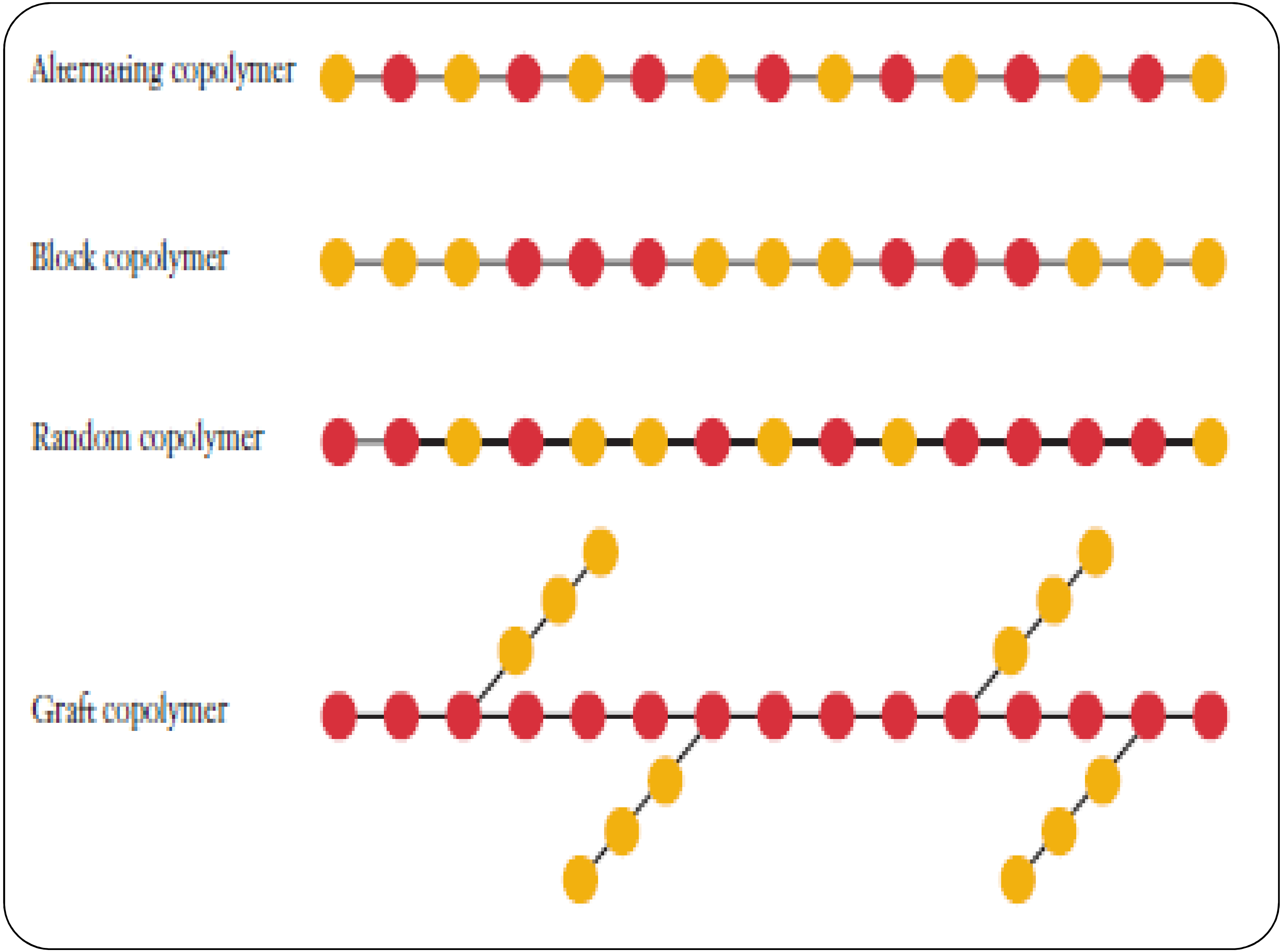
➢ Classification Based on Structure of Polymers:

- [1] ***Linear Polymers***: These polymers consist of long and straight chains. The examples are high density polythene, PVC, etc. Linear polymers are commonly relatively soft, often rubbery substances, and often likely to soften (or melt) on heating and to dissolve in certain solvent
- [2] ***Branched Polymers***: These polymers contain linear chains having some branches, *e.g.*, low density polythene
- [3] ***Cross-linked Polymers***: These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains, e.g. vulcanized rubber, urea-formaldehyde resins, etc. Cross linked polymers are hard and do not melt, soften or dissolve in most cases

➢ Classification Based on Composition of Polymers:

