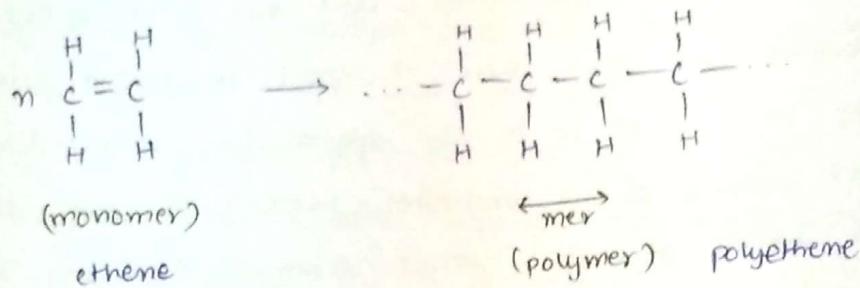


* Polymers : Polymers are macromolecules built by linkage of a large no. of small molecules (monomers).

e.g. Polyethene is a polymer of ethene.

* Monomers : The small molecules which combine to form a polymer are called monomers. The repeating unit is called 'mer'.



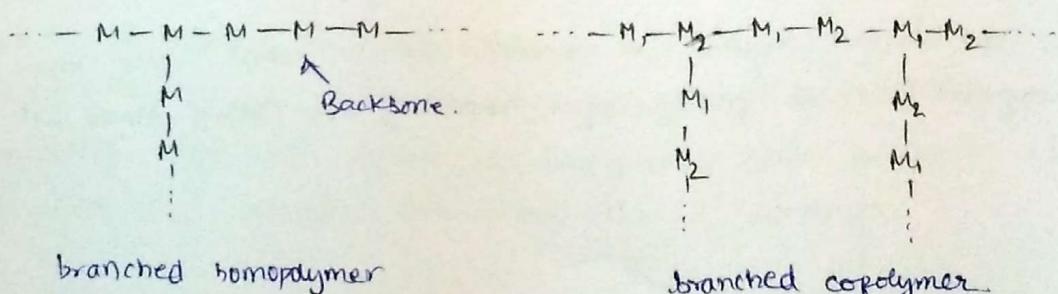
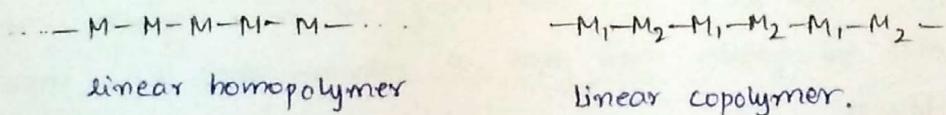
* Degree of polymerisation (DP) : The no. of monomers combined to form a polymer is called degree of polymerisation. (DP). normally, it ranges from 5000-200,000. molecular mass range.

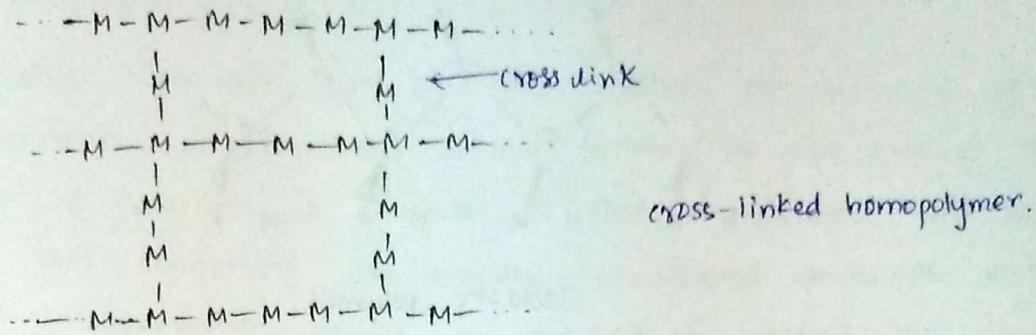
$$\text{DP}(n) = \frac{\text{molecular weight of polymer}}{\text{molecular weight of monomer}}$$

* NOMENCLATURE OF POLYMERS.

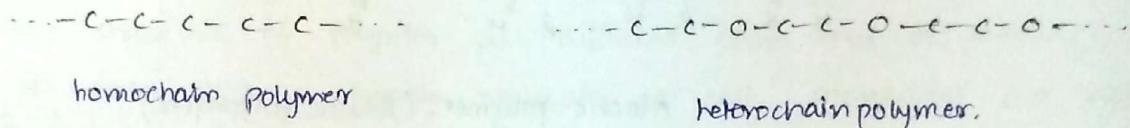
- Homopolymers : polymers whose polymeric chain consists of only one kind of monomer are called homopolymers. e.g. Polyethene.
- Copolymers : polymers whose polymeric chain consists of more than one kind of monomers are called copolymers. e.g. Nylon-6-6.

NOTE : The monomeric unit in polymer may be present in linear, branched or cross-linked structure.

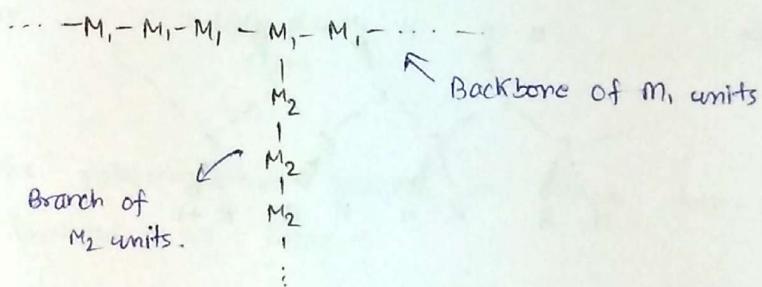




- homochain polymer : If main chain consists of only one species of atoms, then polymer is called homochain polymer.
- heterochain polymer : If main chain consists of more than one species of atoms then polymer is called heterochain polymer.



