Polymer and Composites

❖Introduction, definition, degree of polymerization (D_p), concept of molecular weight (number average, weight average & numerical based on them), glass transition temperature.

❖Classification of polymers: polymerization mechanism: (step and chain polymers)

❖Polymerization Reaction: addition and condensation,.

❖Thermal behavior: Thermoplastic and thermosetting,

❖types of monomers: linear, branched and cross-linked polymers, homo and copolymers.

Commercial Polymers: **s**ynthesis, properties and application, polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), m phenol Formaldehyde (PF), epoxy resin.

Specialty polymers: basic concept applications of conductive polymers, biodegradable polymers, recycling of polymers

Composites: classification, fiber and particle reinforced composites.

Types of materials

Metals / Alloys

Ceramics

Polymers

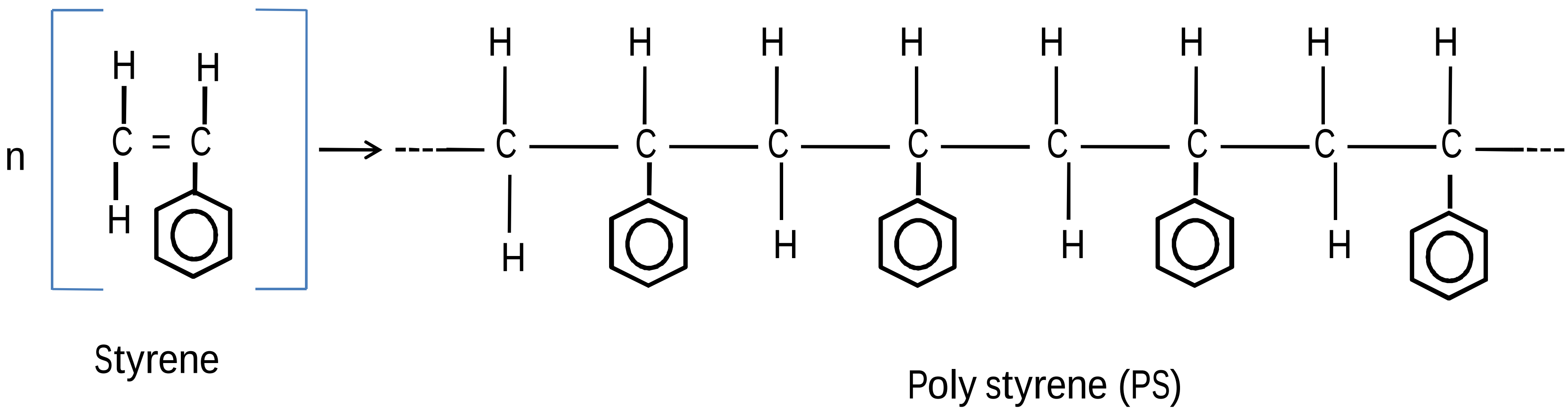
Introduction

Polymer → **Poly + meros**

Defined as high molecular weight compounds formed by combination of large number of one or more types of molecules of low molecular weight

Polymers are giant molecules of high molecular weight called as macromolecules which are built up by linking together large number of small molecules called as monomers and the reaction by which the monomers combine to form polymers is called as polymerization.

$$-(x\text{-}x\text{-}x\text{-}x\text{-}x\text{-}x\text{-}x\text{-}x\text{-}x\text{-}x\text{-})_n$$


n
H
H
C = C
H
Styrene
H
C
H
C
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C
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C
H
C
Poly styrene (PS)

