

## 9. Understanding of Polymer Chemistry

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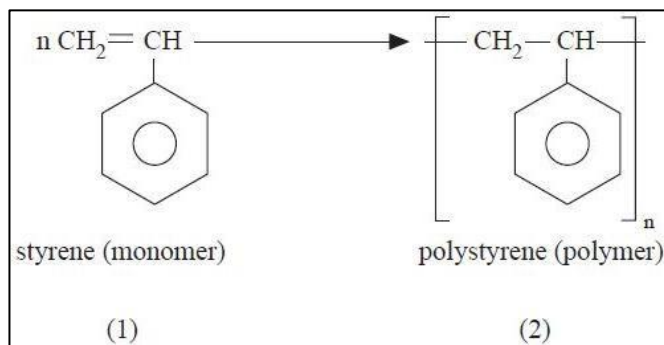
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### 9.1 Introduction:

Polymers have been with us from the beginning of time, and form the building blocks of life. Animals, plants- all classes of living organisms - are composed of polymers. However in the middle of the 20th century we began to understand the true nature of polymers. This understanding came with the development of plastics, which are true man-made materials that are the ultimate tribute to man's creativity and ingenuity. Subsequently polymers have changed our lives. It is hard to visualize today's world with all its luxury and comfort without man-made polymeric materials. Polymers are high molecular weight compounds whose structures are made up of a large number of simple repeating units. The interlinking of many units has given the polymer its name 'Poly' means many, mers means units=polymer. Small molecules are combined to form a big molecule i.e., polymers. A Polymer consists of a large chain of repeating molecules (monomers) that are attached in an end to end fashion.



Other examples of polymers of this type are polyethylene, polyacrylonitrile and polypropylene.

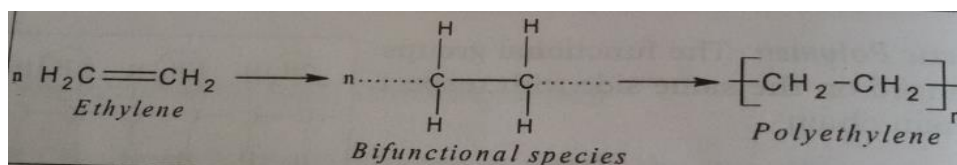
Polymers may either be naturally occurring or purely synthetic. Enzymes, nucleic acids, proteins, carbohydrates are polymers of natural origin. Their structures, are normally very complex. Starch, cellulose, and natural rubber, on the other hand, are examples of polymers of plant origin (natural) but have relatively simpler structures than those of enzymes or proteins.

## 9.2 Types of Polymerizations:

The reaction in which monomers combine to give polymers is known as polymerization. It can be broadly classified into three categories as

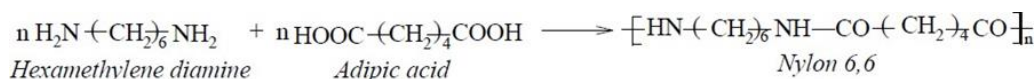
### 9.2.1 Addition Polymerization:

Monomers having multiple bonds (double or triple bond) undergo addition polymerization. Monomers combine to give polymer through addition reaction without elimination of any smaller molecules. Therefore, the molecular weight of the resulting polymer will be an integral multiple of the molecular weight of monomers. Eg: Ethylene to polyethylene.