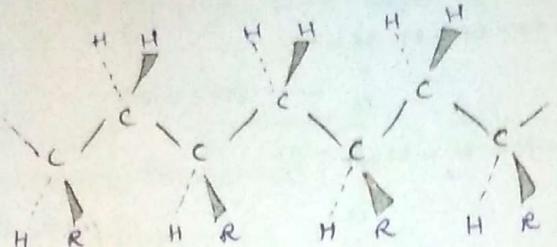
- Craft copolymers : The branched polymers in which monomer units in the branches differ from that present in backbone.



- TACTICITY : The side groups can be arranged either in orderly manner or in random manner around the main polymeric chain. This steric order or steric orientation is called tacticity. Due to tacticity, physical properties differs. Three types of Tacticity possible are :

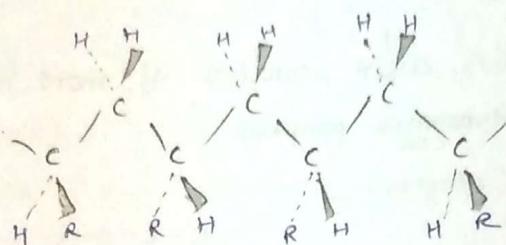
- i) isotactic polymer
- ii) Atactic polymer
- iii) Syndiotactic polymer.

- i) Isotactic polymer : If all the side groups (functional groups) are present on same side of the polymeric main chain, polymer is called isotactic polymer.
eg: Isotactic polypropene.



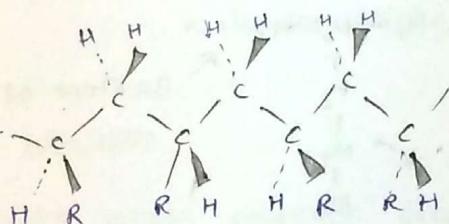
Isotactic polymer.

ii) Atactic polymer: If side groups (functional grp) are present on randomly around polymeric chain, then it is called Atactic polymer.



Atactic polymer. (Atactic polypropene)

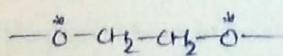
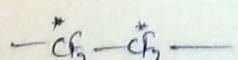
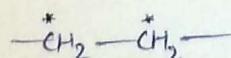
iii) syndiotactic polymer: If side groups are present in an alternate fashion around polymeric chain, it is called syndiotactic polymer.
eg. Gutta percha.



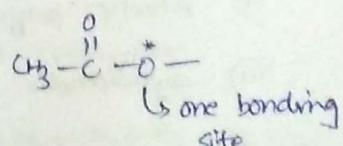
Syndiotactic polymer.

* Functionality of a polymer: The no. of bonding sites in a monomer is called functionality of monomer.

For molecule to act as monomer, it must be atleast bifunctional



functionality of polymer = 2
(can act as monomer)

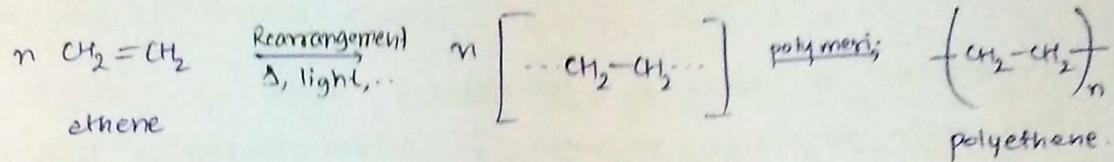


(Monofunctional)

(cannot act as polymer)
monomer.

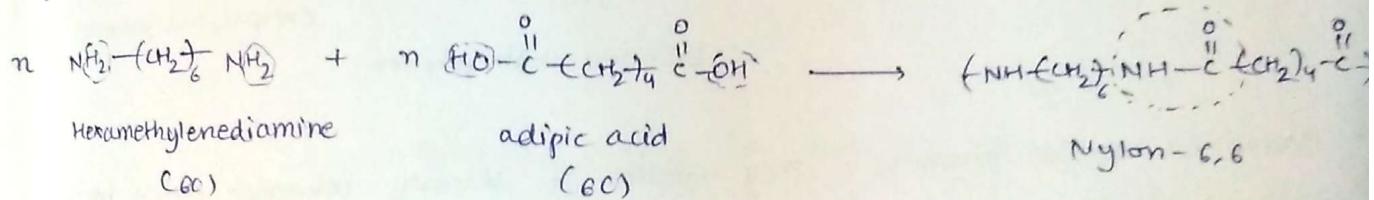
-^{gas} of polymerisation

- * Types of polymerisation : In this type of polymerisation, the molecules of same and different monomers add together, without forming the side product. The ultimate structure of polymer is identical to that of monomer and it takes place very fast. Monomers are usually unsaturated compounds and e. this kind of polymerisation occurs in presence of catalyst, heat etc.

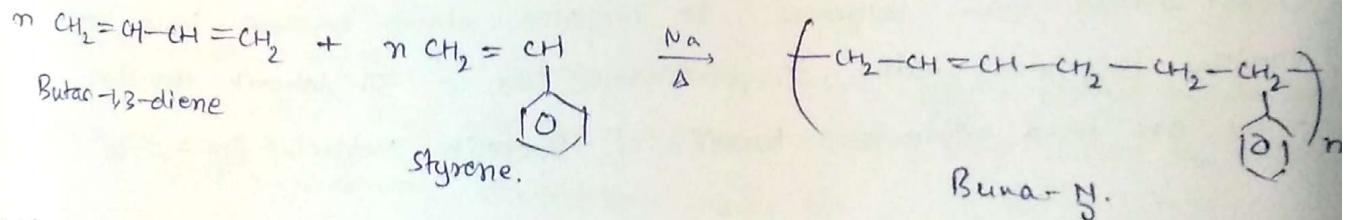


- condensation polymerisation : In this type of polymerisation, molecules react to form polymer along with elimination of small molecules like H_2O , HCl , CO_2 . The ultimate structure of polymer is different from that of monomer because in each step a simple molecule is lost. monomers are usually saturated compounds and there is no need of catalyst.

