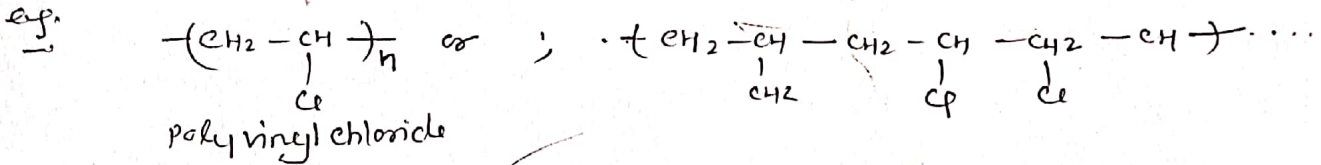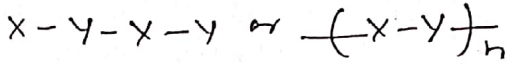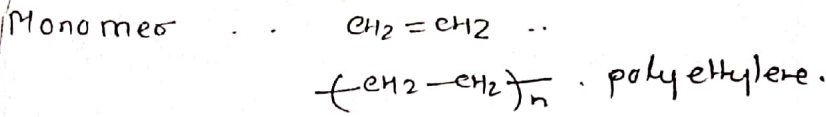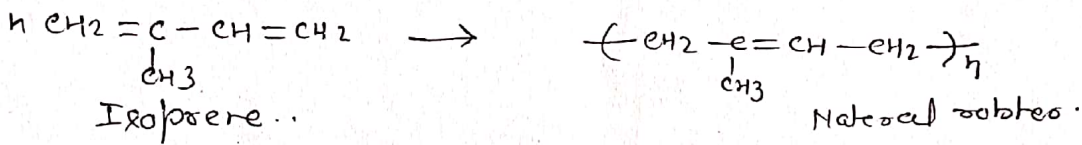# Polymers :-

Introduction, Classification, structure of organic and inorganic polymers, polymers of industrial importance, liquid crystalline and star polymers etc.
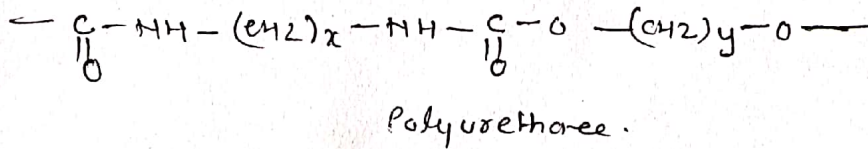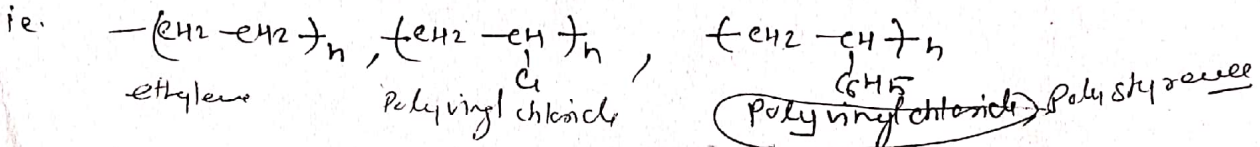

Monomer $\quad$ $CH_2 = CH_2$

$$-(CH_2 - CH_2)_n \cdot \text{polyethylene}$$

$$X - Y - X - Y \quad \text{or} \quad -(X - Y)_n$$

eg.

$$-(CH_2 - \underset{Cl}{CH})_n \quad \text{or} \quad ; \quad \cdot -(CH_2 - \underset{CH_2}{CH} - CH_2 - \underset{Cl}{CH} - CH_2 - \underset{Cl}{CH})- \cdots$$
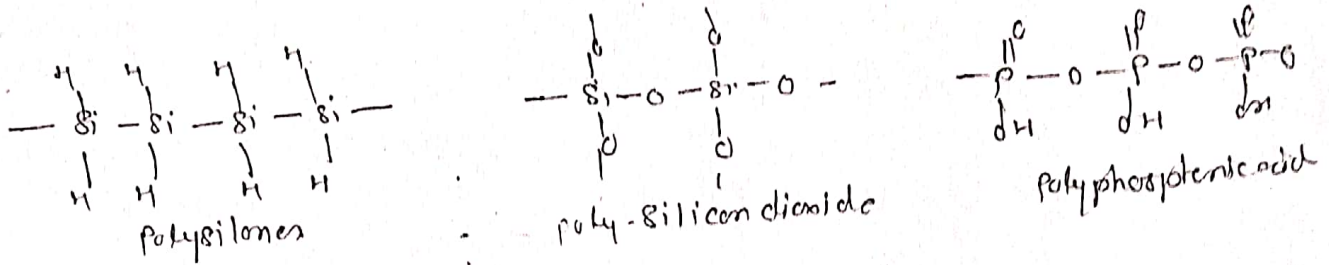
poly vinyl chloride

Classification of Polymer :-

① **Natural Polymer** → occur in nature ie they have vegetable or an animal origin, ie rubber, proteins, cellulose. of polysaccharides, wood and silk. cellulose of starch are the polymers of glucose. Proteins are the macromolecules containing the a large number of amino acids. Natural rubber contain isoprene (2-methyl-1,3-butadiene) repeat unit.

$$n \, CH_2 = \underset{CH_3}{C} - CH = CH_2 \quad \longrightarrow \quad -(CH_2 - \underset{CH_3}{C} = CH - CH_2)_n$$

$\qquad$ Isoprene .. $\qquad\qquad\qquad\qquad\qquad$ Natural rubber.

Synthetic or Organic Polymer :- ie. man-made polymer. ie. containing carbon, hydrogen, oxygen, nitrogen, sulphur and halogen atoms in the backbone or main chain.

ie. $\quad -(CH_2 - CH_2)_n$, $-(CH_2 - \underset{Cl}{CH})_n$, $-(CH_2 - \underset{C_6H_5}{CH})_n$

