POLYMERS / MACROMOLECULES

PART- I

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Sem V Honours

Polymer = ‘Poly’ (many) + ‘mer’ (part)

- Name a polymer used in daily life

  Polythene

- Name a biological polymer

  Proteins, DNA, RNA, cellulose

- Monomers are the building blocks of polymers.

Ethylene is the monomers of polythene.

Propylene is the monomer of polypropylene.

Styrene is the monomer of polystyrene.

- A polymer may be composed of a single type of monomer or more than one type of monomer.

Hexamethylene diamine and adipic acid are the monomers of Nylon 6,6.

Amino acids are the monomers of proteins.

The terms **polymer** and **macromolecule** are not synonymous.

A polymer is substance composed of macromolecules.

Macromolecules usually have a range of molar masses (g mol^{-1}) , the distributions of which are indicated by Dispersity.

CLASSIFICATION OF POLYMERS

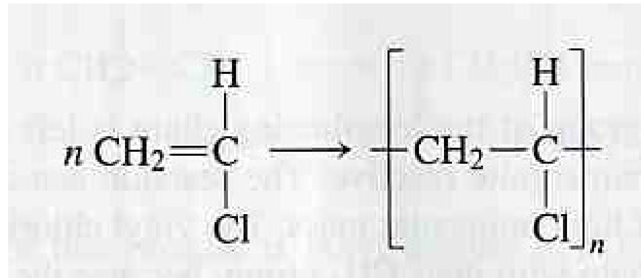
BASIS OF CLASSIFICATION	TYPES OF POLYMERS
Mode of formation	Addition, condensation
Chemical Structure	Homopolymer, co-polymer
Polymeric line structure	Linear, branched, cross-linked
Arrangement of monomers	Block copolymer, graft copolymer
Tacticity	Isotactic, syndiotactic, atactic
Thermal Behaviour	Thermoplastic, thermosetting
Origin	Natural, semi-synthetic, synthetic

MODE OF FORMATION

ADDITION/CHAIN-GROWTH POLYMERIZATION: The addition polymers are formed in a chain reaction of monomers containing double bonds. There is no net loss of atoms in this case.

Eg: polyethylene

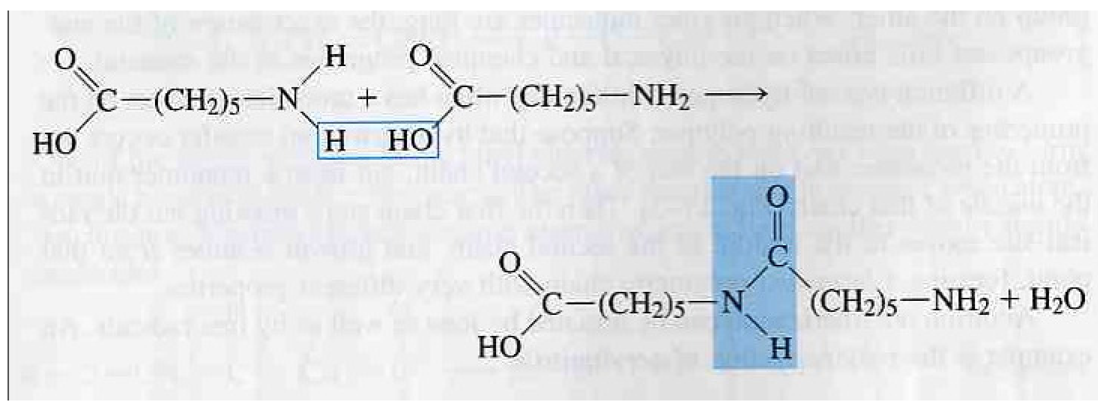
polypropylene



CONDENSATION/STEP-GROWTH POLYMERIZATION: The condensation polymers are formed by reaction between two difunctional or polyfunctional monomers with elimination of a small molecule such as water etc.

Eg: polyamides

polyester



Criteria of a monomer

- have unsaturation (double/triple bond)
- be polyfunctional (at least difunctional)

Number of functional groups (active site) present per molecule of the monomer defines its functionality.

