

CYI101

Common CHEMISTRY(Organic)

Macromolecules: Basics of Polymer Chemistry

Polymer: *Basic Terminology*

Polymer:

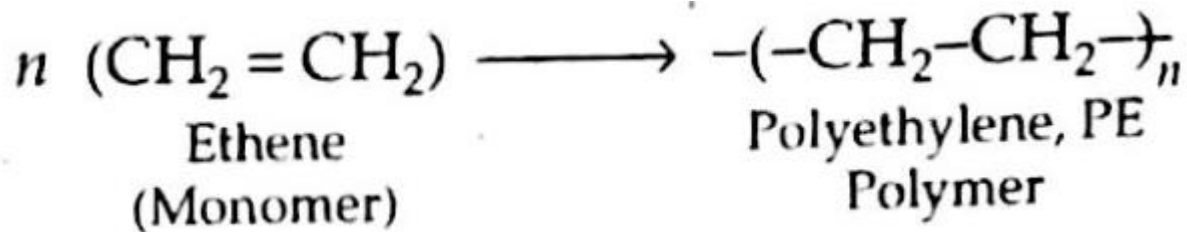
A large molecule having high molecular mass formed by joining a repeating unit of smaller molecules (monomers) through a covalent bonding is called as **polymer**.

Monomer:

Monomer is small individual repeating unit or molecules are called **monomers**.
Monomer is basic unit of polymer.

Polymerization:

The process by which polymers are formed by linking monomers through chemical reaction called **polymerization**.



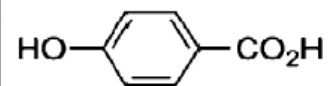
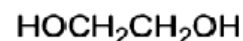
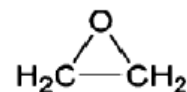
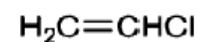
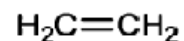
Polymer: *Basics*

$n \cdot [\text{Monomer}] \rightarrow \text{Polymer}$

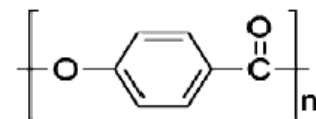
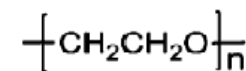
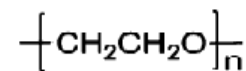
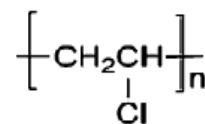
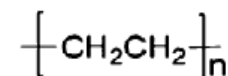
Some examples of polymer listed in the following table

Sr. No.	Monomers	Polymers
1	Ethylene	Polyethylene
2	Vinyl chloride	Polyvinyl chloride (PVC)
3	Styrene	Polystyrene
4	Butadiene	Polybutadiene
5	Propylene	Polypropylene
6	Acrylonitrile	Polyacrylonitrile
7	Caprolactam	Nylon-6
8	Glycol and Terephthalic acid	Terylene or Decron
9	Hexamethylenediamine and Adipic acid	Nylon-6,6
10	Phenol and Formaldehyde	Novolac

(a) Monomer



(b) Polymer



Polymer: Nomenclature

1. Simple vinyl polymers are designated by attaching the prefix poly to the monomer name. To name a polymer prefix **“poly”** to the monomer from which the polymer derived.

Examples:

Sr. No.	Name of monomer	Name of polymer
1	Styrene	Polystyrene
2	Ethylene	Polyethylene
3	Propylene	Polypropylene

2. When the monomer name consists of more than one word or is preceded by a letter or number, the monomer is enclosed by parentheses preceded by the prefix **“poly”**.

Example: The polymer obtained from the polymerization of 4-chlorostyrene is **poly(4-chlorostyrene)** and that from vinyl acetate is **poly (vinyl acetate)**.

3. Tacticity may be noted by prefixing the letter *i* (*isotactic*) or *s* (*syndiotactic*) before prefix **“poly”** as in ***i*-polystyrene**.

4. Geometric and structural isomers may be indicated by using the appropriate prefixes, *cis* or *trans* and 1,2- or 1,4-, before prefix **“poly”**. **Example: *trans*-1,4-poly(1,3-butadiene)**.