$\qquad$ ethylene $\qquad\qquad$ Polyvinyl chloride $\qquad$ (Polyvinyl chloride) Polystyrene

$$-\underset{O}{\overset{}{C}} - NH - (CH_2)_x - NH - \underset{O}{\overset{}{C}} - O -(CH_2)_y - O -$$
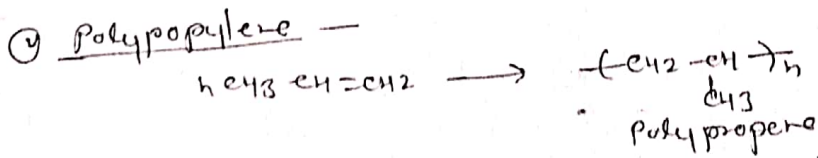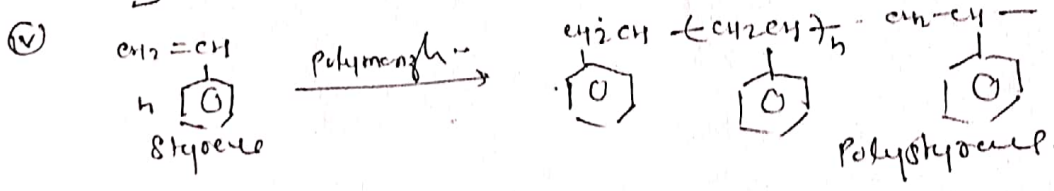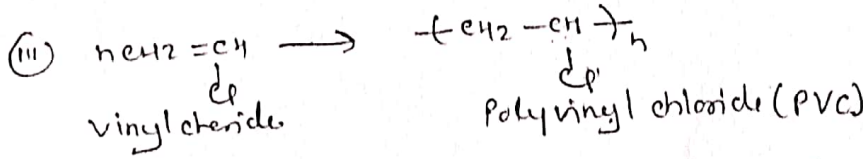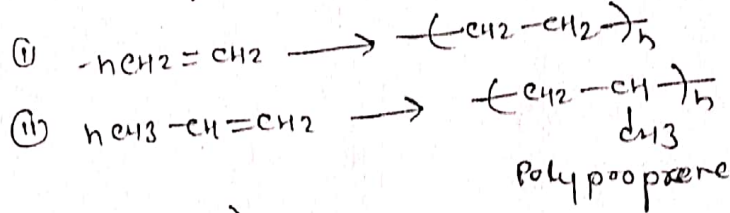
$\qquad\qquad\qquad\qquad$ Polyurethane.

(iii) __Inorganic Polymers__ :— These polymers contain no carbon atom ie. atoms joined by chemical bonds weak inter- molecular forces act Adleuce the chair.

Polysilones · poly-Silicon dioxide · Polyphosphoric acid

__Addition Polymers__ :—

Polyalkenes

(i) $- nCH_2 = CH_2 \longrightarrow \left(CH_2 - CH_2 \right)_n$

(ii) $n CH_3 - CH = CH_2 \longrightarrow \left(CH_2 - CH \right)_n$ ⎪ CH_3 Polypropene.

(iii) $n CH_2 = CH$ ⎪ Cl vinyl chloride $\longrightarrow \left(CH_2 - CH \right)_n$ ⎪ Cl Polyvinyl chloride (PVC)

(iv) $CH_2 = CH$ — Styrene — Polymerization — Polystyrene.

(v) __Polypropylene__ —

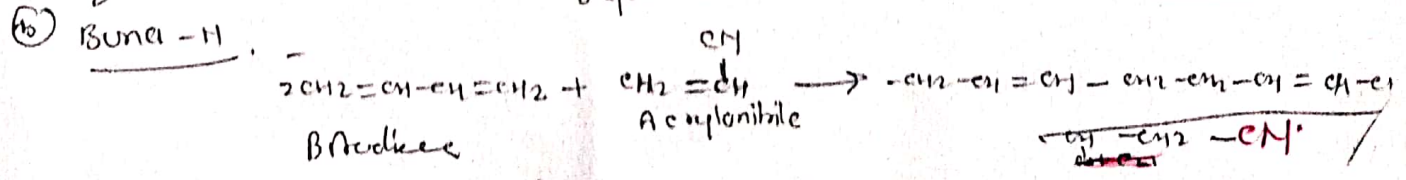$n CH_3 CH = CH_2 \longrightarrow \left(CH_2 - CH \right)_n$ ⎪ CH_3 Polypropene

__Properties & Uses__ :— Polypropene is quite resistent to acid and alkalies. It has high tensile strength, it is harder and stronger than polyethylene.

__Polydiens__ :— These polymers are obtained from the polymerization of __unsaturated__ hydrocarbons with two double bonds or

(i) __Synthetic Rubbers__ —
   (a) Buna Rubber   (b) Butyl Rubber.

(i) __Buna - S__

$n [CH_2 = CH - CH = CH_2] + n CH = CH_2$ ⎪ C_6H_5 Styrene / Butadiene $\xrightarrow{Na}$ $\left(CH_2 - CH = CH - CH_2 - CH - CH_2 \right)_n$ ⎪ C_6H_5 Buna - S.

(b) __Buna - H__

$2 CH_2 = CH - CH = CH_2 + CH_2 = CH$ ⎪ CN Acrylonitrile $\longrightarrow CH_2 - CH = CH - CH - CH_2 - CH = CH - CH_2 - CN$

(iv) Butyl Rubber :-

$$n\ CH_2 = CH - CH = CH_2 + (CH_3)_2 - C = CH_2 \longrightarrow \left(CH_2 - CH = CH - CH_2 - \underset{\underset{(CH_3)_2}{|}}{C} - CH_2 \right)_n$$

isobutyl-   Butyl rubber.

(v) Polyacrylates ..