25



- Copolymerisation : The polymerisation process in which two or more species of monomers are involved. e.g.: Buna-S.



- * Difference between Addition and Condensation polymerisation.

Addition polymerisation	Condensation polymerisation.
Only growth $\rightarrow x^n$ adds repeating units once at a time to chain.	Any two molecular species can react
No. of units ↓ steadily through out x^n .	No. of monomers disappears early in x^n
Structure of polymer identical to monomer.	Not identical.
No side product formed.	Side product formed.
Need of catalyst.	No need of catalyst.
Unsaturated monomer.	Saturated monomer.

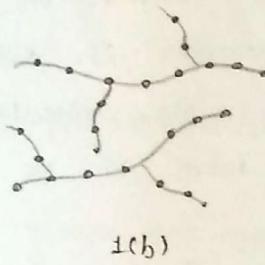
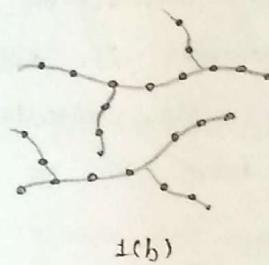
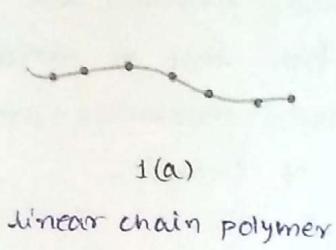
* CLASSIFICATION OF POLYMERS.

i) classification on the basis of source:

- Natural polymers : which are found in nature in plants & animals.
e.g. starch (polymer of α -D-glucose), cellulose (polymer of β -D-glucose), nucleic acids and natural rubber (polymer of cis-isoprene).
- Synthetic polymers : man-made polymers like Polyethene, polypropene, PVC, polystyrene (PS), nylon etc.

ii) classification on basis of structure:

- Linear chain polymers : polymers in which monomeric units are joined in form of long straight chains. e.g. High density polyethene (HDPE), nylons, polyesters etc. They possess high mp, tensile strength, density.



- Branched chain polymers : They consists of linearly polymeric chain having some branches. Due to poor presence of polymeric chain (por packing), they have low mp, density and tensile strength. e.g. LDPE (low density polyethene), amylopectin etc.

- Cross-linked chain polymers : It contains strong covalent bonds b/w various polymeric chains to give rise to a 3D-network structure. They are hard, rigid and brittle. e.g. Bakelite, Melamine-formaldehyde resin

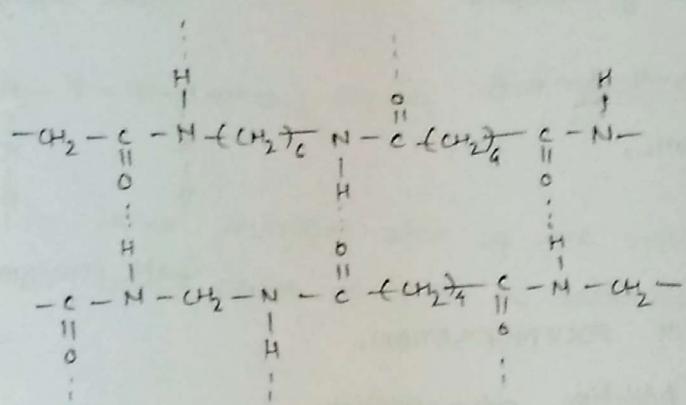
iii) classification on basis of their methods of synthesis :

- Addition polymers : polymers which are formed from addition polymerisation method. These are formed by repeated addition of monomeric units (unsaturated) to yield a long chains. NO side product is obtained.
e.g : Polyethene, polypropene, PS, PVC etc.
- Condensation polymers : polymers which are formed from condensation polymerisation method. It involves loss of small molecules like H_2O , HCl etc.
e.g : Nylons, polyester etc. Monomers are saturated compounds.

iv) classification on basis of intermolecular forces :

- Elastomers : Those polymers in which intermolecular forces b/w various polymeric chains is weakest vander waal force are called elastomers. They have high degree of elasticity i.e. they have ability to be stretched out 10 times their normal length and return back to their original length when applied forces are withdrawn. The weakest vander waal forces permit polymeric chains to be stretched out and cross-links helps to regain its normal position. e.g. vulcanised Rubber, Buna-N, Buna-S etc.

- Fibre : Those polymers in which intermolecular forces b/w various polymeric chains are strongest H-Bonding or dipole-dipole interaction are called fibres. e.g. Nylon, polyester etc.



Hydrogen bonding in Nylon-6,6 (fibre).

- * Thermoplastics : these are linear, long chain polymers, which can be softened on heating and hardened on cooling i.e. they are capable of going reversible changes. e.g. polyethylene (PE), PP, PVC, PS etc.

- * Thermosetting plastic : there are cross-linked polymers, which cannot be softened on heating, insl rather they gets hardened on heating and cannot be softened again. e.g. Bakelite, melamine formaldehyde resin etc.

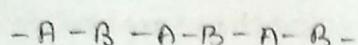
Thermoplastics	Thermosetting plastics
They soften on heating rapidly.	They do not soften on heating, on prolong heating, they burn.
They are long-chain linear molecules.	They have cross-linked structure joined by covalent bonds.
Formed by addition polymerisation.	Formed by condensation polymerisation.
They can be resoftened, reshaped, reused.	They can't be resoftened, reshaped, reused.
They are soft, weak, less brittle.	They are hard, strong, more brittle.
They are soluble in some organic solvents.	They are not soluble in most of organic solvents.