Monofunctional: CH_3COOH (acetic acid), CH_3CH_2OH (ethyl alcohol)
Bifunctional: H_2NCH_2COOH (glycine)
$OHCH_2CH_2OH$ (ethylene glycol)
$CH_3CH(OH)COOH$ (lactic acid)
Trifunctional: $HOOCCH_2CH(OH)COOH$ (malic acid)
$HOOCCH_2CH_2CH(NH_2)COOH$ (glutamic acid)

CHEMICAL STRUCTURE

- HOMOPOLYMER: identical monomers

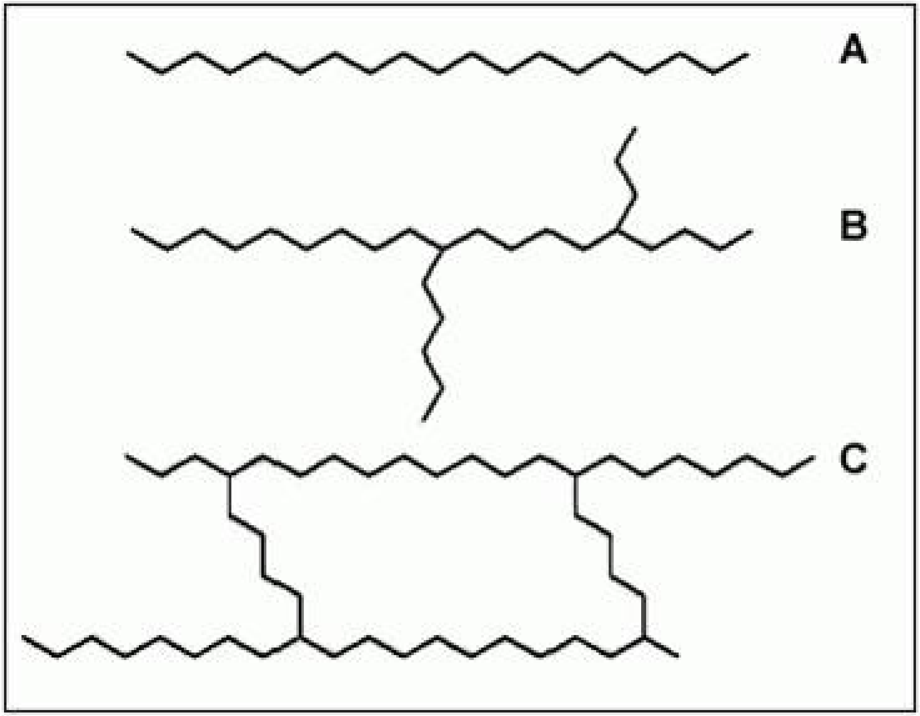
---A—A—A—A—A—A—A—

- COPOLYMER: more than one types of monomers

--A—B—A—B—A—B—A—B---

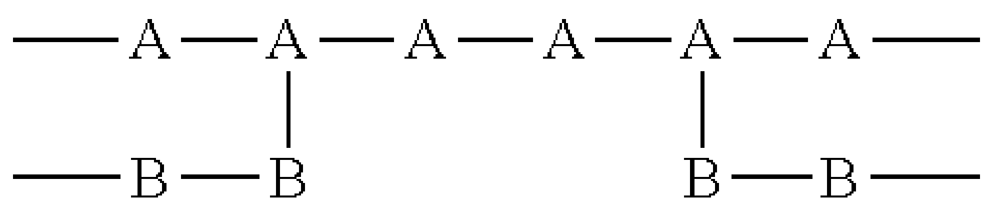
POLYMERIC LINE STRUCTURE

- LINEAR: represented by lines of finite lengths **A**
- BRANCHED: represented by lines of finite lengths with short or long branched structures of repeat unit **B**
- CROSS-LINKED: represented by a network structure (planar/space) **C**



ARRANGEMENT OF MONOMERS

- **BLOCK COPOLYMER:** Linear polymers in which identical monomeric units occur in relatively long sequences.
- **GRAFT COPOLYMER:** Branched copolymers in which monomer segments on the branches and backbone are not the same.