(a) **Poly methyl methacrylates** -

$$n \left[CH_2 = \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \right] \xrightarrow{polymerisation} \left[CH_2 - \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \right]_n$$
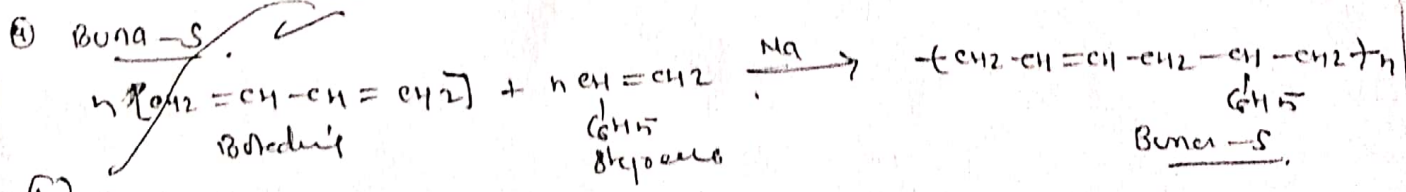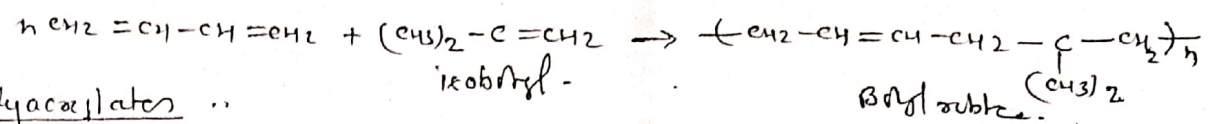
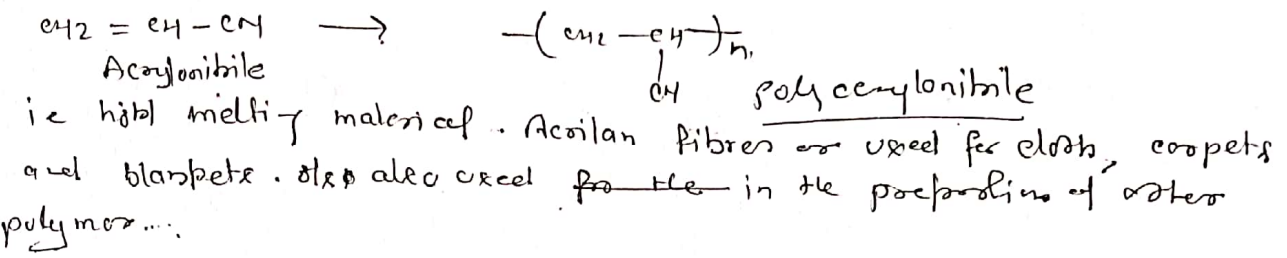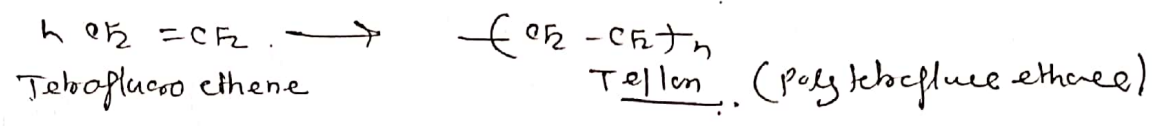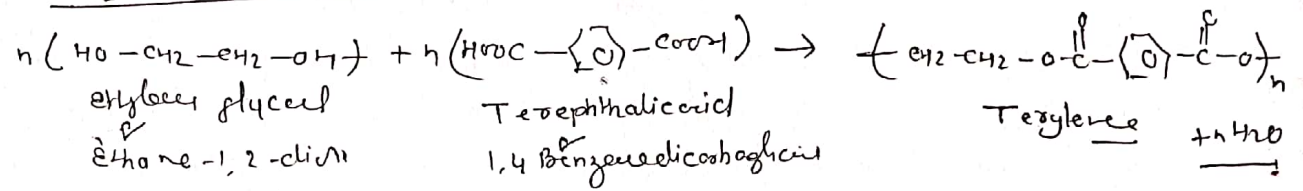Methyl methacrylate.   Poly methyl methoxylyf
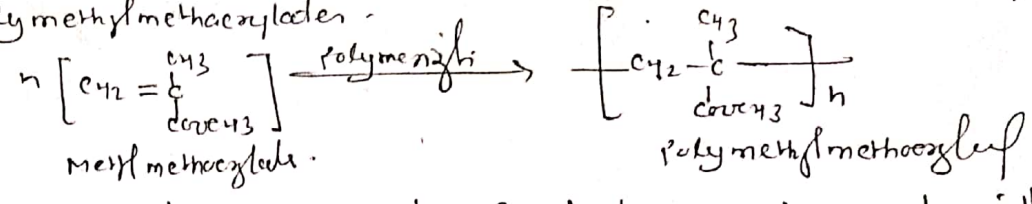
⊛ is hard_ transparent with high optical clarity - It has good resistance to effect of light and ageing. It is useful for lenses, transparent domes and skylights, dentures aircraft windows and protective coatings. Its commercial names are lucit lucite, plexiglass, acrylite - perspex.

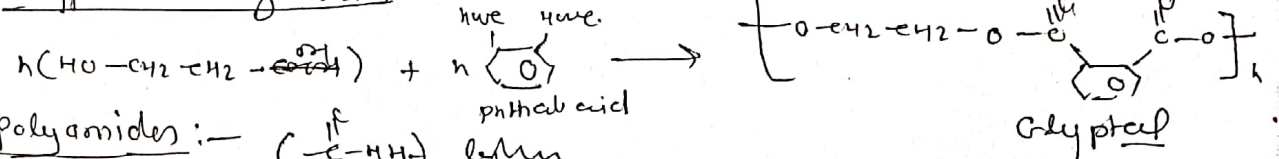$$n\ CF_2 = CF_2 \longrightarrow \left(CF_2 - CF_2 \right)_n$$
Tetrafluoro ethene   Teflon. (polytetrafluoro ethene)

$$CH_2 = CH - CN \longrightarrow \left(CH_2 - CH \right)_n$$
Acrylonitrile $\overset{\overset{|}{CN}}{}$ poly acrylonitrile

ie high melting material. Acrilan fibres or used for cloth, carpets and blankets. Also also used for the in the preparation of other polymer...

CONDENSATION Polymers.

① **Polyester** - $\left(R - \overset{\overset{O}{||}}{C} - O - R' \right)$

(a) **Terylenes (or decron)** :—

$$n\ (HO - CH_2 - CH_2 - OH) + n\ (HOOC - \langle O \rangle - COOH) \longrightarrow \left(CH_2 - CH_2 - O - \overset{\overset{O}{||}}{C} - \langle O \rangle - \overset{\overset{O}{||}}{C} - O \right)_n$$
ethylene glycol   Terephthalic acid   Terylene
ethane-1,2-diol   1,4 Benzenedicarboxylic   + n H_2O

(b) **Glyptal or alkyd resin** —

$$n(HO - CH_2 - CH_2 - OH) + n \underset{phthalic acid}{\overset{\overset{HOOC \quad COOH}{\langle O \rangle}}{}} \longrightarrow \left[O - CH_2 - CH_2 - O - \overset{\overset{O}{||}}{C} \underset{\langle O \rangle}{} \overset{\overset{O}{||}}{C} - O \right]_n$$
                                                                                                        Glyptal

② **Polyamides** :— $\left(\overset{\overset{O}{||}}{C} - NH \right)$ bylen

(a) **Nylon - 6** —

cyclohexane $\xrightarrow{oxidation}$ [benzene ring with O] $\xrightarrow{NH_2OH}$ [ring with N-OH] $\xrightarrow[Rearr]{H_2SO_4 \ Beckmann}$ [7-membered ring with $\overset{H}{N}$, =O]
                      cyclohexane   cyclohexanone   caprolactam
                                                                      oxime