### 9.2.2 Condensation Polymerization:

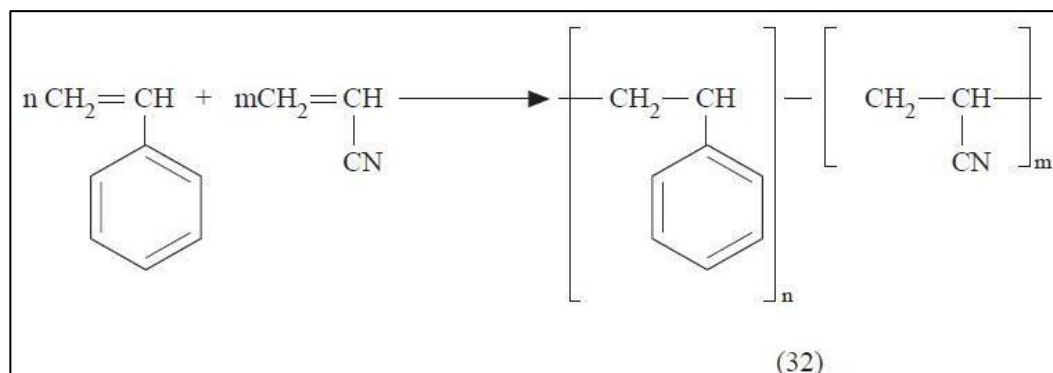
Monomers having same or different types of functional groups undergo condensation polymerization. The polymerization proceeds by step wise reaction between reactive functional groups and small molecules are eliminated. Eg: polymerization reaction of nylon66.



The differences between two major polymerization methods are tabulated as follows:

Sr. No.	Addition Polymerization	Condensation Polymerization
1	E.g. PVC	E.g. Nylon 6,6
3	Monomers are adding together to form polymers.	Monomers are condensed to form polymer.
4	No elimination of other molecules.	Elimination of smaller molecules occur.
5	At least one multiple bond presence is essential condition.	Monomers must have two or more functional groups.
6	Homo polymers are formed.	Hetero polymers are formed.
7	Thermoplastics are formed.	Thermo set plastics are formed.
8	Molecular weight of the polymer is the integral multiple of monomers.	Need not be so.

**Copolymerization:** It is a special kind of polymerization, otherwise known as “Joint polymerization”. The product is known as ‘Co-polymers’. This is superior to other polymerization because it is used to alter the hardness, strength, rigidity and crystallinity of the monomers.



### 9.3 Classification of Polymers:

#### A. Based on their sources they are classified into:

**Natural polymers:** The polymers, which are obtained from natural sources such as plants and animals, are called natural polymers.

Egs. Wood, cellulose, Cotton, Wool, Silk, Proteins, Natural rubber etc.

**Synthetic polymers:** The polymers, which are synthesized from simple molecules are called synthetic polymers.

Egs: Nylon6,6, PVC, Polystyrene, Teflon, Polyesters, Polyethylene etc.

**B. Based on their thermal behaviour they are classified into:**

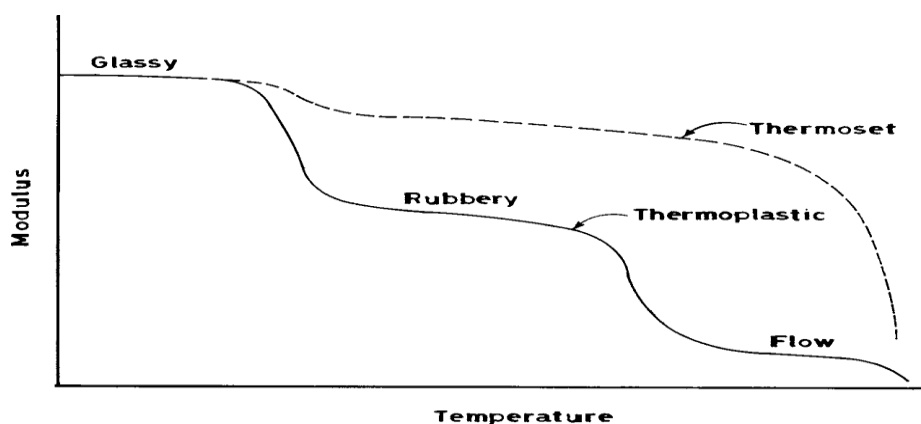
On the basis of thermal (thermomechanical) response polymers can be classified as thermoplastics and thermosets. As the name suggests, **thermoplastic polymers** soften and flow under the action of heat and pressure. Upon cooling, the polymer hardens and assumes the shape of the mold (container). Thermoplastics, when compounded with appropriate ingredients, can usually withstand several of these heating and cooling cycles without suffering any structural breakdown. This behaviour is similar to that of candle wax.