Nomenclature rules for non-vinyl polymers such as condensation polymers are generally more complicated than for vinyl monomers. The non-vinyl polymers are usually named according to the initial monomer or the functional group of the repeating unit.

Example: The most important commercial nylon, commonly called **nylon-6,6** is more descriptively called **poly(hexamethylenedipamide)** with adipic acid.

1.7 Nomenclature

A. Types of Nomenclature

a. **Source name** : to be based on names of corresponding monomer

Polyethylene, Poly(vinyl chloride), Poly(ethylene oxide)

b. **IUPAC name** : to be based on CRU, systematic name

Poly(methylene), Poly(1-chloroethylene),
Poly(oxyethylene)

c. **Functional group name** :

Acoording to name of functional group in the polymer backbone

Polyamide, Polyester

1.7 Nomenclature

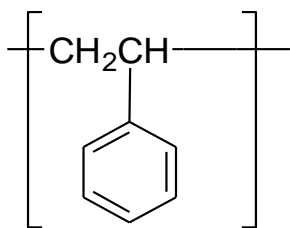
- d. **Trade name** : The commercial names by manufacturer Teflon, Nylon
- e. **Abbreviation name** : PVC, PET
- f. **Complex and Network polymer** : Phenol-formaldehyde polymer
- g. **Vinyl polymer** : Polyolefin

1.7.1 Vinyl polymers

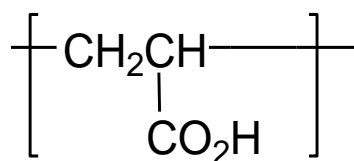
A. Vinyl polymers

- a. **Source name** : Polystyrene, Poly(acrylic acid),
Poly(α -methyl styrene), Poly(1-pentene)
- b. **IUPAC name** : Poly(1-phenylethylene), Poly(1-carboxylatoethylene)
Poly(1-methyl-1-phenylethylene), Poly(1-propylethylene)

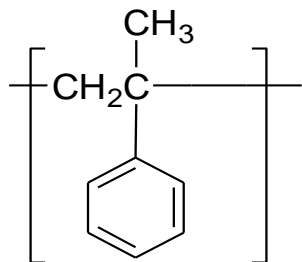
Polystyrene



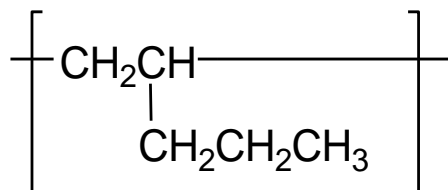
Poly(acrylic acid)



Poly(α -methylstyrene)

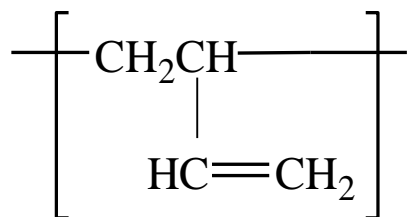


Poly(1-pentene)

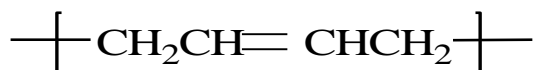


1.7.1 Vinyl polymers

B. Diene monomers



1,2-addition




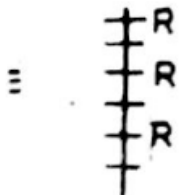
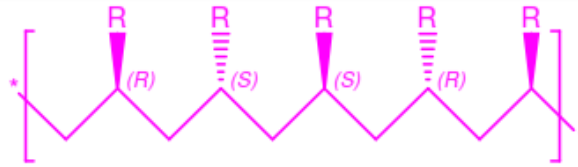
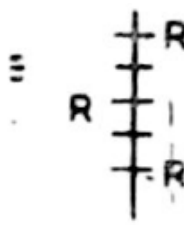

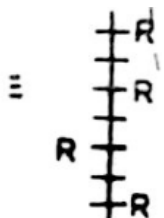
1,4-addition

Source name : 1,2-Poly(1,3-butadiene) 1,4-Poly(1,3-butadiene)