Natural Polymers

Cellulose (Present in wood)
Polyphosphates (Present in bones)
DNA
Rubber

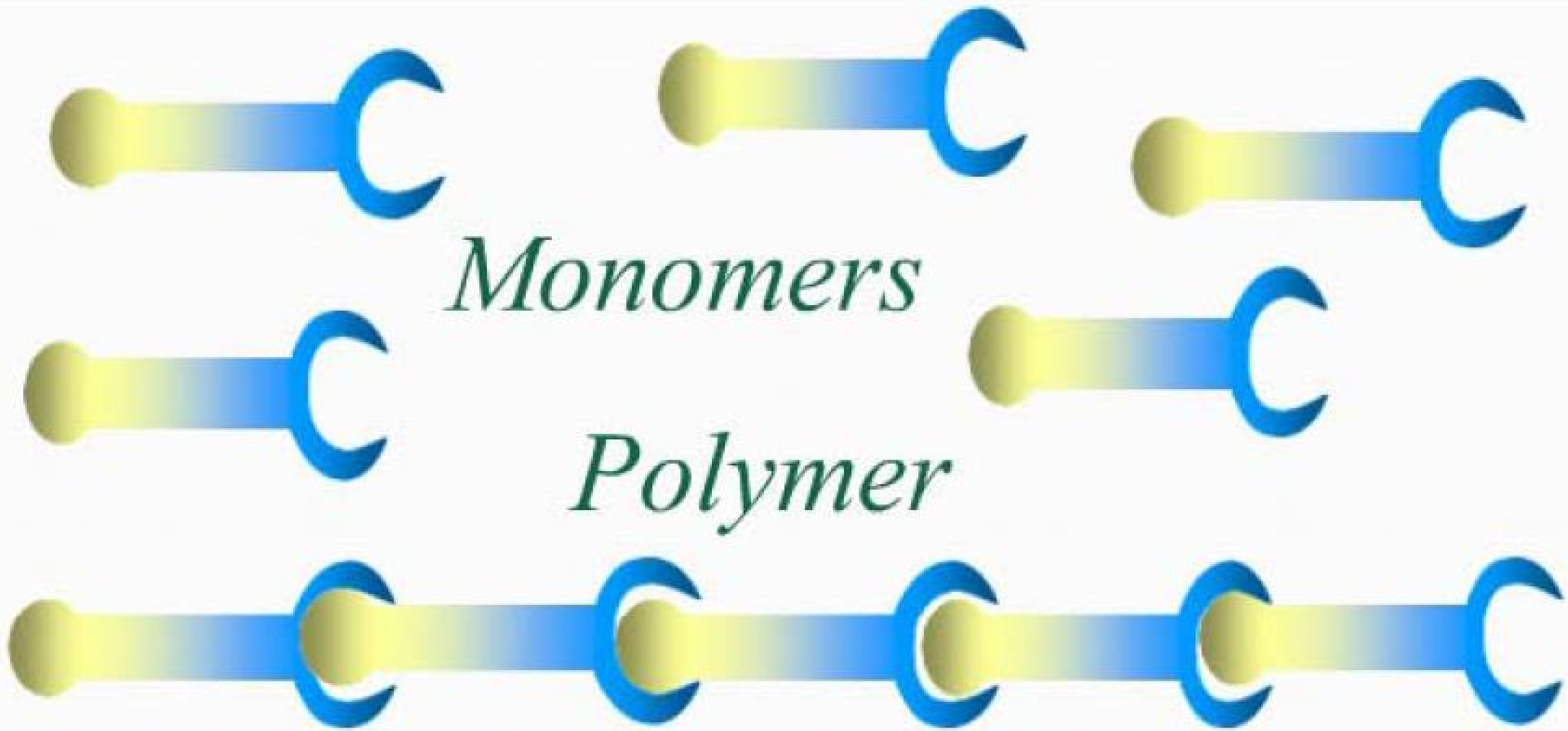
Synthetic Polymers

Polyethylene
Polypropylene
Nylon
Polyesters , PVC

Polymers

- The earliest synthetic polymer was developed in 1906, called Bakelite.
- The development of modern plastics started in 1920s using raw material extracted from coal and petroleum products (Ethylene). Ethylene is called a building block.
- Polymers are long-chain molecules and are formed by polymerization process, linking and cross linking a particular building block (***monomer***, a unit cell).
- The term polymer means many units repeated many times in a chain-like structure.
- Most monomers are organic materials, atoms are joined in covalent bonds (electron-sharing) with other atoms such as oxygen, nitrogen, hydrogen, sulfur, chlorine,….