- Classification on basis of monomer
- Homopolymer : polymeric chain consists of only one kind of monomer.
- Copolymer : polymeric chain consists of more than one species of monomer.

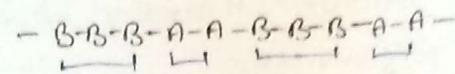
vi) classification on basis of stereochemistry:

- Isotactic polymer
 - Atactic polymer
 - Syndiotactic polymer
- } (discussed earlier).

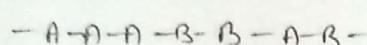
vii) on basis of arrangement of monomer: copolymer can be classified as



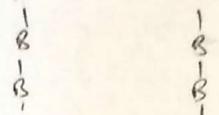
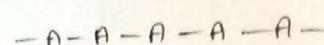
alternating copolymer



Block copolymer



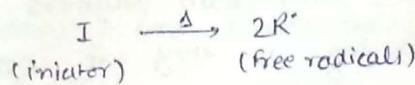
random.



Graft copolymer

* MECHANISM OF POLYMERISATION.

- Free radical Addition polymerisation
- Initiation: It consists of two reactions. First, is the homolytic dissociation of initiator (or catalyst) to produce free radicals.

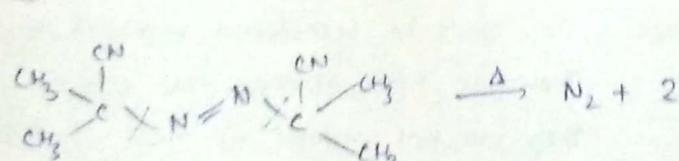
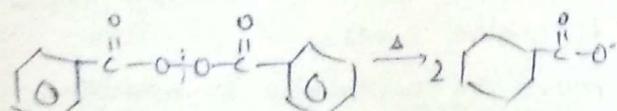
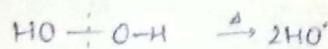


Adding of free radical to first monomer molecule takes place.

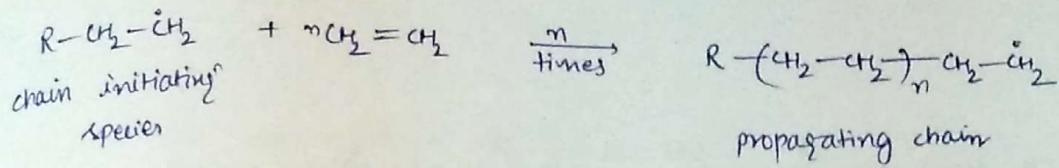


(chain initiating species)

e.g. of some initiators, H_2O_2 , Benzoyl peroxide & 2,2-Azobis isobutyronitrile

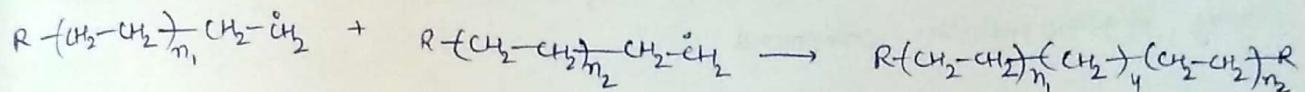


Step 2: Propagation : Propagation of chain takes place by successive addition of a large no. of monomer molecules.

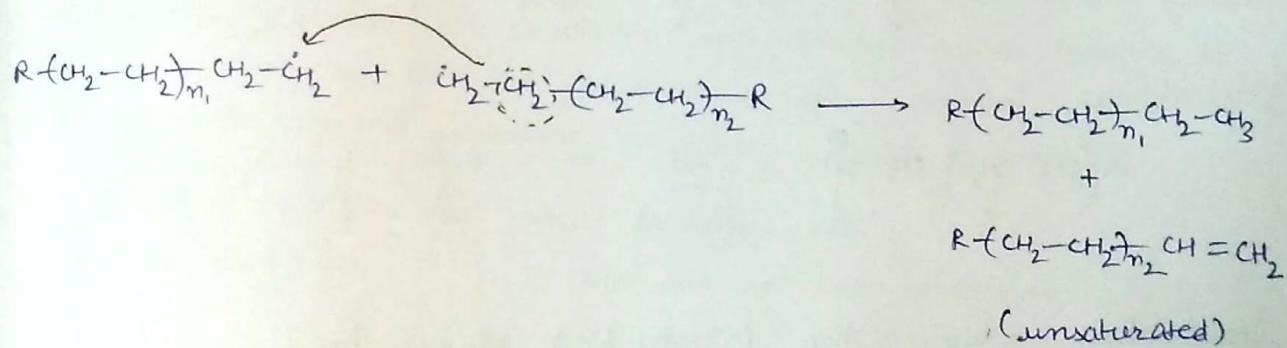


Step 3: Termination : The growth of chain stops at some points and terminates. Termination can take place in two ways:

(i) By coupling of two polymeric chains:



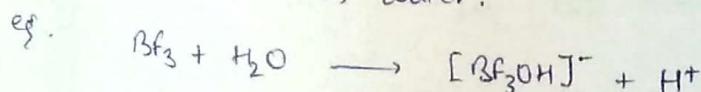
(ii) By disproportionation in which hydrogen atom of one radical centre is transferred to other radical centre to form a saturated and other unsaturated polymer.



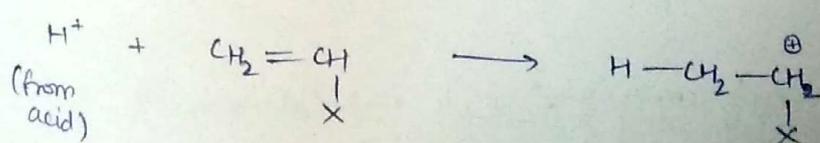
• NOTE : Dead polymer means cessation of growth of propagating radical.