nylon - 6, $\left(\overset{\overset{O}{||}}{C} - NH - (CH_2)_5 \right)_n \longleftarrow$ Polymerisation
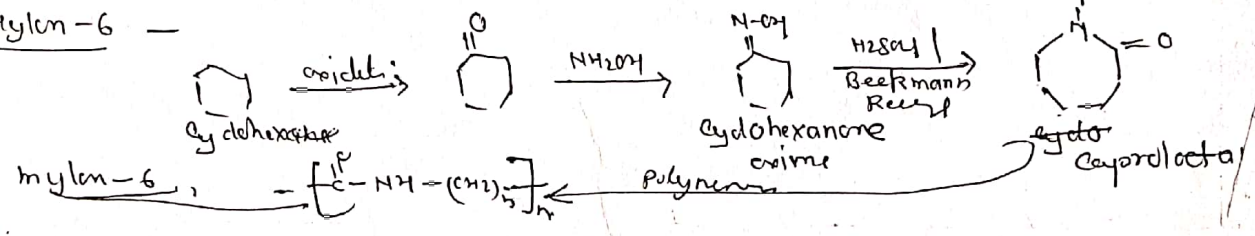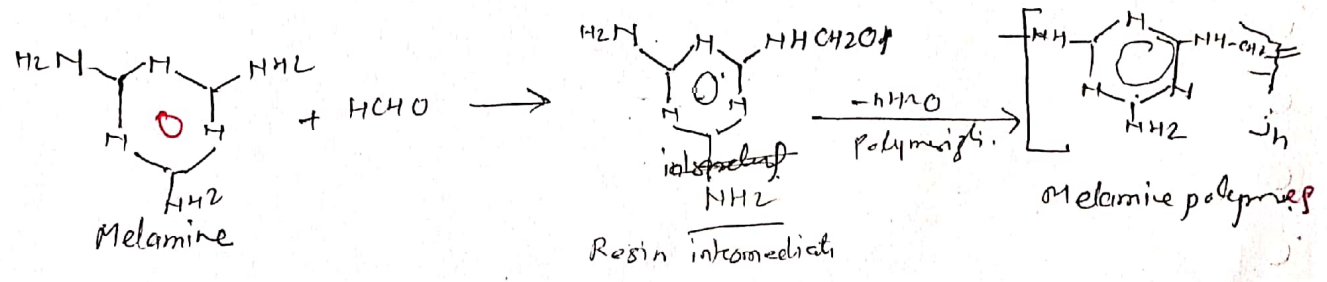
(4) **Formaldehyde Resins:** — Formaldehyde resins are typical thermosetting (4) plastics. This class of plastics include phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins. On heating these resins become highly cross-linked thereby forming infusible, and insoluble product.
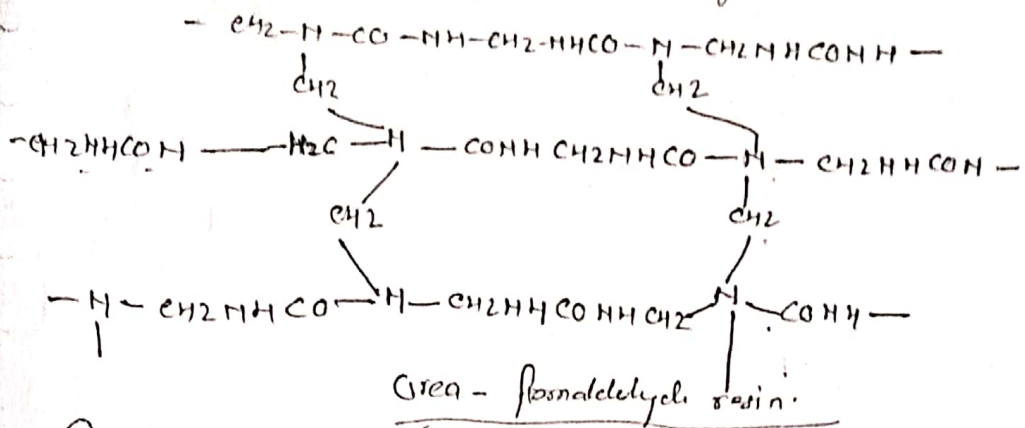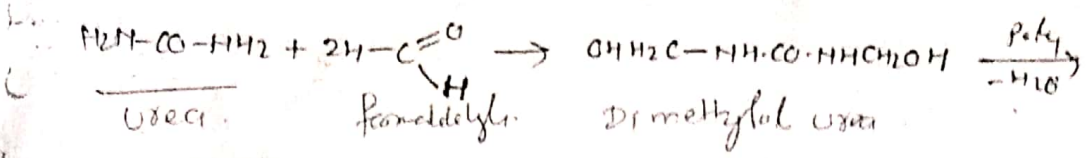
(a) **phenol-formaldehyde resins**

formation of linear

both up cross-linked

o-hydroxy benzyl alcohol   p-hydroxy Benzyl alcohol

polyoslup →

linear poly--

copdy---
-h'ho

high degree of polymerisation leads to the formation of hard bakelite which are used for making. combs, fountain-pen, barrels, phonograph records, electric goods, formica table-tops and. Gear wheels for steel rolling and paper miles, protective coatings of electrical apparatus. They can be laminated with paper, leather in order to obtain products with high resistance to impact.

(Part of Bakelite cross linked)

(b) **Melamine-formaldehyde resins** —

Melamine   + HCHO →   Resin intermediate   -h'ho / Polymerisation →   Melamine polymer

$$n\ HO-\overset{O}{\overset{||}{C}}-(CH_2)_4-\overset{O}{\overset{||}{C}}-OH + n\ H_2N-(CH_2)_6-NH_2 \longrightarrow n\left[\bar{O}-\overset{O}{\overset{||}{C}}-(CH_2)_4-\overset{O}{\overset{||}{C}}-\bar{O}\ H_3\overset{+}{N}-(CH_2)_2-\overset{+}{N}H_3\right]$$

Adipic acid   Hexamethyl diamine   1:1 Salt (Nylon)

$$\xrightarrow[\text{polyms}]{\text{heat}} -O-\overset{O}{\overset{||}{C}}-(CH_2)_4-\overset{O}{\overset{||}{C}}\left[-NH-(CH_2)_6-NH-\overset{O}{\overset{||}{C}}-(CH_2)_4-\overset{O}{\overset{||}{C}}-\right]NH-(CH_2)_6-NH_2$$

         nylon 66 $+\ (2n-1)\ H_2O$

③ **Polycarbonate:**

$$HO-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\langle O\rangle-OH + Cl-\overset{O}{\overset{||}{C}}-Cl \xrightarrow[-HCl]{\text{Pyridine}} H\left[-O-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\langle O\rangle-O-\overset{O}{\overset{||}{C}}\right]_n-O-Ph-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-Ph-OH$$

Bisphenol A   phosgene   polycarbonate

Co-polymerization :→ Copolymerization is the combined polymerization of two or more monomer species.

       —A—A—A—A—   Homo polymere

       —A—B—A—A—   Copolymere.