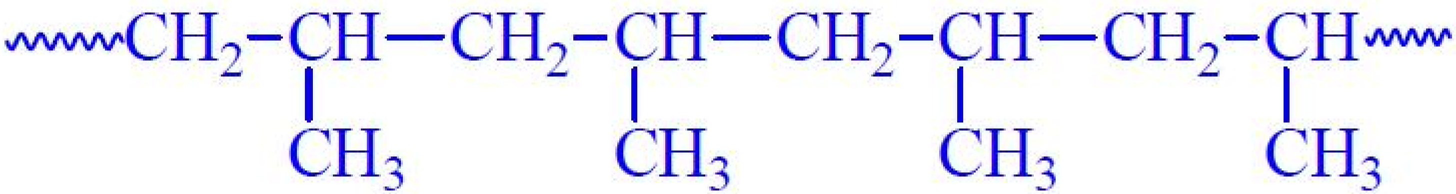
Monomer to Polymer



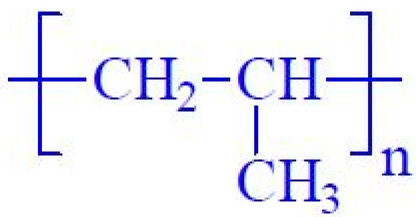
The word, polymer, implies that polymers are constructed from pieces (monomers) that can be easily connected into long chains (polymer).

Structure units are connected to one another in the polymer molecule, or polymeric structure, by covalent bonds.

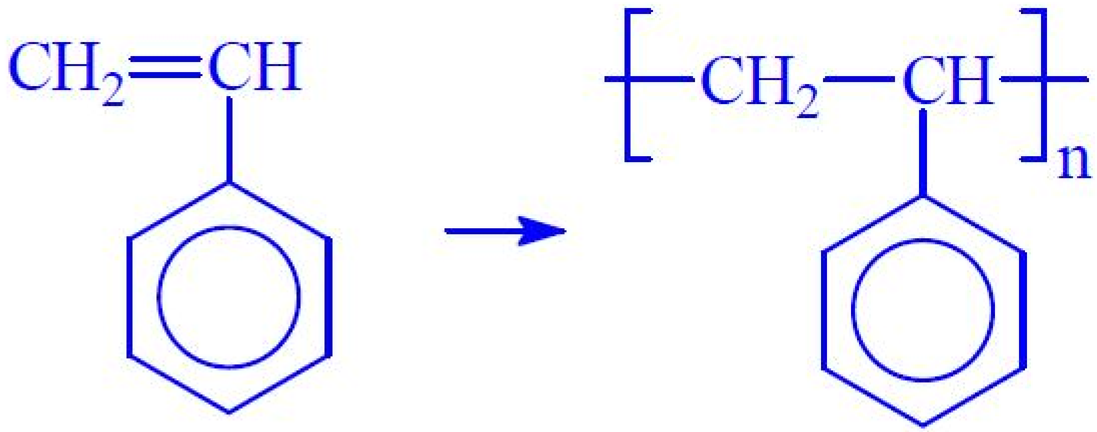
Repeat unit: The atoms that make up the backbone of a polymer chain come in a regular order, and this order repeats itself all along the length of the polymer chain. For example, look at polypropylene :



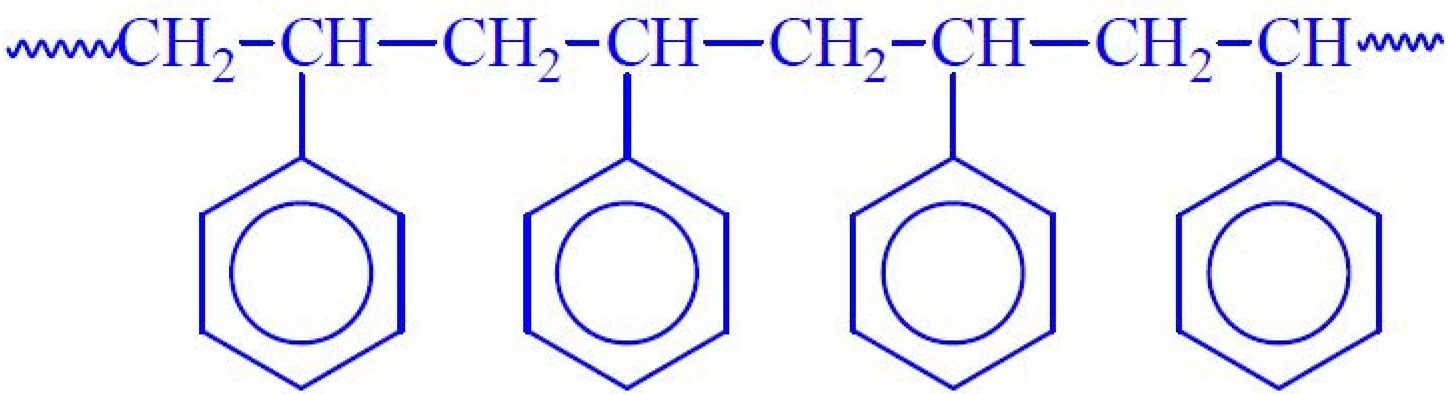
Its backbone chain is made up of just two carbon atoms repeated over and over again. One carbon atom has two hydrogen atoms attached to it, and the other carbon atom has one hydrogen atom and one pendant methyl group (CH_3). This is called the *repeat structure* or the *repeat unit*. To make things simple, we usually only draw one unit of the repeat structure, like this:



Another example: styrene monomers join together to make polystyrene:



Styrene monomer Polystyrene repeat unit



Degree of Polymerization

The number of repeating units (n) in the polymer chain is known as the degree of polymerization.
Degree of polymerization is related to the molecular weight of the polymer [M] by the relation

$$D_p = \frac{M}{m} \quad \text{Or} \quad D_p \times m = M$$

Where m is the molecular weight of the monomer
M is the molecular weight of the Polymer
D_p is the degree of polymerization

Most of the polymers have molecular weights ranging from 5000-200000

Functionality of the Monomer

Reactive Positions in a monomer

- These reactive positions are useful for joining large number of monomers to form a polymer.
- Easily reacting positions present in the form of functional groups or in the form of C= C

Functional groups present in monomer organic molecules are

-OH	*-COOH*
$-NH_2$	*-C≡N*
-Cl	*-COOR*

Functionality of the Monomer

❖The number of active bonding sites or the number of reactive positions in a monomer is referred to as its functionality.

✓Monomers having 2 reactive positions are called as bifunctional
✓Monomers having 3 reactive positions are called as trifunctional
✓Monomers having 4 reactive positions are called as tetrafunctional

Examples of bifunctional monomers

$CH_2 = CH_2$

$HO-CH_2-CH_2OH$ (Ethylene glycol)

$HOOC-(CH_2)_4-COOH$ (Adipic acid)

$CH_2=CHCl$ (Vinyl Chloride)

Examples of trifunctional monomers

$CH_2 = CH_2$

$HO-CH_2-CHOH-CH_2OH$ (glycerol)

Examples of tetrafunctional monomers

$CH \equiv CH$ (acetylene)

NH2-CO-NH2 (Urea)

$$CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$$

$$CH_2 = CH_2 + Cl_2 \longrightarrow CH_2Cl - CH_2Cl$$

Bifunctional (because Reacting with 2 hydrogen atoms or halogen atoms)

$$CH{\equiv}CH + 2H_2 \longrightarrow CH_3 - CH_3$$

$$CH{\equiv}CH + 2Cl_2 \longrightarrow CHCl_2 - CHCl_2$$

Tetrafunctional (because Reacting with 4 hydrogen atoms or halogen atoms)

Nomenclature of Polymers

- A polymer may consist of monomer of identical or different chemical structures. They are known as homopolymers and copolymers respectively.
- Copolymerization is the combined polymerization of 2 or more monomer species.