- [1] ***Homopolymer:*** A polymer resulting from the polymerization of a single monomer; a polymer consisting substantially of a single type of repeating unit
- [2] ***Copolymer:*** When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer
- **Copolymerization:** A ***heteropolymer*** or ***copolymer*** is a polymer derived from two (or more) monomeric species, as opposed to a homopolymer where only one monomer is used
- Copolymerization refers to methods used to chemically synthesize a copolymer. Commercially relevant copolymers include ABS plastic, SBR, Nitrile rubber, styrene-acrylonitrile, styrene-isoprene-styrene (SIS) and ethylene-vinyl acetate

- In an ***alternating copolymer***, the two monomers are arranged in an alternating fashion
- In a ***random copolymer***, the two monomers may following any order
- In a ***block copolymer***, all of one type of monomers are grouped together, and all of the other are grouped together
- In ***graft copolymer***, a block copolymer can be thought of as two homopolymers joined together at the ends: branched copolymers with one kind of monomers in their main chain and another kind of monomers in their side chains



Alternating copolymer
Block copolymer
Random copolymer
Graft copolymer

➢ Classification Based on Mode of Polymerisation:

- Two sub groups; (a) ***Addition*** and (b) ***Condensation Polymers***.
- **Addition Polymers:** The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, *e.g.*, the formation of polythene from ethene and polypropene from propene
- However, the addition polymers formed by the polymerisation of a single monomeric species are known as homopolymer, *e.g.*, polythene
- The polymers made by addition polymerisation from two different monomers are termed as copolymers, *e.g.*, Buna-S, Buna-N, etc

- **Condensation Polymers:** The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units
- In these polymerisation reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place
- The examples are terylene (dacron), nylon 6, 6, nylon 6, etc
- For e.g., nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid
- It is also possible, with three functional groups (or two different monomers at least one of which is tri-functional), to have long linkage sequences in two (or three) dimensions and such polymers are distinguished as ***cross linked polymers***

➢ Classification Based on Molecular Forces:

- The mechanical properties of polymersare governed by intermolecular forces, *e.g.*, van der Waals forces and hydrogen bonds, present in the polymer, these forces also bind the polymer chains
- Under this category, the polymers are classified into the following groups on the basis of magnitude of intermolecular forces present in them, they are
- (i) ***Elastomers***
- (ii) ***Fibers***
- (iii) ***Liquid resins***
- (iv) ***Plastics*** [(a) ***Thermoplastic*** and (b) ***thermosetting plastic***].

- **Elastomers:** These are rubber – like solids with elastic properties
- In these elastomeric polymers, the polymer chains are random coiled structure, they are held together by the weakest intermolecular forces , so they are highly amorphous polymers
- These weak binding forces permit the polymer to be stretched
- A few ‘crosslinks’ are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber
- The examples are buna-S, buna-N, neoprene, etc

- **Fibers:** If drawn into long filament like material whose length is at least 100 times its diameter, polymers are said to have been converted into ‘fibre’
- Polymeric chains are straight chain polymers, they are held together by the strong intermolecular forces like hydrogen bonding, these strong forces also lead to close packing of chains and thus impart crystalline nature
- Fibres are the thread forming solids which possess high tensile strength and high modulus
- Examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

- **Liquid Resins:** Polymers used as adhesives, potting compound sealants, etc. in a liquid form are described liquid resins, examples are epoxy adhesives and polysulphide sealants.
- **Plastics**: A polymer is shaped into hard and tough utility articles by the application of heat and pressure; it is used as a ‘plastic’
- The intermolecular force between polymeric chains are intermediate between elastomers and fibers, so they are partially crystalline
- Typical examples are polystyrene, PVC and polymethyl methacrylate. They are two types
- (a) Thermoplastic and
- (b) Thermosetting plastic.

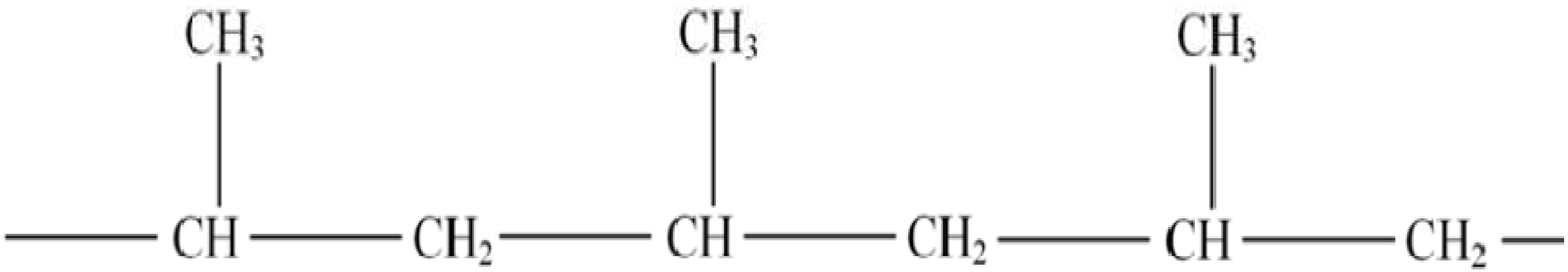
- **Thermoplastic Polymers:** Some polymers soften on heating and can be converted into any shape that they can retain on cooling
- The process of heating, reshaping and retaining the same on cooling can be repeated several times, such polymers, that soften on heating and stiffen on cooling, are termed 'thermoplastics'
- These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling
- These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres
- Polyethylene, PVC, nylon and sealing wax are examples of thermoplastic polymers.