ⓐ **Random Copolymer** —

     A—B—B—A—B—A—A—B—B—A—A—B—B —

           Random Sequence.

    ex. butadiene and styrene, butadiene and acrylonitrile

ⓑ **Alternative Copolymer** —

       —A—B—A—B—A—B—A—B— — — — ·

         AB—AB—AB— — —

   ex. polyesters, polyamides, styrene–acrylonitrile, styrene–maleic anhyd

ⓒ **Block Polymer** —

         —A-A-A-A—B-B-B-B-A-A-A-A—

ⓓ **Graft Copolymer** —

     —A—A—A—A—A—A—A—A—A— —

           | |

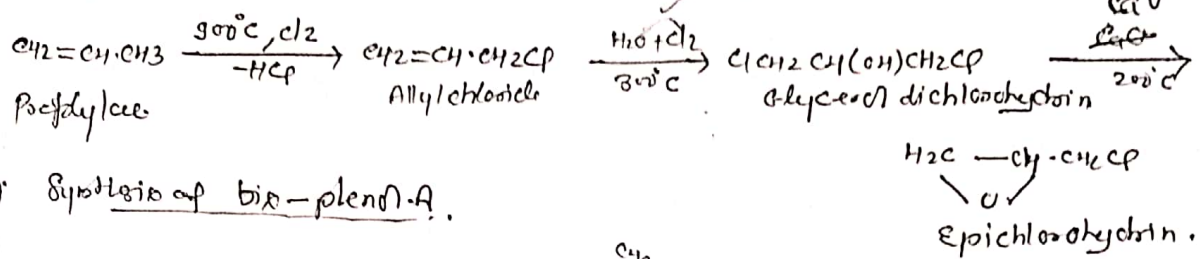   B   B

           B   B

           B   B
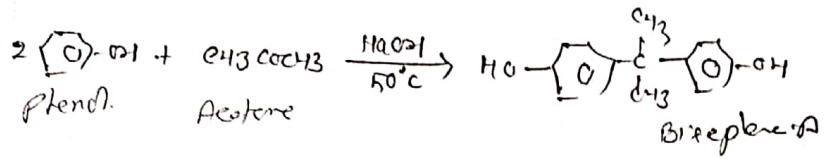
           B

(C) Urea formaldehyd – (Urea formaldehyde resin)

$$H_2N-CO-NH_2 + 2H-C\!\!\begin{smallmatrix}O\\H\end{smallmatrix} \longrightarrow OH H_2C-NH\cdot CO\cdot NHCH_2OH \xrightarrow[-H_2O]{Poly}$$

Urea   formaldehyde   Dimethylol urea

$$-CH_2-N-CO-NH-CH_2-NHCO-N-CH_2NHCONH-$$
$$\qquad\quad CH_2 \qquad\qquad\qquad CH_2$$

$$-CH_2NHCON-\!\!-H_2C-H-CONH\,CH_2NHCO-N-CH_2NHCON-$$
$$\qquad\qquad\qquad CH_2 \qquad\qquad\qquad\qquad CH_2$$

$$-N-CH_2NHCO-N-CH_2NHCONH CH_2-N-CONH-$$

Urea – formaldehyde resin.

(5) **Epoxy Resins:** — (Polyether)

(a) Synthesis of epichlorohydrin —

$$CH_2=CH\cdot CH_3 \xrightarrow[-HCl]{500^\circ C, Cl_2} CH_2=CH\cdot CH_2Cl \xrightarrow[30^\circ C]{H_2O+Cl_2} ClCH_2 CH(OH)CH_2Cl \xrightarrow[200^\circ C]{CaO/CaCl}$$

Propylene   Allyl chloride   Glycerol dichlorohydrin

$$H_2C-CH\cdot CH_2Cl$$ (epoxide)
Epichlorohydrin.

(b) Synthesis of bis-phenol-A.

$$2 \langle O\rangle\text{-}OH + CH_3COCH_3 \xrightarrow[50^\circ C]{HaOH} HO-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{C}}-\langle O\rangle-OH$$

Phenol   Acetone   Bisphenol-A

Bisphenol-A + $H_2C-CH\cdot CH_2Cl + HO-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{C}}-\langle O\rangle-OH \xrightarrow[condensation, abu\ 60^\circ C]{aq.\ NaOH\ (catalyst)}$

$$H_2C-CH-CH_2\left[O-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{C}}-\langle O\rangle-O-CH-CH_2\right]_h O-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{C}}-\langle O\rangle-OH$$

Epoxy resin.

or

$$\left[O-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{C}}-\langle O\rangle-O-CH_2-\underset{OH}{\overset{}{C}}-CH_2\right]_n O-$$

epoxy resin.
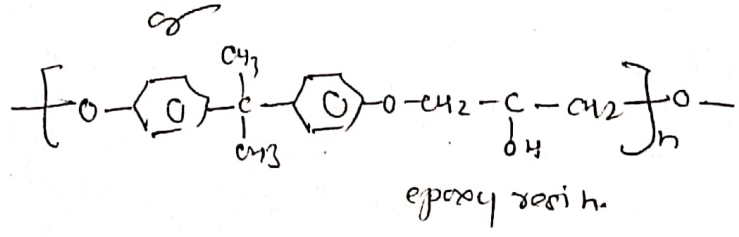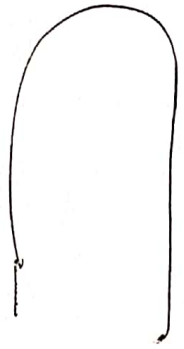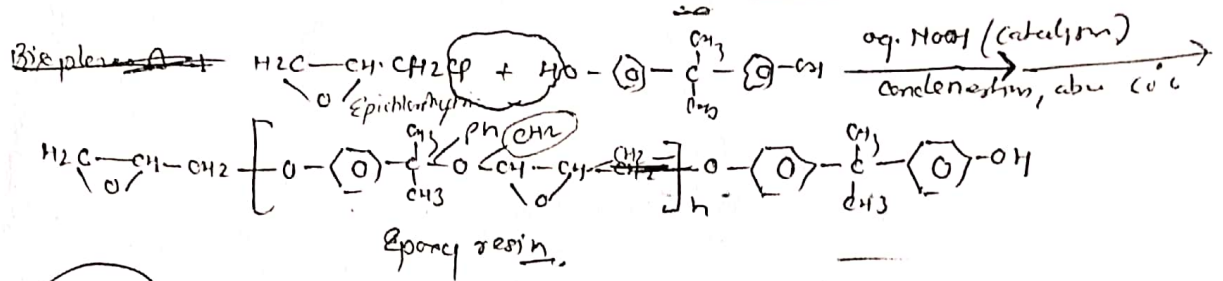
Molecular Weight of Polymers :-

M.W. of a polymer influences various properties of a polymer such as solution viscosities, softening temp; tensile and impact strength and heat resistance. The low M.W. polymers are generally soft and gum like resins. The high M.W. polymers are tougher and more heat resistance, thus control if molecular weight of a polymer is often important for industrial polymerization. The M.W. of polymer depends upon the number of simple molecules joined together during polymerization reactions i.e. upon the degree of polymerization. But the polymerization chains are broken at different stages, therefore the final product will contain the macromolecules of different weights Most of the polymers are polydisperse ie. the molecules of the polymers sample do not have identical molecular weights (M). Hence it is necessary in their case to take average molecular weight. There are two type of average molecular weights.