Homopolymer- only one monomer (repeating unit)

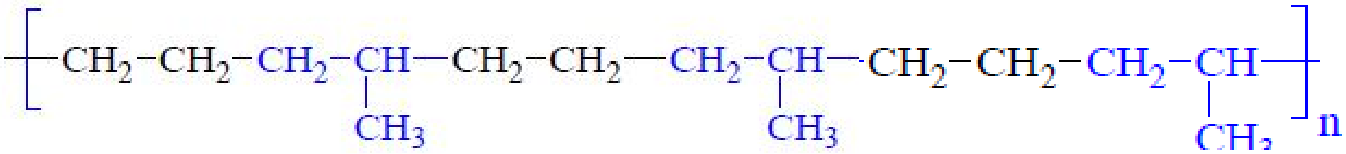
-A – A – A – A – A – A – A –

Copolymer – more than one monomer

Copolymers

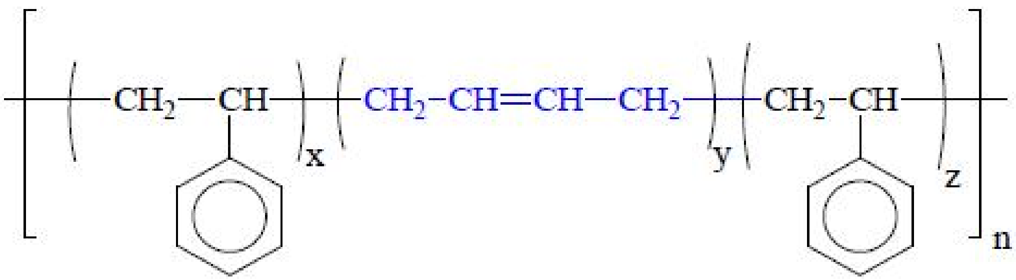
- Alternating and random

  - A – B – A – B – A – B – A – B -



Block

-A-A-A-A-A-B-B-B-B-B-A-A-A-A-A-



-A-A-A-A-A-A-A-B-B-B-B-B-B-B-

Random copolymer: The monomer units are <u>randomly distributed</u> along the polymer chain.

..-A-B-B-A-A-A-A-B-A-A-B-B-B-B-B-A-B... (RANDOM SEQUENCE)

Examples: commercial polymer such as butadiene and styrene, butadiene and acrylonitrile.

Alternate copolymer: The monomer units are <u>arranged in an regular alternating manner.</u>