- **Thermosetting Polymers:** Some polymers, on the other hand, undergo some chemical change on heating and convert themselves into an infusible mass
- They are like the 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.
- These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible
- These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.

1.3.6 Tacticity:-

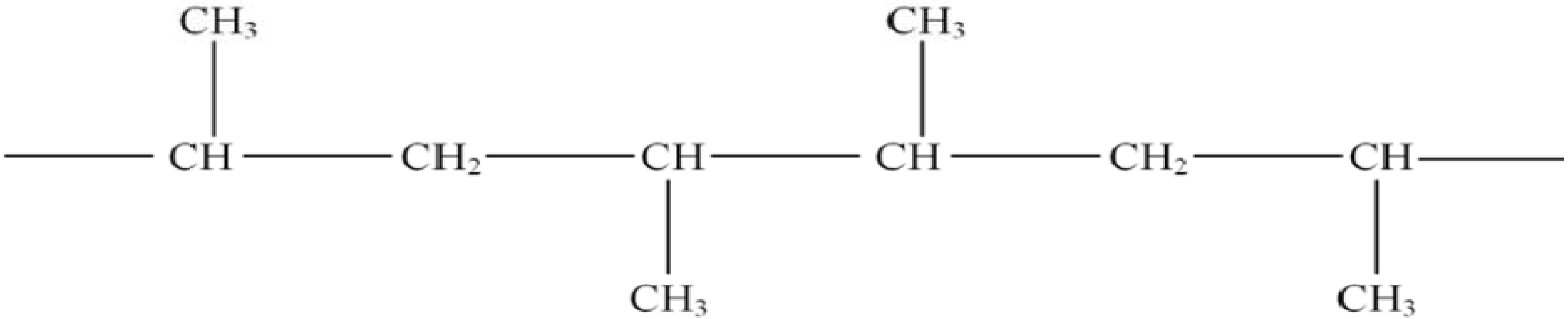
It may be defined as the geometric arrangement (orientation) of the characteristic group of monomer unit with respect to the main chain (backbone) of the polymers. On the basis of structure, polymer may be classified into three groups:-

A. Isotactic polymer:- It is the type of polymer in which the characteristic group are arranged on the same side of the main chain.



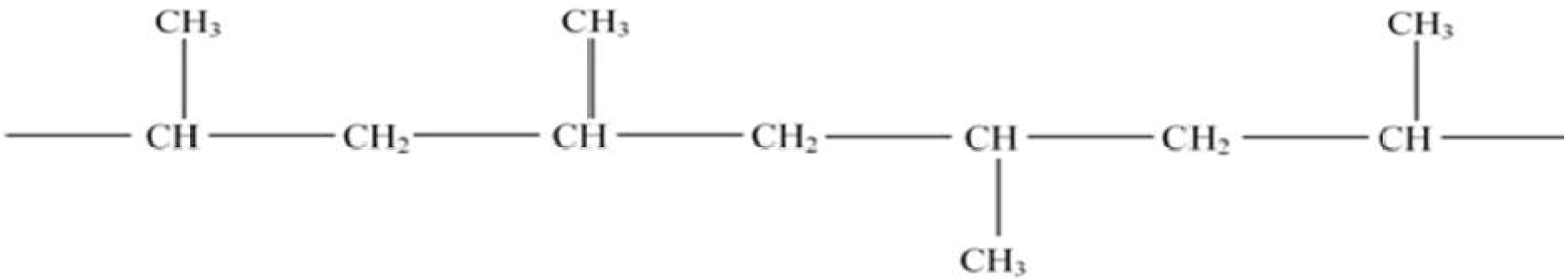
Isotactic Polypropene

B. Syndiotactic polymer:- A polymer is said to be syndiotactic if the side group (characteristic group) are arranged in an alternate fashion.



Syndiotatic Polypropene

C. Atactic polymer:- A polymer is said to be atactic, if the characteristic groups (side group) are arranged in irregular fashion (randomness) around the main chain. It has proper strength and more elasticity.



Atactic Polypropene

The end