① **The no. average molecular weight. (Mn) -**

$$M_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \cdots}{n_1 + n_2 + n_3 + \cdots}$$

where $n_1, n_2, n_3 \cdots$ are the numbers of molecules having masses $M_1, M_2, M_3, \cdots$ respectively..

$$\sum \overline{M_n} = \frac{\sum n_i m_i}{\sum n_i} \qquad -①$$

② **The Weight-Average Molecular Weight ($\overline{M_w}$),**

$$\overline{M_w} = \frac{m_1 M_1 + m_2 M_2 + m_3 M_3 + \cdots}{m_1 + m_2 + m_3 + \cdots}$$

if $n_1, n_2, \cdots$ denote the number of molecules having masses $M_1, M_2, \cdots$ then, $m_1 = n_1 M_1, \quad m_2 = n_2 M_2$ (also $m_i = n_i M_i$)

$$\overline{M_w} = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \cdots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \cdots}$$

$$\sum \overline{M_w} = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\sum w_i M_i}{\sum w_i} \qquad -②$$

from ① & ② it is clear that $\overline{M_w}$ is always greater than $\overline{M_n}$ for polydisperse systems. For monodisperse system $\overline{M_w} = \overline{M_n}$, then the ratio $\overline{M_w}/\overline{M_n}$ is known as distribution ratio as an index of polydispersity.

⑭ Z-average M.W. ($\overline{M_z}$) -
$$\overline{M_z} = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} \qquad -③$$

$\overline{M_z} > \overline{M_w} > \overline{M_n}$ is real polymer system.

$\overline{M_n} : \overline{M_w} : \overline{M_z} = 1 : 1.306 : 1.617$

Question 1 → # A polyaverage sample polydispersate re prepared by mix — three monodisperse sample in the following proportion.

1g — 10,000 M.w.
2g — 50,000 M.w
2g — 1,00,000 M.w

A polydisperse sample of polystyrene is prepared by mixing —

Using this above proportion, calculate the number average (m.w), weight average m.w.

Soln:)

(i) $$\overline{M_n} = \frac{\sum\limits_{i=1}^{3} N_i m_i}{\sum\limits_{i=1}^{3} N_i} = \frac{\sum\limits_{j=1}^{3} w_j}{\sum\limits_{j=1}^{3} \left(\frac{w_j}{m_j}\right)} = \frac{1+2+2}{\left(\frac{1}{10,000} + \frac{2}{50,000} + \frac{2}{1,00,000}\right)} = 31,250$$

(ii) $$\overline{M_w} = \frac{\sum\limits_{j=1}^{3} N_i m_i^2}{\sum\limits_{j=1}^{3} N_i m_i} = \frac{\sum\limits_{j=1}^{3} w_i m_i}{\sum\limits_{j=1}^{3} w_i} = \frac{10,000 + 2(50,000) + 2 \times (1,00,000)}{5} = 62,000 \frac{g}{mol}$$

Q.2

1g — 20,000 m.w
2g — 40,000 m.w
3g — 80,000

$$\overline{M_n} = \frac{1+2+3}{\frac{1}{20,000} + \frac{2}{40,000} + \frac{3}{80,000}} = \frac{6}{0.00005 + 0.00005 + 0.0000375}$$

$$= \boxed{43636 \cdot 364}$$

$$\overline{M_w} = \frac{(1) \times 20,000 + 2 \times (40,000) + 3 \times (80,000)}{1+2+3} = \boxed{56666 \cdot 67}$$

(i) Molecules weight in next page.

(ii) Secondary Valency forces :- s. Vander waall forces, affect the mechanical strength of polymers. The strength of these forces increases with the increase polarity and decreases sharply with increasing distance. The individual engies in straight chain and branched chain polymer are low but the cumulative effect of large number of these bonds along the polymer chain results in large electrostatic fields of attraction. Such polymers exhibit mechanical strength only when chain length is greater than 150 to 200 atoms in a line. Usually the low m.w.p. are soft, brittle and low heat resistant. The strength of the straight chain polymers depends on the deformation power. Polyvinyl chloride is a hard and stronger polymer than polyethylene because of polar atom chlorine. The cross linked polymers are most strong and hard, because of sharp covalent covalent bonds which restrict the slipping of one molecule over the Mol.

(3) Mechanical Properties (Deformation) →

Generally the deformation is found in thermoplastics polymers on application of heat or pressure or both as they are low heat resistant. At low strain (<1 %), the deformation of most polymers is elasto elastic meaning that the deformation is homogeneous and full recovery can occur over a finite time. The linear polymers without bonded or cross linked structure show the greatest degree of deformation because of the weak intermolecular forces prevails in these polymers. At high temp, the Vander Waals forces become weak and consequently easy deformation occurs. While in case of cross-linked and branched polymers which are having more covalent bonds than weaker intermolecular forces, deformation does not occur on heating. These are generally the thermosetting polymers. Such polymers are, at higher strains, the deformations are not reversible unless the polymer is heated above its glass transition temp. (tg).

Crystallinity in Polymers :-

Some polymers cooled from the melt can organise into regions crystalline structure. The polymers show a coarse structure and called crystalline polymers. The crystalline polymers of high m.w. have perfect organization than crystals of low m.w.p. crystallized from the solution. The basic units of crystalline polymer morphology are crystalline lamella consisting of arrays of folded chains. Crystalline regions occur when several polymer molecules or structures of polymer molecules are oriented parallel to each other. Under these conditions weak interchain forces hold the molecules together conferring strength on the polymer. On the other hand the polymer molecules are not sufficiently close to each other for the inter-chain forces to operate. These regions are formed as amorphous.
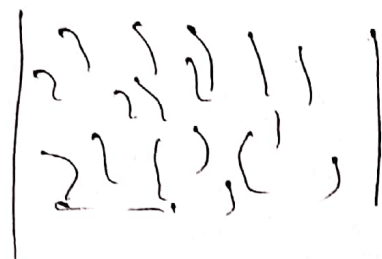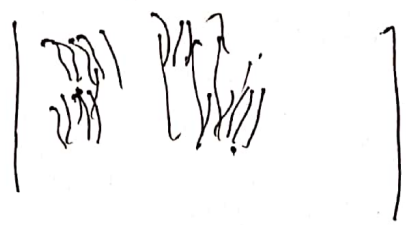
(a) amorphous.   (b) crystalline polymer.   crystal polymer. embedded in an amorphous matrix.

- Plastic is mainly amorphous and a fibre is a highly crystalline.

Some point for crystalline polymer :-

(i) Some polymers crystallised from the melt or from concentrated solution, crystallites can organise into larger spherical structure called spherulites.