IUPAC name : Poly(1-vinylethylene) Poly(1-butene-1,4-diyl)

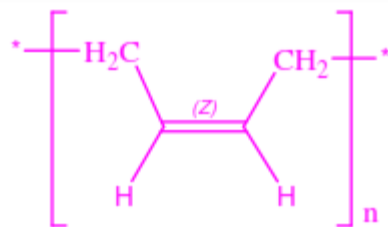
Polymer Structure: *Tacticity*

Tacticity: The difference in configuration due to the orientation of different functional groups with respect to the main chain is called **tacticity**. In addition to the type, number, and sequential arrangement of monomers along the chain, the spatial arrangement of substituent groups is also important in determining properties.

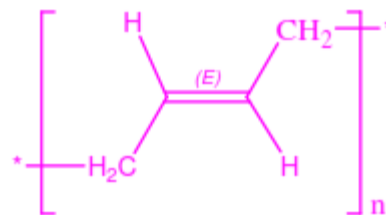
Polymer	structure	Model	Description
<i>Isotactic</i>			all the functional groups are arranged on the same side of main chain
<i>Syndiotactic</i>			all the functional groups are arranged in the alternative fashion of main chain
<i>Atactic</i>			all the functional groups are arranged in random of main chain

Polymer Structure: *Geometric isomers*

Geometric isomerism: Polymers with unsaturated sites double bond in the repeat unit in chain give rise to different geometric isomers. 1,3-butadiene can be polymerized to give poly(1,2-butadiene) or either of two geometric isomers of poly(1,4-butadiene). These two polymers are called *cis* and *trans*-poly(1,4-butadiene). In the *cis*-polybutadiene, first and four carbons lie on the same side of central double bond while in *trans*-polybutadiene, first and four carbon lie on the opposite side of central double bond.



Cis-1,4-polybutadiene



Trans-1,4-polybutadiene

Polymer Classification: *Based on sources*

Classification Based on Source: Based on the source of polymer they are classified into three sub categories.

a) Natural polymers

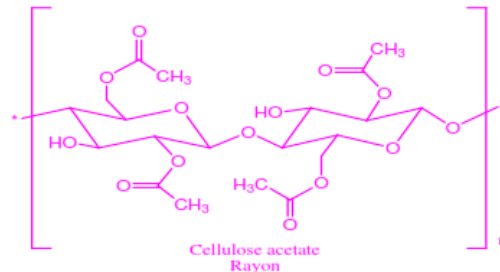
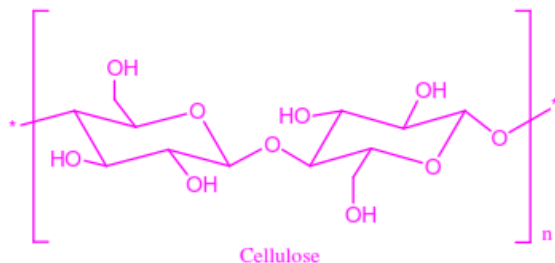
Polymers which are isolated from natural origin are called natural polymers. These polymers are found in plants and animals. E.g. Proteins, cellulose, starch, some resins and rubber.

b) Semi-synthetic polymers

The polymers are obtained by chemical treatment of natural polymer to improve their physical properties are called semisynthetic polymers. Semisynthetic polymers are simply chemically modified natural polymers. E.g. Cellulose acetate (rayon) and cellulose nitrate from cellulose.

c) Synthetic polymers

Polymers are synthesized in laboratory from monomers are called synthetic polymers. E.g. Polyethylene, Nylon 6,6, Buna-S, Polystyrene, Terylene, etc



Polymer Classification: *Based on Structure of Polymers*

On the basis of the polymers structure they are divided into three subgroups.