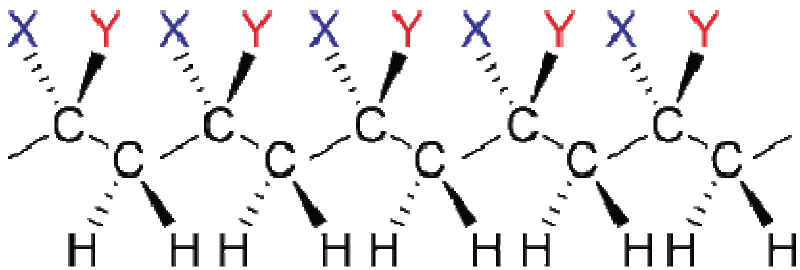
Graft Copolymer

Block Copolymer

TACTICITY

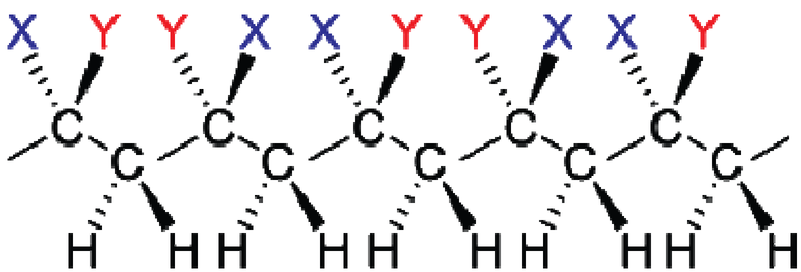
Orientation of monomer units in space is termed as tacticity

isotactic



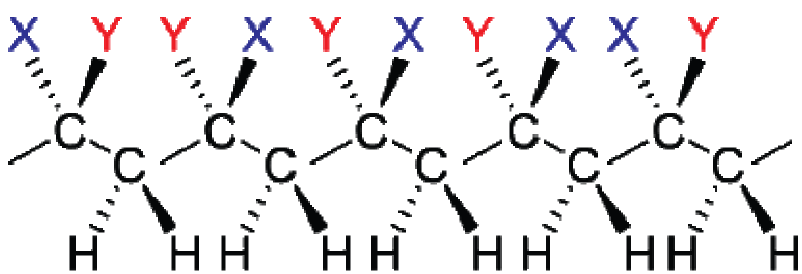
side groups of the monomers
lie on the same side of the chain

syndiotactic



side groups of the monomers
are arranged in alternate fashion
around the main chain

atactic



side groups of the monomers
are arranged randomly around
the main chain

THERMAL BEHAVIOUR

- **THERMOPLASTICS:** Polymers which soften on heating and become plastic so that they can be converted to any shape by moulding.

  eg: nylons, poly(vinyl chloride) etc.

- **THERMOSETS:** Polymers which change irreversibly into hard and rigid materials on heating and cannot be reshaped, once they are set.

  eg: polyesters, epoxy resins etc.

ORIGIN

- NATURAL: Available in nature.

  eg: natural rubber, cellulose, starch, protein.

- SEMISYNTHETIC: Chemically modified natural polymers.

  eg: hydrogenated/halogenated natural rubber

- SYNTHETIC: Prepared synthetically.