(ii) Since no polymer is completely crystalline, which may exhibits both a glass transition temp. (tg) corresponding to large scale segmental motion in the amorphous region and a crystalline melting temp (tm) at which crystallites are destroyed and an amorphous disordered melt is formed.
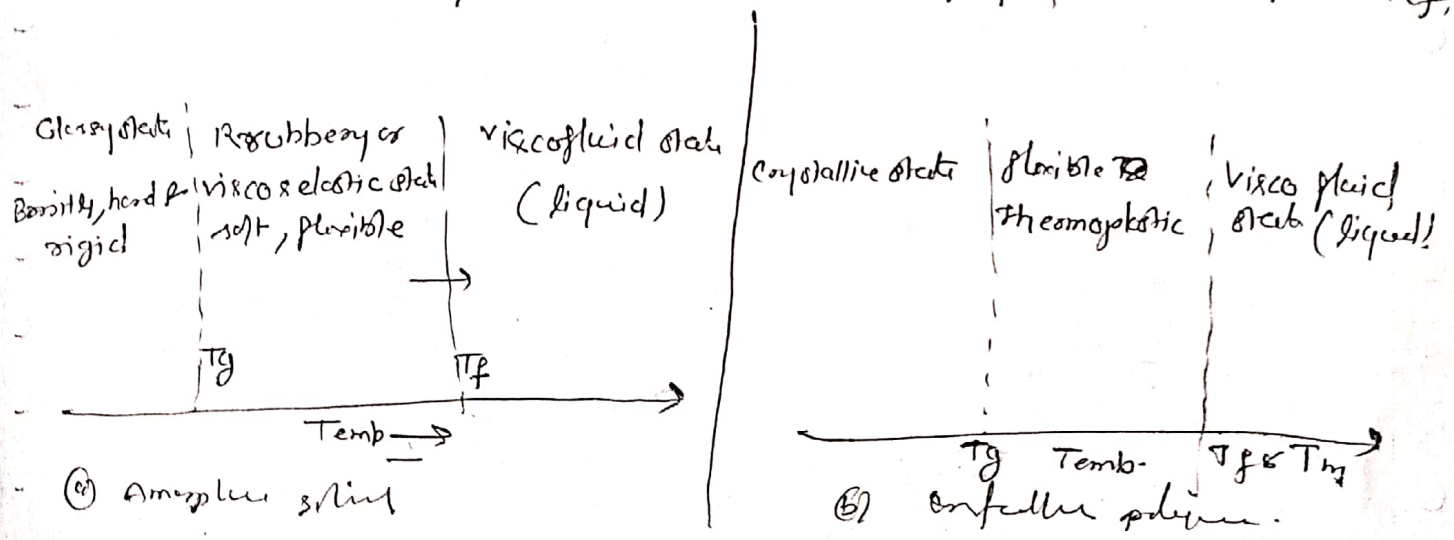
(iii) In fibrous polymeric structures, the small aggregated crystallites that are large enough to appear as a small thread like units are called fibrils.

(4) transparency of crystalline polymers is more or less directly dependent on the size of spherulites. Larger size spherulites decrease the transparency of a given polymer.

(or)

→ **The Amorphous State:** — Completely amorphous polymers exist as long, randomly coiled, interpenetrating chains. These are capable of forming stable, flow restricting entanglements at sufficiently high m.w. The liquid phase state is characterized by the absence of any two long range order. Two situations here are ① where molecular mobility is frozen, and ② where molecular mobility is activated. In both the situations, no long range order is exhibited. When the substance does not possess any molecular mobility, it exists as a physical solid, but it does not possess any long range order, so it is unable to crystallise. So i.e. amorphous solids.

An amorphous substance cannot exhibit crystallinity, but can exist as a glassy solid (liquid phase state) or as a molten liquid and the transition from the glassy solid to molten liquid occurs at a temp.

GLASS TRANSITION TEMPERATURE: — The temp that marks the transition from the amorphous solid state to the melt state is called the glass transition temp. (T_g). The T_g below which polymer is hard, brittle and rigid glassy state and above which it is soft, flexible. The T_g marks in isoviscous state i.e., viscosity increases rapidly as a polymer is cooled from the melt state. At T_g point, on further heating the polymer without boiling or cools linked onen, becomes a highly viscous liquid and starts flowing. This state is termed as viscofluid state, the transition taking place at its flow temp.

Glassy state	Rubbery or	Viscofluid state
Brittle, hard &	viscoelastic state	(liquid)
rigid	soft, flexible	

T_g T_f

Temp →

(a) Amorphous solid

| Crystalline state | flexible | Visco fluid |
| | Thermoplastic | state (liquid) |

T_g Temp. T_f & T_m

(b) Crystalline polymer.

- In case of amorphous polymers, there is no any clear melting point. When a polymer changes from one state to another, there is a gradual change in many of its physical (specific volume, specific heat, density, dielectric constant, etc.). ...

(a) Highly crystalline. (b) Amorphous. (c) Partially crystalline.
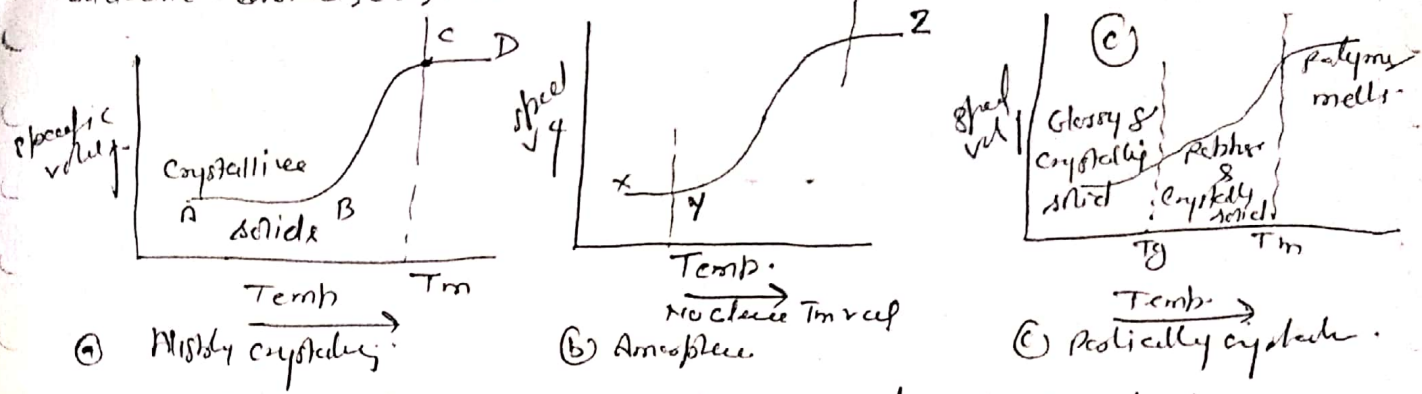
- The following factors which influence the glass transition temp.

① Segmental and chain mobilities are easier in noncrystalline polymers than in crystalline polymers.

② Linear polymer chains made of single bonds have a high degree of freedom for rotation, thus they have higher **segmental mobility** than the bulkier, aromatic co cyclic structure polymers.

③ The polymers having more secondary valency forces are having higher mobility.

④ Those polymers having polar segments show lower mobility.

- The t_g (temp) of polymer is influenced by its **molecular weight** upto around a value of 20,000.