a) Linear polymers

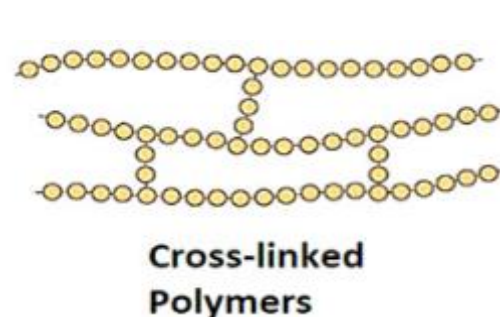
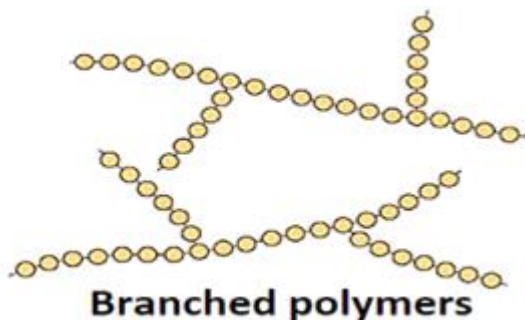
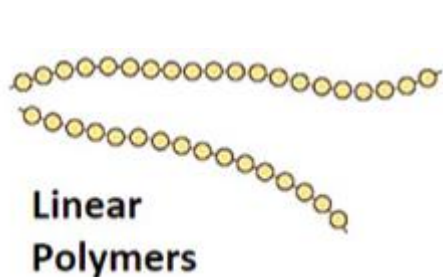
These polymers consist of long and straight chains well packed structure. The examples are high density **polythene**, **polyvinyl chloride**, etc. They have high melting point, high densities and high tensile strength.

b) Branched chain polymers

These polymers contain linear chains having some branches and irregular packed structure. e.g., **low density polythene** and **glycogen**. They have low tensile strength, low density and lower melting point in comparison with linear polymers.

c) Cross linked or Network polymers

These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains. They are hard and rigid. E.g. **Bakelite**, **melamine**, etc.



Polymer Classification: *Based on Mode of Polymerization*

On the basis of the polymers structure they are divided into two subgroups.

a) 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 polypropylene from propene.



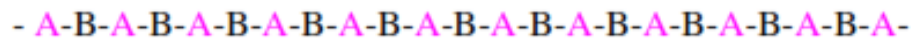
Homopolymer:

When all the monomers are the same, the molecule is called a Homopolymer. A homopolymer consist of identical monomers. When monomer A joined to form polymer, such kind of polymer is known as homopolymers. Examples: **Polystyrene**, **Polypropylene**, **Polybutadine**, **Polyvinyl chloride**, etc.



Copolymer:

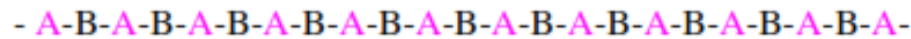
When there is more than one type of monomer present, the molecule is called copolymer. A copolymer consists of monomers of different chemical structure. When two different monomers A and B joined to form polymer is known as copolymers.



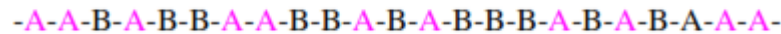
Copolymer: *Classification*

Copolymers are classified according to the distribution of monomers in the macromolecule. In copolymerization different monomers incorporated during the growth of the polymer chain can lead to:

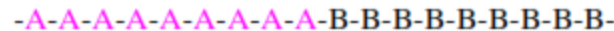
a. Alternating copolymer: there is alternate pattern to the distribution of monomer units in a alternating copolymer.



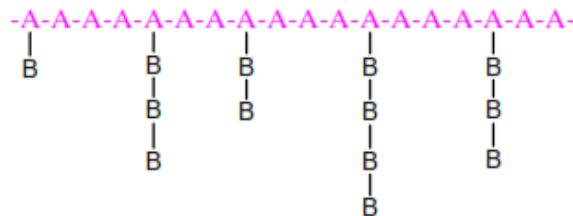
b. Random copolymers: As the name implies, there is no pattern to the distribution of monomer units



c. Block copolymers: The main chain contains sections (blocks) of repeating units derived from different monomers. The sequence:



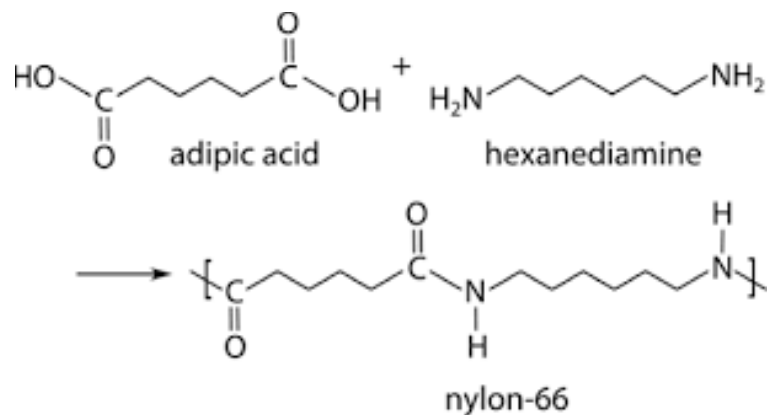
d. Graft copolymer: If main chain consists of one monomer and branched chain consists of other monomers are called Graft copolymers. The main chain bears branches (grafts) that are derived from a different monomer.



Polymer Classification: *Based on Mode of Polymerization*

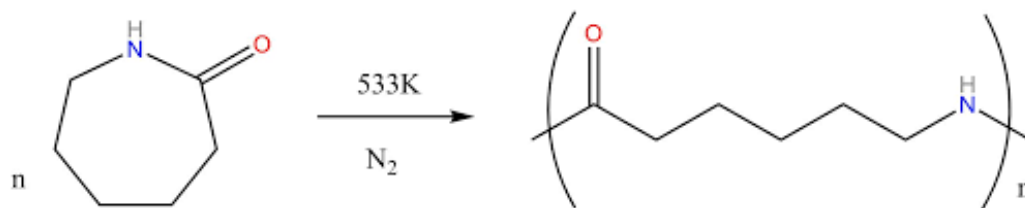
b) Condensation polymers: The condensation polymers are formed by repeated condensation reaction between two different bifunctional or tri-functional monomeric units. In these polymerization reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. The examples are terylene (dacron), **nylon6,6** etc. For example, nylon 66 is formed by the condensation of hexamethylenediamine with adipic acid

Nylon 66 is a type of polyamide or nylon. It, and nylon 6, are the two most common for textile and plastics industries. **Nylon 66** is made of two monomers each containing 6 carbon atoms, **hexamethylenediamine** and **adipic acid**, which give **nylon 66** its name.

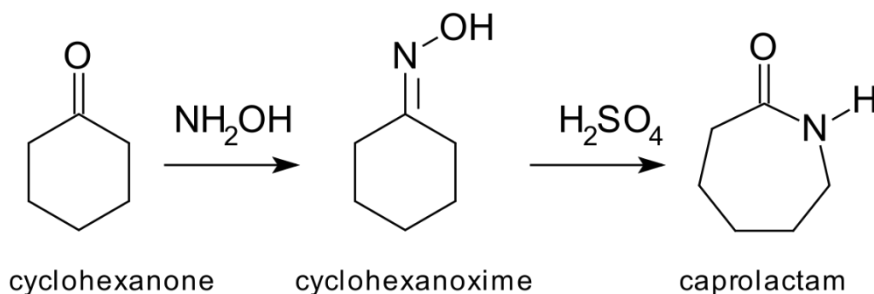


Polymer Classification: *Based on Mode of Polymerization*

Nylon 6 is polyamide made from **caprolactam**. Unlike most other nylons, **nylon 6** is not a condensation polymer, but instead is formed by **ring-opening polymerization**; this makes it a special case in the comparison between condensation and addition polymers.



When **caprolactam** is heated at about 533 K in an inert atmosphere of nitrogen for about 4-5 hours, the ring breaks and undergoes polymerization.