Examples of thermoplastic polymers are Polyethylene, polystyrene and Nylon.

A **thermoset** is a polymer that, when heated, undergoes a chemical change to produce a cross-linked, solid polymer. Thermosets usually exist initially as liquids called prepolymers; they can be shaped into desired forms by the application of heat and pressure, but are incapable of undergoing repeated cycles of softening and hardening. Examples of thermosetting polymers include urea–formaldehyde, phenol– formaldehyde, and epoxies.

The basic structural difference between thermoplastics and thermosets is that thermoplastic polymers are composed mainly of linear and branched molecules, whereas thermosets are made up of cross-linked systems. Recall from our previous discussion that linear and branched polymers consist of molecules that are not chemically tied together. It is therefore possible for individual chains to slide past one another. For cross-linked systems, however, chains are linked chemically; consequently, chains will not flow freely even under the application of heat and pressure.

The differences in the thermal behavior of thermoplastics and thermosets are best illustrated by considering the change in modulus with temperature for both polymers. At low temperatures, a thermoplastic polymer (both crystalline and amorphous) exists as a hard and rigid glass. As the temperature is increased, it changes from a glass to a rubbery elastomer to a viscous melt that is capable of flowing.



Thermoplastics: Plastics which soften on heating and harden on cooling. They retain their structure when subjected to heat and pressure. Hence they can be remolded into new shapes without any loss of their physical properties.

Eg: PVC, polyethylene.

**Thermosetting plastics:** Plastics which get hardened during moulding process and cannot be softened by reheating. They also soften on heating but on standing acquire a cross-linked structure which make them stable to heat. Thus, they cannot be remolded into new shapes.

E.g. Phenol formaldehyde resin(Bakelite), Urea-Formaldehyde etc.

### **C. Based on their mechanism of polymerization they are classified into**

**Addition polymers:** A polymerization reaction in which monomers containing one or more double bonds are linked to each other without the elimination of any by products, usually in the presence of initiators is called addition polymerization.

Eg: PVC, Polyethylene etc.

**Condensation polymers:** It is brought by linking together different monomers accompanied by the elimination of small molecules like H<sub>2</sub>O and HCl..

Eg: Nylon6,6, Polyester etc.

### **D. Based on their configuration:**

#### **Stereospecific polymer or Tacticity:**

Tacticity describes the relative stereochemistry of chiral centers in the neighbouring structural units within a polymer. The classification is based on the orientation of the monomeric units or functional groups with respect to the main chain of the polymer. The orientation of the substituents can be in an orderly fashion or disorderly fashion. Based on this there are three types of polymers:

**Isotactic polymer:** It is a polymer with all substituents on the same side with respect to the main chain of the polymer. Example: Polypropylene, cis-polyisoprene

**Atactic polymer:** It is a polymer with the random orientation of the substituents with respect to the main chain of the polymer. Example: Polypropylene, trans-polyisoprene

**Syndiotactic polymer:** It is a polymer having substituents that are alternatively placed with respect to the main chain of the polymer. Example: Polypropylene

### **E. Based on their monomers:**

**Homopolymers:** When all the repeating units in a particular polymer have the same structure, that polymer is called a homopolymer.

Eg: poly vinyl chloride.