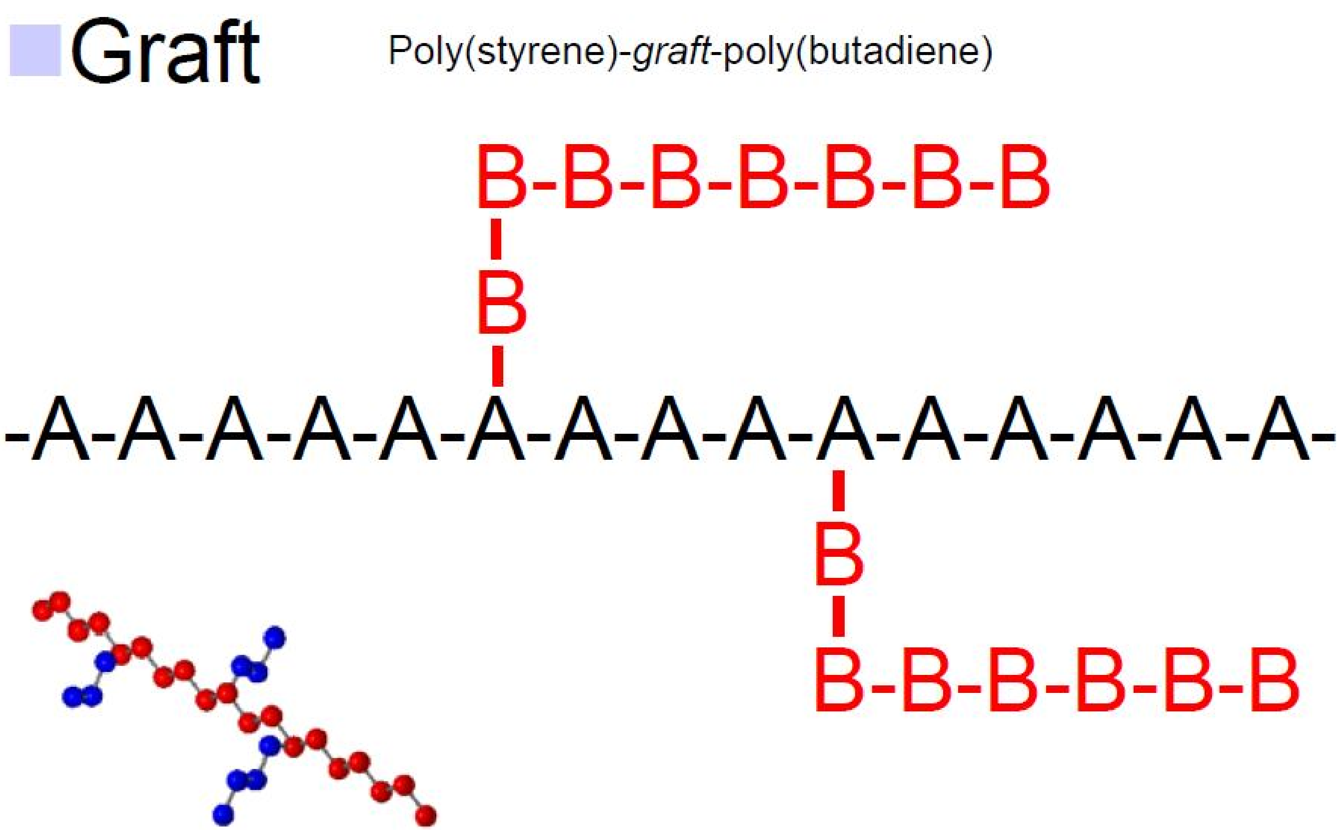
<u>....-A-B-A-B-A-B-A-B-A-B-A-B..</u>

Examples: Polyesters, polyamides, styrene-acrylonitrile..

Block copolymer: In this a block of repeating unit of one monomer is followed by a block of repeating unit of another monomer.

<u>..-A-A-A-A-B-B-B-B-A-A-A-A-B-B-B-B-A-A-A-A..</u>

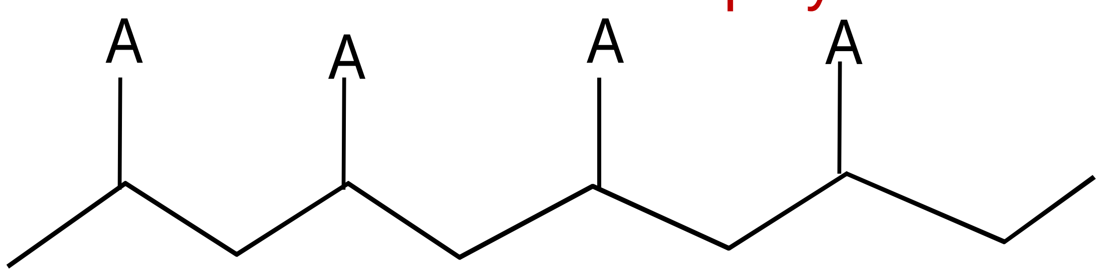
Graft copolymer: The polymer is formed by one type of repeating unit of monomer is grafted on a chain of monomer units of another types acting as backbone of the polymer.



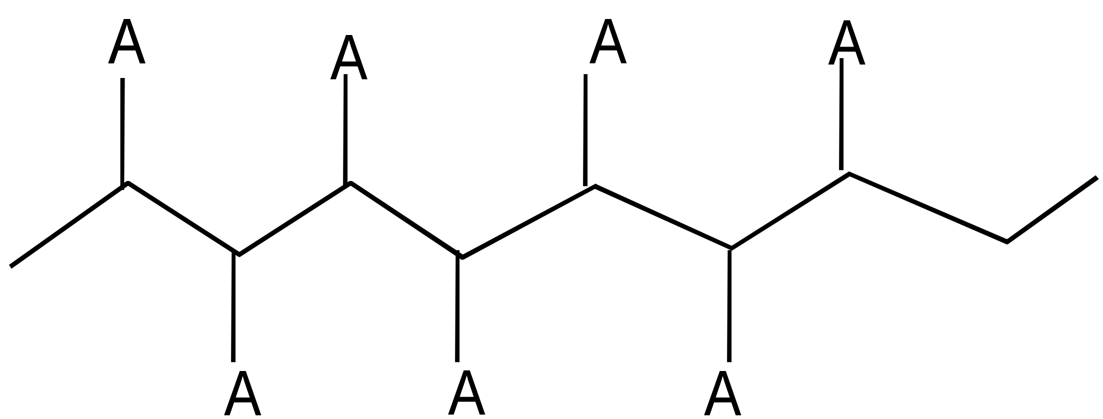
Tacticity (stereoisomerism) of polymers

The orientation of the monomeric units in a polymer molecule w.r.t. to main chain is called as the tacticity of the polymer.