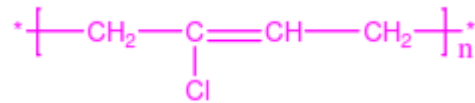
Caprolactam is prepared in a process comprising a **Beckmann rearrangement** of **cyclohexanone oxime**

Polymer Classification: *Based on Molecular Forces*

A large number of polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forces i.e. van der Waals forces and hydrogen bonds present in the polymer. Under this category, the polymers are classified into the following four sub groups:

a) Elastomers:

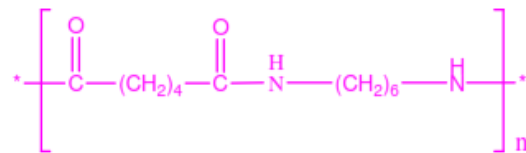
Elastomers are also known as rubbers. These are solids with elastic properties. The examples are buna-S, buna-N, neoprene, etc. There are number of man-made elastomers in addition to natural rubber.



Neoprene

b) Fibers:

Fibers are the thread forming solids which possess high tensile strength and high modulus. Example: Nylon 6, 6, Terylene, etc.

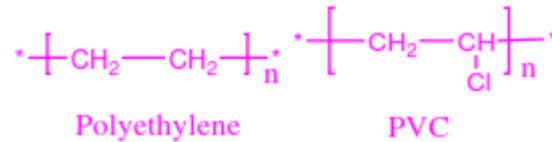


Nylon 6,6

Polymer Classification: *Based on Molecular Forces*

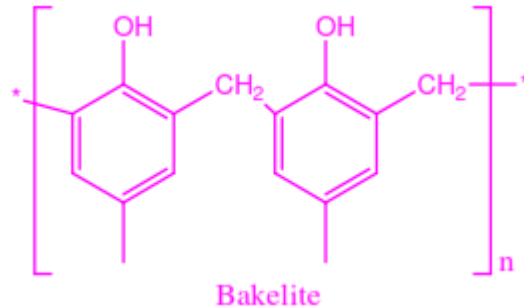
c) Thermoplastic polymers:

These plastics soften when heated and harden when cooled. Example: polythene, polystyrene, polyvinyls(PVC), acrylics, nylons, polypropylene, polymethyl methacrylate etc



d) Thermosetting plastic polymers:

They are not soft on heating under pressure and not remolded.



Polymer : *Thermoplastic vs Thermosetting*

S. No.	Thermoplastics	Thermosetting Plastics
1	Formed either by addition or by condensation polymerization reactions	Formed by condensation polymerization reactions
2	They have either linear or branched structures.	They have three-dimensional cross-linked network structures
3	Adjacent polymer chains are held together by either vanderwaals forces, or by dipole dipole forces or by hydrogen bonds	Adjacent polymer chains are held together by strong covalent bonds called crossed-links
4	They soften on heating and stiffen on cooling	They do not soften on heating.
5	Low molecular weight thermoplastics are soluble in their suitable solvents.	They are insoluble in any solvent.
6	They can be remoulded, re-shaped and re-used.	They can be reclaimed from waste i.e., they can be recycled
7	There is no change in chemical composition and structure during moulding process.	They undergo chemical changes such as further polymerization and cross-linking during moulding process.
8	They are soft and flexible	They are hard, rigid and infusible.
9	They can be reclaimed from waste i.e.; they can be recycled.	They cannot be reclaimed from waste. They cannot be recycled.
10	They undergo reversible changes, on the application of heat.	They undergo irreversible changes on the application of heat.
11	They swell or dissolve in organic solvents.	They neither dissolve nor swell in organic solvents.
12	They are tough materials.	They are brittle materials.
13	The moulded articles are to be cooled to room temperature before taking out from the moulds to avoid deformation.	The moulded articles can be taken out of the moulds even when they are still hot without any deformations
14	Curing can be done by cooling.	Curing can be done by applying heat and pressure.
15	Examples: Polyethylene (PE), Bakelite.	Examples: Phenol- formaldehyde resin (PF), urea- formaldehyde resin

Polymer : *Classifications*