**Copolymers:** When different repeating units make up the polymer chain, the polymer is called a copolymer. A- A-B-B-B-A-B-A-A-B—

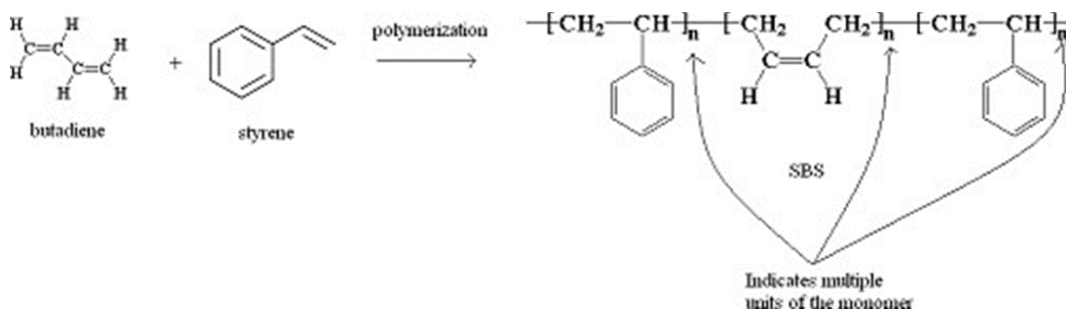
Eg: styrene butadiene copolymer

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

- Alternating copolymers(A-B-A-B-A-B-)
- Block copolymers (A-A-A-A-B-B-B-B)
- Random copolymers(A-B-B-B-A-A-B-B-)

a. Alternating 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-**



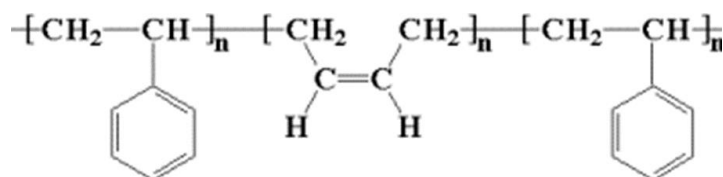
b. Random Co-polymers: In this type of copolymers, the different repeating units are not arranged in a systematic manner but are randomly arranged, e.g.

**-ABAABABBAAABA-**

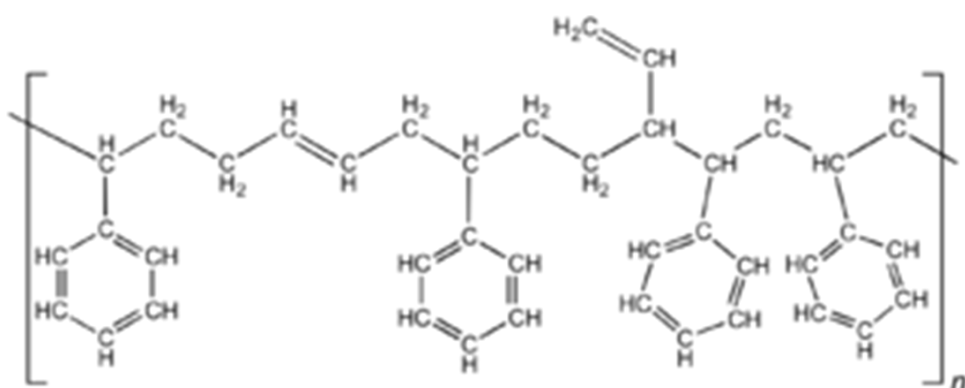
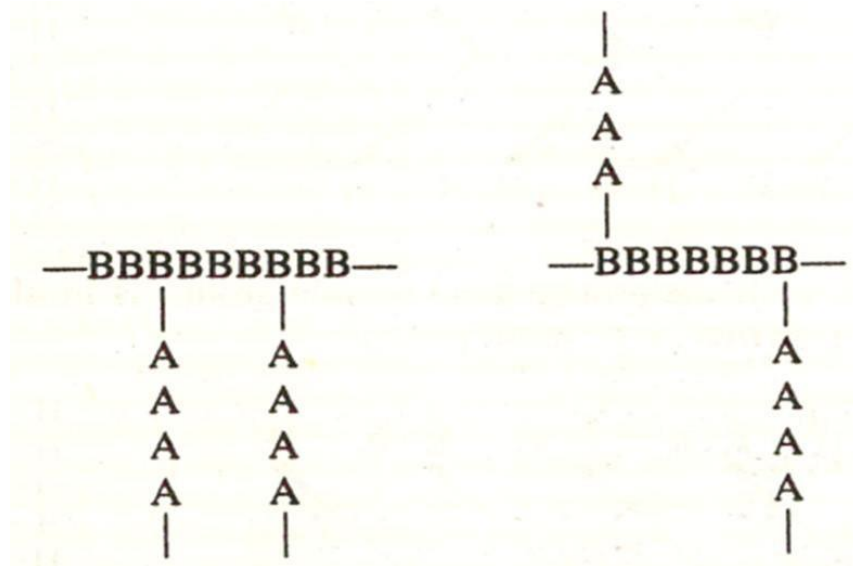
Eg; commercial copolymers of butadiene and acrylonitrile