CATIONIC ADDITION POLYMERISATION :

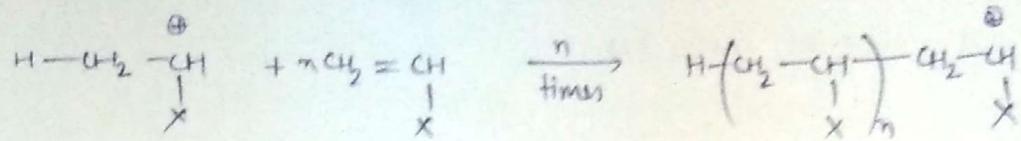
Such rxn takes place in place of presence of strong Lewis acid or protic acid and traces of water.



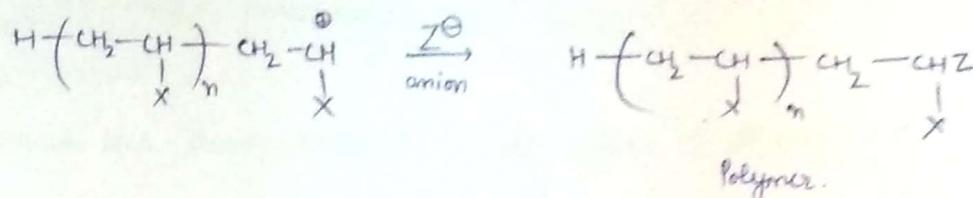
Initiation :



Propagation :



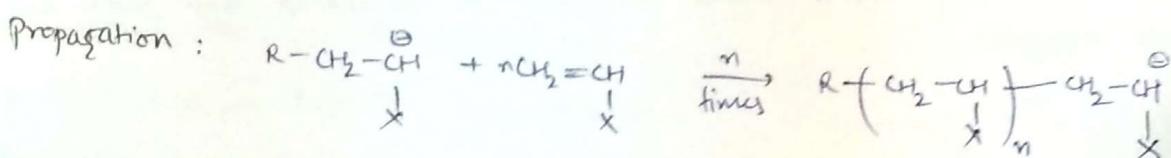
Termination :



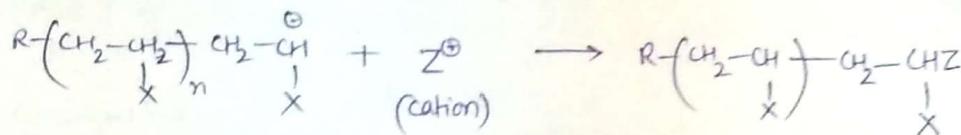
- Anionic Addition polymerisation.

The required carbanion is generated from Grignard reagent or from any organometallic compound.

Initiation :

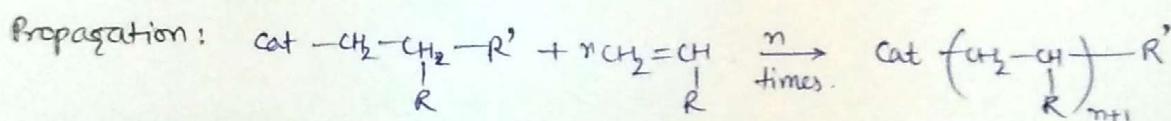
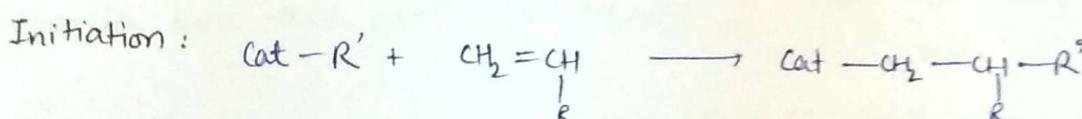


Termination :

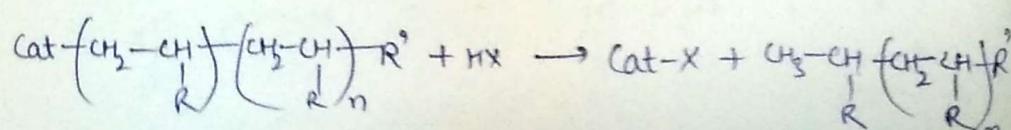


- Coordination polymerisation (Zeigler-Natta polymerization).

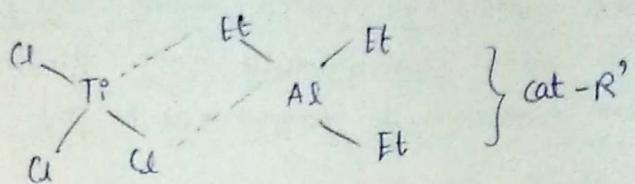
In the presence of transition metal halides and organometallic comp. Stereospecific polymers can be obtained. This is called stereospecific polymerisation.



Termination :
(using Active
hydrogen
compound)



NOTE : Ziegler - Natta Catalyst ($Ti^2O_3 + AlEt_3$). (Can be used for ppⁿ of PE, PP etc.)



- Atactic polymers are soft, others are dense.
- Using suitable solvent, catalyst and temp, desired stereospecific polymer can be obtained.

* METHODS OF POLYMERISATION

Due to difference in mechanism of addition and condensation polymerisation the polymerisation techniques employed are different.