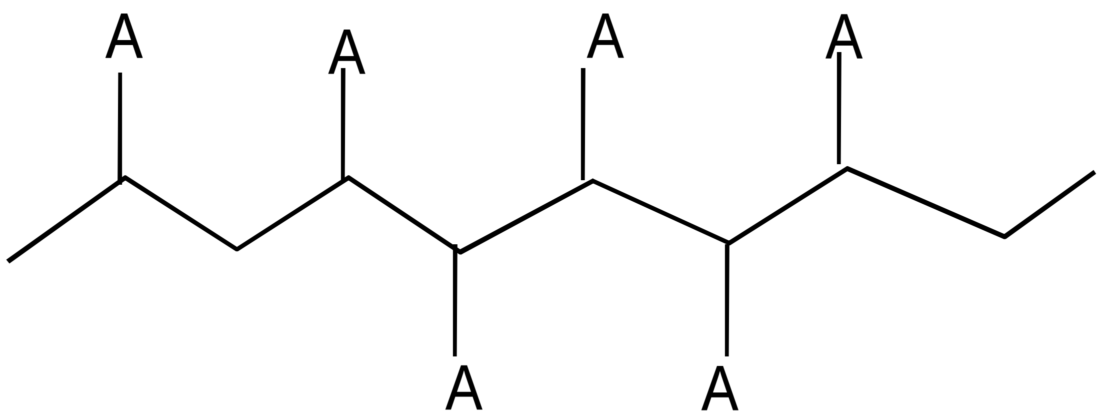
When all the functional groups or side groups are present on the same side of the polymer chain it is called as isotactic polymer



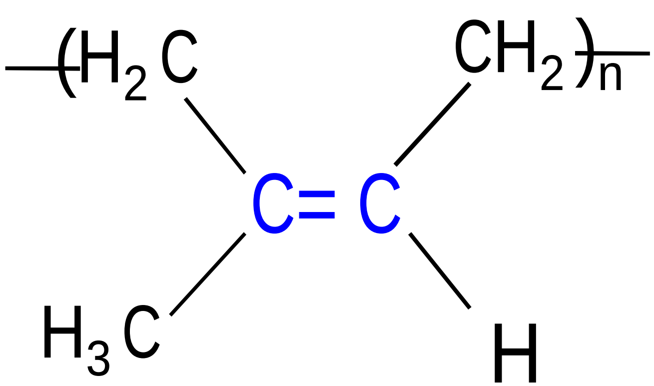
When the functional groups or side groups are present in an alternating manner it is called as syndotactic polymer



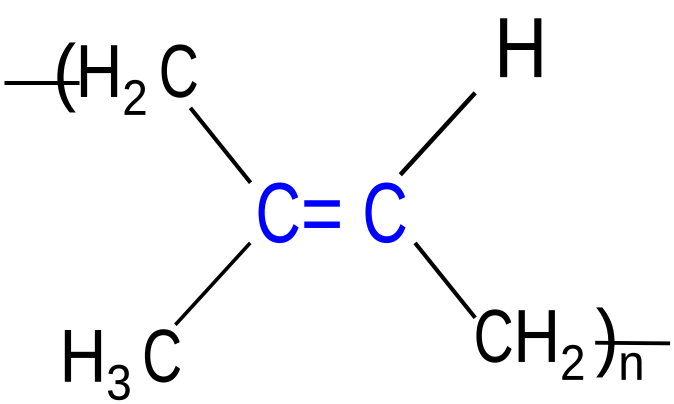
When the functional groups or side groups are present in random manner it is called as atactic polymer



Cis and Trans Isomer



Cis 1,4 polyisoprene (natural rubber)



Trans 1,4 isoprene (synthetic Rubber)

Molecular Weight of Polymers

- ❖Most of the properties of polymers such as viscosity, softening temperature, heat resistance, are influenced by the molecular weight.
- ❖Low molecular weight polymer are soft and gum like resins where as high M.W polymers are tough and exhibit better heat resistance.
- ❖Thus controlling M.W. is of great importance for industry and research.
- ❖However in the polymerization process all the polymer chains do not grow to same size.
- ❖The process of chain growth termination is random process and hence the chains have different molecular weights.