- The (Tm) is the temp of the crystalline polymer where it melts to the liquid state.

CHEMICAL PROPERTIES OF POLYMERS :→

The chemical structure of a polymer determines whether it will be crystalline or amorphous.

① Solubility, like dissolve like:
- (a) polymers of more aliphatic character are more soluble in aliphatic solvents; while aromatic ones are more soluble in aromatic solvents.

② Solubility of polymers in a given solvent decreases with increase in M.W. of polymer as the viscosity of the solution increases.

ⓒ Greater the degree of cross-linking in the polymer, lesser is its solubility.

ⓓ Polar polymers are soluble in polar solvents like water, alcohol, phenols, etc.

ⓔ Non-polar polymers are soluble in nonpolar solvent like benzene, toluene, petrol etc.

W-Average:- The average molecure weight $\bar{M}$, may we express as ...

$$\bar{M} = \frac{\sum_i N_i M_i^{\alpha}}{\sum N_i M_i^{\alpha-1}} \qquad -①$$

where N_i indicates the number of moles of molecules with a molecular weight of M_i and the parameter α is a weighting factor that defines a particular average of the M.W. distribution. The weight W_i, of molecules with molecular weight M_i be then.

$$W_i = N_i M_i \qquad -②$$

M.W. that are important in determining polymer properties are the number average, $\bar{M}_n$ $(\alpha=1)$, the weight-average, $\bar{M}_w$ $(\alpha=2)$, and the z-average, $\bar{M}_z$ $(\alpha=3)$, and M.W.

(fig. .. continuous distribution of m.w as plot of the no. of moles of chains N, having m.w. M, against M.)

. from eqn ① that the number average M.W. for a discrete distribution of m.w. is given as

$$\bar{M}_n = \frac{\sum\limits_{i=1}^{N} N_i M_i}{\sum\limits_{i=1}^{N} N_i} = \frac{\sum\limits_{i=1}^{N} W_i}{\sum\limits_{i=1}^{N} (W_i / M_i)}$$

where N is the total no. of molecular weight species in the distribution.
the expression ie. the number average molecular weight

$$\bar{M}_n = \frac{\int_0^{\infty} N M \, dM}{\int_0^{\infty} N \, dM}$$

the respective relationship. For the weight-average average M.W of a discrete and a continuous distribution etc.

$$\overline{M_w} = \frac{\sum\limits_{i=1}^{N} N_i M_i^2}{\sum\limits_{i=1}^{N} N_i M_i} = \frac{\sum\limits_{i=1}^{N} w_i M_i}{\sum\limits_{i=1}^{N} w_i} \quad\text{—(I)}$$

and,

$$\overline{M_w} = \frac{\int_0^\infty N M^2 \, dM}{\int_0^\infty N M \, dM} \quad\text{—(V)}$$

In the case of high-M.W. polymer, the number-average m.w. is directly determined by membrane osmometry, while the weight-average M.W. is determined by light scattering and other scattering technique.

To measure of the breadth of the M.W. distribution is given by the ratios of M-W. averages. For this purpose, the most commonly used ratio is $\overline{M_w}/\overline{M_n}$, which is called the poly dispersity index.
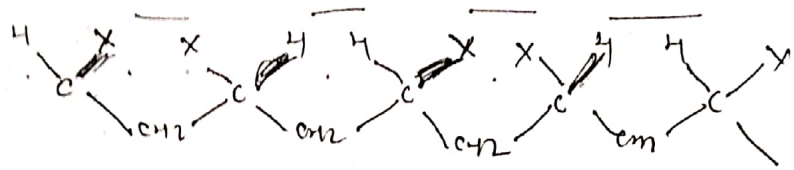
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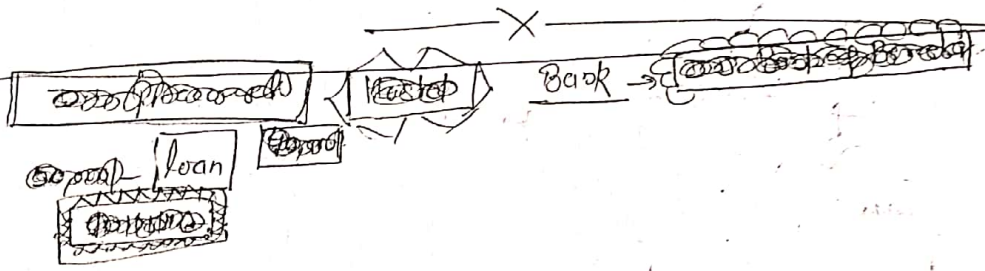
(i) **Isotactic** — The head to tail configuration in which the functional groups are on the same side of the chain.

same side of plane
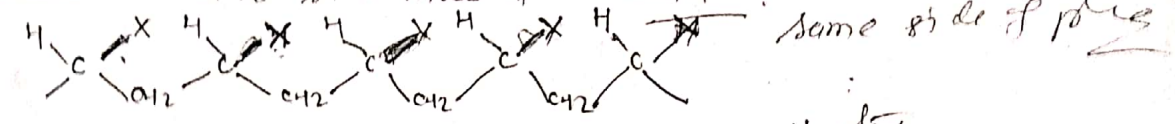
(ii) **Syndioctactic** — arrmt of side groups are at random alternating around the main chain

(iii) **Atactic** —

Aloctic

, random

→ If the arrmt of side groups is in alternating position, one at, it is called syndiotac

Tacticity → The orientation of monomer units in a polymer molecule can take place in an orderly or disorderly (tacticity) fashion with respect to main chain. The difference in configuration do effect their physical properties.

(i) **Isotactic** → The arrangement of functional groups are all on the same side of the chain.
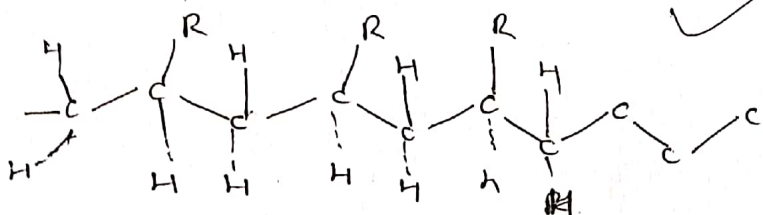
(ii) **Atactic** → arrangemt of functional group are at random around the main chain it is called atactic.
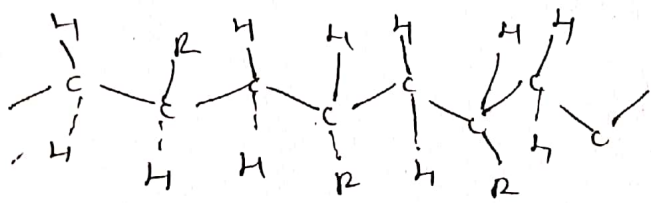
(iii) **Syndiotactic** → The arrangmt of side groups is in alternating fashion,