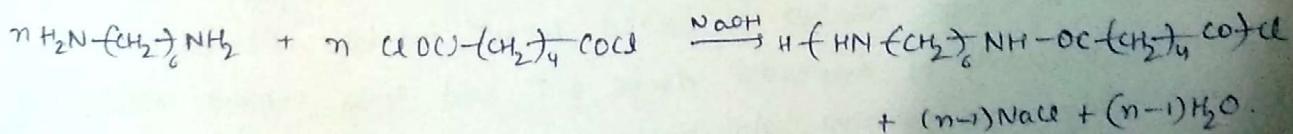
• Condensation polymerisation.

i) High-temperature method: Monomers in suitable stoichiometric proportions are added into an autoclave (heating container) and heated at high Temp ($> 200^\circ C$) at slightly high Temp. Viscosity stabilizers and dehydrating agent are added. As the rxn proceeds, viscosity \uparrow and escaping tendency of volatile products \downarrow . At this stage, pressure is decreased and heated more strongly in vacuum to complete the rxn. As polymerisation gets completed, entire mass is pushed out from autoclave, quenched in water, washed & dried.

NOTE: high purity monomers are required (99.5%)

to avoid oxidation, it is carried out in inert atmosphere.

ii) Low-temperature method: Monomers are heated separately in at high temp. to provide requisite amount of Energy of activation. Then, they are mixed & stirred till rxn is complete. If reactivity of monomers is high, then it can also take place at ordinary Temp. e.g.: Nylon-6,6 can also ppd. using acid chloride of it instead of Adipic acid.



• Addition polymerisation.

Four types of polymerisation techniques involved are:

i) Bulk polymerisation: It is the simplest method in which monomer & initiator are used as main components. It involves two stages.

Pre-polymerisation (1st stage) in which nitrogen atmosphere is maintained around reaction vessel, which is heated using hot jackets (not water coils), & monomer is added continuously with stirring at suitable rate in vessel where monomer is polymerized to 30%.

Post-polymerisation (2nd stage): The polymerization mix is fed in upper end of vertical reactor, divided into zones which are heated using superheated steam except lowest one which is heated electrically to get high temp. enough to complete the rxn. Successfulness of rxn depends on residence of mixture in different zones. The highest conversion of monomer is carried out in lowest zone. The resultant molten polymer is taken out, conveyed in water cooling system, following chipping and grinding. PVC, PS, PMA are polymerised by this method.

ii) solution polymerisation: It involves dissolution of monomer in suitable solvent and then initiator is added to start polymerization rxn. The heat of polymerisation is dissipated as evaporation of solvent. The polymer mixture is precipitated by adding a non-solvent to it. It is then filtered off, washed, dried before use. N-vinyl pyrrolidone & acrylonitrile.

iii) emulsion polymerisation: Monomers are dispersed as fine droplets (10^{-5} to 10^{-6} mm) in large amount of water and then emulsified by addition of soap / detergent / protective colloids. Then initiator is added which is either water or monomer soluble. Persulphates are used which gives SO_4^{2-} in emulsion. These react with monomer and micelle formation and polymerisation occurs. It is broken by adding electrolyte, then washing and drying. PVC, PVA are made by this.

Advantages: Rapid production of polymer
high average molecular weights.
ease of Temp. control.

iv) Suspension polymerisation: Monomers are dispersed as relatively large droplets (0.01 to 1 mm) in water. It is kept in suspension by mechanical agitation. Catalyst is added & rxn initiates. As polymerisation proceeds, viscosity of dispersed drops ↑ and they become sticky. At this stage, suspension stabilizer are added. When rxn gets completed, rxn product is washed & dried. PVC & PS are ppd. by this method.

* MOLECULAR-MASS OF A POLYMER.

All the polymeric chains in a polymer sample does not have the same molecular weight. So, in that case, we find average molecular mass of a polymer. Moreover, this can also be classified in three :

- i) number-avg. molecular mass (\bar{M}_n)
- ii) weight-avg. molecular mass (\bar{M}_w)
- iii) viscosity-avg. molecular mass. (\bar{M}_v).

i) number-avg. molecular mass : determined by measuring colligative properties. It is defined as total mass of all molecules in sample divided by total no. of molecules present. mathematically,

$$\bar{M}_n = \frac{\sum N_i^o M_i}{\sum N_i^o}$$

where, N_i^o is no. of molecules of mass M_i

ii) weight-avg. molecular mass : determined by light-scattering & ultra-centrifugation techniques. It is different from \bar{M}_n in the fact that bigger molecules contribute more to the total mass of polymer than small polymers do. Mathematically,

$$\bar{M}_w = \frac{\sum w_i^o M_i}{\sum w_i^o}$$

w_i^o is weight fraction of molecules whose mass is M_i .

also, $\frac{\sum N_i^o M_i^2}{\sum N_i^o M_i} = \bar{M}_w$

* Polydispersity index (PDI) : It is ratio of weight avg. molecular mass to number avg.-molecular mass.

$$\text{i.e. PDI} = \bar{M}_w / \bar{M}_n$$

for monodisperse system (having identical molecular mass of all molecules),

$$\bar{M}_w = \bar{M}_n \therefore \text{PDI} = 1. \text{ Always, } \bar{M}_w \geq \bar{M}_n$$

iii) Viscosity-Avg. molecular mass →

By measuring viscosity, avg. molecular mass can be obtained. Because higher the molecular mass, slower the movement of polymer molecules & hence more viscous will be the solution.

Q) → Why does polymer makes solution viscous ?

Due to their high molecular masses, they move slowly and get in b/w in the path of solvent molecules and blocks their way, making solution viscous. They also makes solvent molecules move slowly by making forces of interaction with them.

$$\bar{M}_v : \text{Mathematically, } \bar{M}_v = \left[\frac{\sum w_i M_i^a}{\sum w_i} \right] = \left[\frac{\sum N_i M_i^{a+1}}{\sum N_i M_i^a} \right]^{\frac{1}{a}}.$$

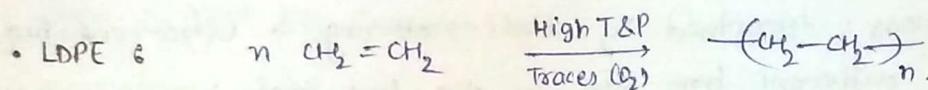
where a is constant.

for $a=1$, $\bar{M}_v = \bar{M}_w$ and normally $\bar{M}_v < \bar{M}_w$ because a is 0.5-0.9.