Molecular Weight of Polymers

As the polymer formed is of same chemical type but have different degree of polymerization (D.P) size and molecular weight, the average value of their molecular weight is taken.

- ❖Number average molecular weight
- ❖Weight average molecular weight

Lets say that the total number of molecules in a polymer is **N**

If N1 molecules in the polymer have molecular weight M1
N2 molecules have molecular weight M2
N3 molecules have molecular weight M2 and so on

$\therefore$ Total number of molecules $= N = N_1 + N_2 + N_3 + \ldots\ldots.N_i$

The molecular weight of N_1 molecules will be N_1M_1
The contribution by N_1 molecules will be

$$= \frac{N1\,M_1}{\sum N_i}$$

Similarly the molecules with different molecular weights n2, n3…

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \ldots.NiMi}{\sum n_i} = \frac{\sum \mathbf{Ni\,M_i}}{\sum \mathbf{N_i}}$$

❖Number average molecular weight ($\overline{M}_n$)

It is defined as the total mass (Mi) of all the molecules (Ni) in a sample divided by the total number of molecules present.

$$\overline{M}_n = \frac{\sum Ni\, M_i}{\sum N_i}$$

Determined by measurement of colligative properties such as

- ❖Freezing point depression
- ❖Boiling point elevation
- ❖Osmotic pressure etc.

Weight average molecular weight

Lets consider a polymer of molecular weight W

Let W_1 = the weight of the N1 polymer molecules having molecular weight M_1

W_2 = the weight of the N2 polymer molecules having molecular weight M_2

W_n = the weight of the *N* polymer molecules having molecular weight M_n

The total weight of the polymer is $W = W_1+W_2+W_3+W_4+W_5....W_i$

$= \sum W_i$

The weight fraction of W_1 Weight $= W_1/W$

The molecular weight contribution of W1 = W_1M_1/W

Similarly the contributions form others will be W_2M_2/W , W_3M_3/W

The average molecular weight $\overline{Mw} = \dfrac{W_1M_1+W_2M_2+W_3M_3+..........}{\sum W_i}$

$$= \frac{\sum W_i M_i}{\sum W_i} \qquad (1)$$

If the weight W1 contains N1 molecules of molecular weight M1 then

$W1 = N1 \times M1$

Similarly $Wi = Ni \times Mi$

Substituting for Wi in equation 1 becomes,

The average molecular weight Mw $= \dfrac{\sum Ni \times Mi \times M_i}{\sum NiMi}$

$$\overline{\mathbf{Mw}} = \frac{\sum \mathbf{NiMi^2}}{\sum \mathbf{NiMi_i}}$$

If a polymer sample has population of
25 molecules of molecular weight each = 15000
20 molecules of molecular weight each = 20000
5 molecules of molecular weight each = 25000

Calculate its number average and weight average molecular mass and find Mw/Mn ratio.

$$\overline{M_n} = \frac{\sum Ni\, M_i}{\sum N_i}$$

$$\overline{M_n} = \frac{[25 \times 15000 + 20 \times 20000 + 5 \times 25000]}{50}$$

$$\overline{M_n} = \frac{375000 + 400000+125000}{50} = \frac{900000}{50}$$

= 18,000

$$\overline{M_w} = \frac{\sum NiMi^2}{\sum NiMi_i}$$

$$\overline{M_w} = \frac{[25 \times (15000)^2 + 20 \times (20000)^2 + 5 \times (25000)^2]}{[25 \times 15000 + 20 \times 20000 + 5 \times 25000]}$$

$$\overline{M_w} = \frac{5625 \times 10^6 + 8000 \times 10^6 + 3125 \times 10^6}{900000}$$

$$\overline{M_w} = \frac{1.675 \times 10^{10}}{900000} = 18611.1$$

Mw/Mn = 18611/ 18000 = 1.033