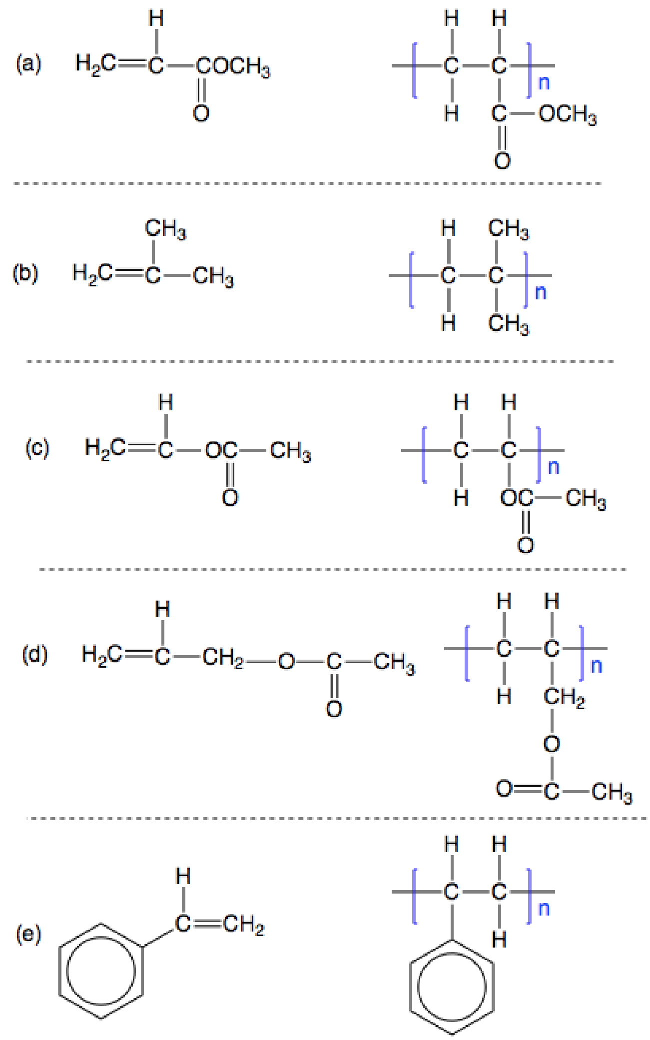
  eg: polyethylene, polystyrene

Relationship between average functionality (f), extent of reaction (p) and degree of polymerization ($\overline{X}_n$)

Carothers' equation

- **This equation is applicable to condensation polymerization reaction only, and <u>not</u> to addition polymerization reaction.**
- **This equation can be used to predict gelation in polyfunctional systems.**
- **The limitation of this equation is that practically gelation starts even at earlier stages than predicted by this equation because of uncontrolled local conditions in the hot viscous reaction mass.**

- Degree of polymerization: The number of repeat units in a given polymer molecule is known as its chain length or degree of polymerization.



- Average Functionality:

Calculated on the basis of stoichiometric equivalence of the two kinds of functional groups.

Consider a reaction between a dicarboxylic acid and trihydric alcohol.

HOOC—A—COOH + HO—B(OH)—OH

To strike stoichiometric equivalence the acid and the alcohol should be taken the molar ration 3:2.

Average functionality

= 12/5 = 2.4

Let N_0 be the total number of reacting molecules initially present giving an average functionality for the system as f.

Initial total number of functional groups = $N_0 f$

The related functional groups are assumed to be present in stoichiometric equivalence.

Let N be the number of molecules present at time t when the extent of reaction is p.

Thus, the number of molecules lost during the process over the time period t is given by $N_0 - N$

For each molecule lost the number of functional group lost is 2 (one of each kind).

Thus, the total number of functional group lost = $2 (N_0 - N)$

Thus, the extent of reaction $p = \frac{2(N_0 - N)}{N_0 f}$

or $$p = \frac{2}{f}\left(1 - \frac{N}{N_0}\right)$$

$\overline{X}_n$ is defined as the average number of structural units per polymer molecule.

Thus, $$\overline{X}_n = \frac{N_0}{N}$$

Therefore, $$p = \frac{2}{f}\left(1 - \frac{1}{\overline{X}_n}\right)$$ **Carothers' Equation**

This is important in understanding and control of the growth of polymers through polycondensation reactions. The critical extent of reaction p_c at the gel point for ($\overline{X}_n \to \propto$) is given by,

$$p_c = \frac{2}{f}$$

Carothers' equation for bifunctional system

f =2 for a bifunctional system.

Thus, the equation reduces to:

$$p = \left(1 - \frac{1}{\overline{X}_n}\right)$$

For *p*=1, $\overline{X}_n$ = ∝, which means that for complete reaction, the average degree of polymerization will be infinity, but short of complete reaction, the degree of polymerization is always a finite quantity.

Polymer obtained in a bifunctional system is under all practical situations, linear and hence soluble and fusible.

Carothers' equation for polyfunctional system

Consider a reaction between a dicarboxylic acid and trihydric alcohol.

HOOC—A—COOH + HO—B(OH)—OH **average functionality =2.4**

Carothers' equation will be:

$$p = \frac{2}{2.4}\left(1 - \frac{1}{\overline{X}_n}\right)$$

Thus, the value of p_c= 2/2.4 =0.83.

This means when the reaction is 83% complete, the polymer being formed in the polycondensation system gets cross linked and, hence, turns into an insoluble, infusible gelled mass. Thus, this condensation reaction should not be allowed to proceed beyond this point, otherwise the reaction mixture would turn into unusable product.