* functional polymers : Polymers to which chemically bound functional groups are attached which can be utilised as reagents, catalysts, protecting groups etc.

* SOME COMERCIALLY USEFUL POLYMERS.

i) Polyethylene (PE)



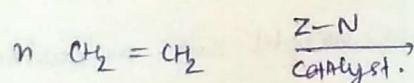
$T = 180-300^\circ\text{C}$ & $P = 1000-3000\text{ atm}$.

LDPE = low density polyethylene.

Applications : as insulations for electric wires & cables.

As packaging material for frozen foods.

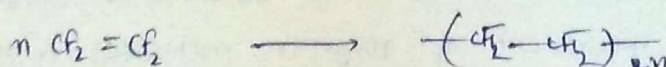
• HDPE : high density polyethylene.



$$\begin{aligned} Z-N &= \text{Ziegler Natta catalyst} \\ &= \text{TiCl}_3 + (\text{C}_2\text{H}_5)_2\text{Al} \end{aligned}$$

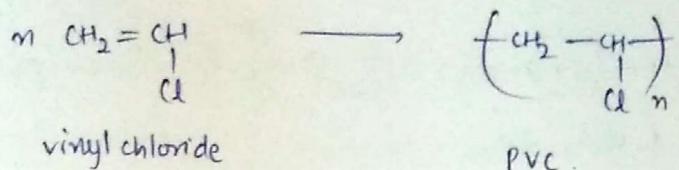
Applications : in making container, toys, bottles etc.

ii) PTFE : Polytetrafluoroethylene



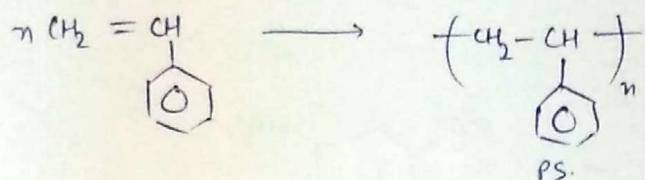
Applications : in non-stick cookwares, insulation materials for motors & transformers.

iii) PVC : Polyvinyl chloride.



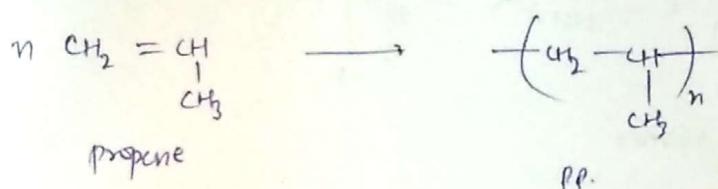
Applications: In making raincoats, bags and pipes, etc.

iv) Polystyrene (PS) :



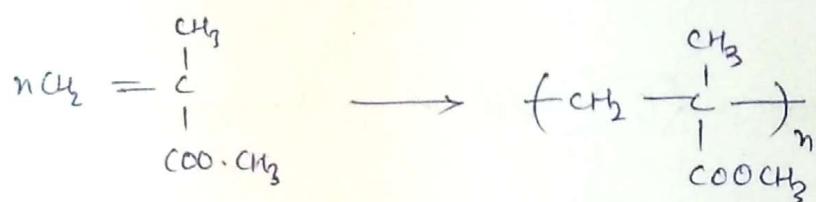
Applications : In making radio & TV boxes as it is resistant to action of moisture, heat, chemical etc.

v) Polypropene : (pp).

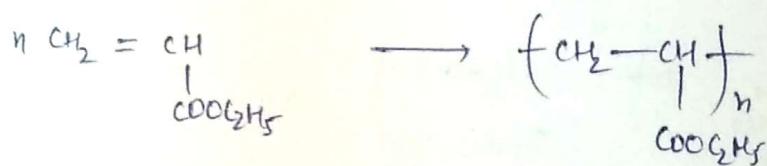


Ans: manufacture of ropes, fibres etc.

vi) PMMA : poly methyl meth acrylate.



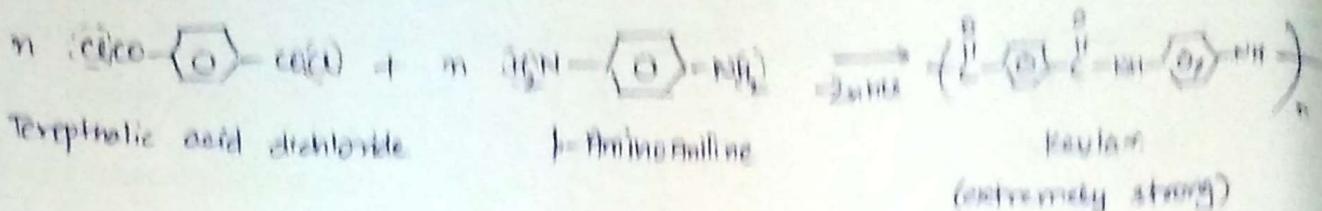
viii) PEA : polyethylacrylate.



Apps of PEA & PMMA:

in making lens, aircraft window, plastic
jewellery etc.