c. Block Co-polymers: In such co- polymers, block of repeating units of one type alternate with block of another type. E.g. SBS.

**-AAAABBBBAAAABBBB-**



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



Eg: Polystyrene

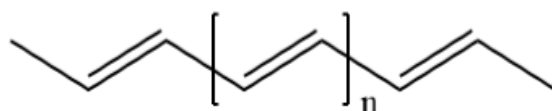
**F. Based on their properties they are classified into:**

- Elastomers; Natural rubber
- Fibres: Wood, Silk etc.
- Resins: Urea- Formaldehyde, Epoxy resins, Phenol- Formaldehyde etc.
- Plastics: Plexiglass, PVC, Teflon etc.

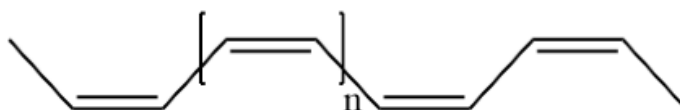
**G. Conducting Polymers:**

Conductive polymers are poly conjugated organic polymers that conduct electricity because of their conjugated  $\pi$ -bonds. Such compounds can have either metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers.

**Polyacetylene:**



trans-polyacetylene



cis-polyacetylene

It is the first conducting polymer to be synthesized. Poly(acetylene) is the simplest conjugated polymer. In its linear form it precipitates as a black, air sensitive, infusible and intractable powder out of solution and cannot be processed.

In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa reported similar high conductivity in oxidized iodine-doped polyacetylene. For this research, they were awarded the 2000 Nobel Prize in Chemistry for the discovery and development of conducting polymers.

Polyacetylene itself did not find practical applications, but drew the attention of scientists and encouraged the rapid growth of the field. Polyacetylenes exist in isomeric forms: cis-polyacetylene and trans-polyacetylene.

In cis-configuration, the hydrogen atoms are bound on the same side of the carbon-carbon double bonds. In trans-configuration, the hydrogen atoms are bound on the alternative sides of the carbon-

carbon double bonds. The scientist, Shirakawa, prepared poly(acetylene) by passing acetylene gas over the Zeigler-Natta catalyst. Zeigler-Natta catalyst is the coordination complex of tetra butoxy titanium,  $[Ti(OBu)_4]$ , an organo metallic compound and triethyl aluminium,  $[Et_3Al]$ .

**Applications:** Conducting polymers have many uses. The most documented are as follows:

- Corrosion Inhibitors
- Compact Capacitors
- Light Emitting Diodes (LEDs)
- Lasers used in flat televisions
- Solar cells
- Displays in mobile telephones and television screens



Conducting Polymers have an immense advantage of being simple to synthesis, with their chemical structure tailored to alter their physical properties, such as their band gap. They exhibit an extensive range of electrical conductivity and can exhibit metallic to insulator property, so that they have many application such as solar cell, sensor and corrosion solar cells devices.