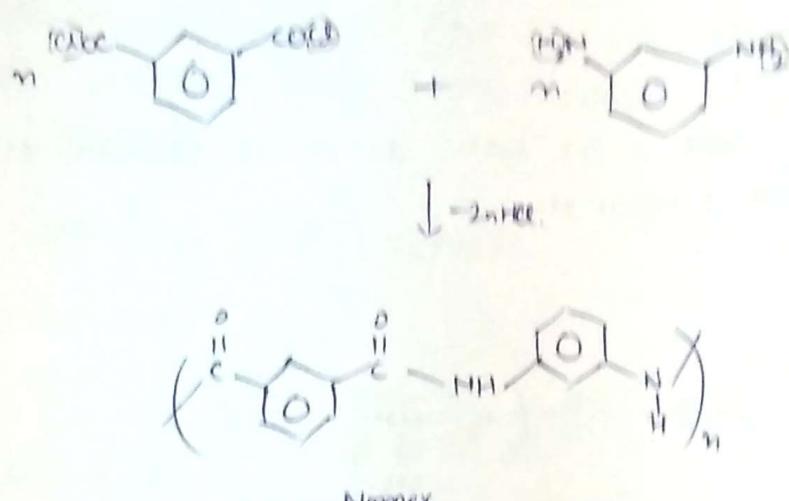
* KEVVAE *



APPS: used in aircraft & aerospace industries
& car parts.

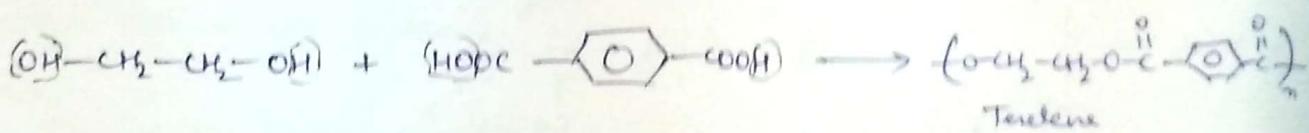
High stability & flexibility

* NOMEY.



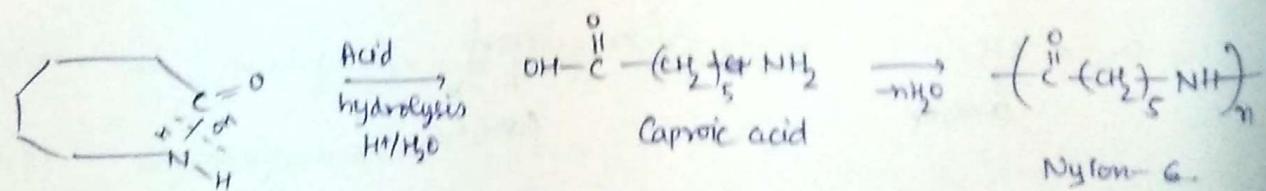
• insulating paper for electrical motors.
• Sewing thread.

* DACRON (Terelene)



Apps: used for making, safety belts, helmets, magnetic recording tapes.

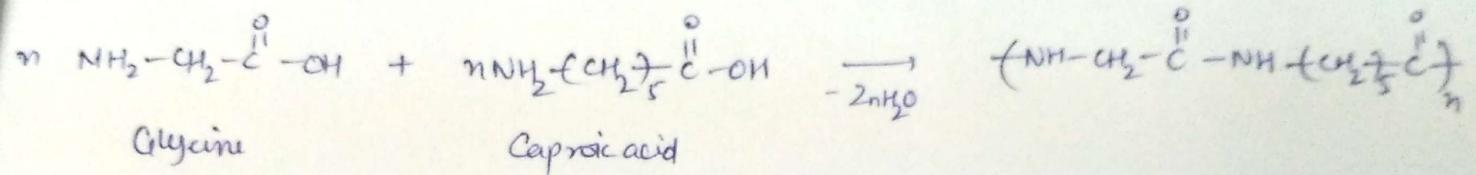
* NYLON 6



(7 membered heterocyclic ring)

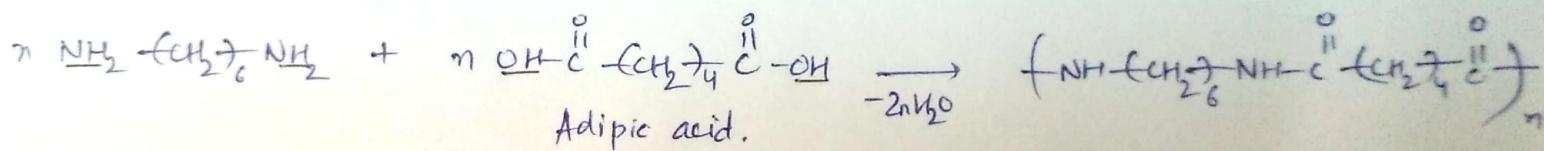
Coprolactum (monomers)

* Nylon-2,6

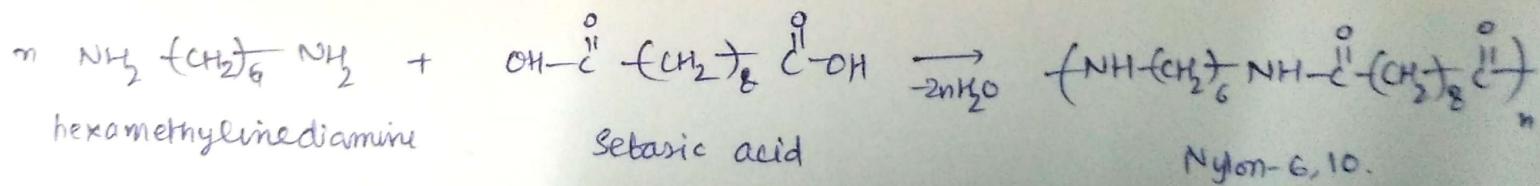


Apps: fibre, plastics, ropes

* Nylon - 6, 6.



* Nylon - 6, 10



use: fibre, plastics, ropes etc.