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 (3) ^{initial}
 B. Jayanthi
 I MSc Chemistry
 8.30 to 9.15
 5 Set
 1 BR-2

i) Oligo polymers :

Polymers with only a few no of repeating units is called Oligo polymers. It is usually less than from 2 to 10. [Molecular mass 500 to 15000].

ii) High polymers :

Polymers with high degree of polymer are called high polymers. Molecular mass ranges from 10^4 to 10^6 .
 Difference :
 Thermosetting - Thermoplastic
 Addition - Condensation
 Diff. case

Linear, branched & network polymers :

Depending upon the origin, Polymers are classified into 2 types i) Natural & ii) Synthetic

i) Natural polymers :

Polymers which are isolated from natural material is called natural polymer.

Eg - Rubber, wood, Cellulose, starch & protein.

These polymers has some disadvantages

Their physical properties are fixed by the nature of the particular material & cannot be varied.

(i) Their supplies are limited by agricultural considerations, & the materials are often expensive & occurs rapid fluctuations in price.

ii) Synthetic polymers :

These Polymers which are synthesized from low molecular weight compounds are called synthetic polymers. Eg: Polyethylene, PVC, nylon & terylene.

These are manufactured from cheap & readily available petroleum fractions.

Synthetic polymers are classified into 3 types.

- i) Linear polymer
- ii) Branched polymer
- iii) Network polymer (a) Cross linked
- iv) Comb polymer & v) Ladder polymer.

Monomers :

The individual small molecule from which polymers is formed known as monomer.

- 1 Self poly condensation
- 2 Preparation of copolymers
- 3 Co-polymerization
- 4 Reactivity Ratio Co-polymerization
- 5 Rate of Co-polymerization

9.15 to 9.45

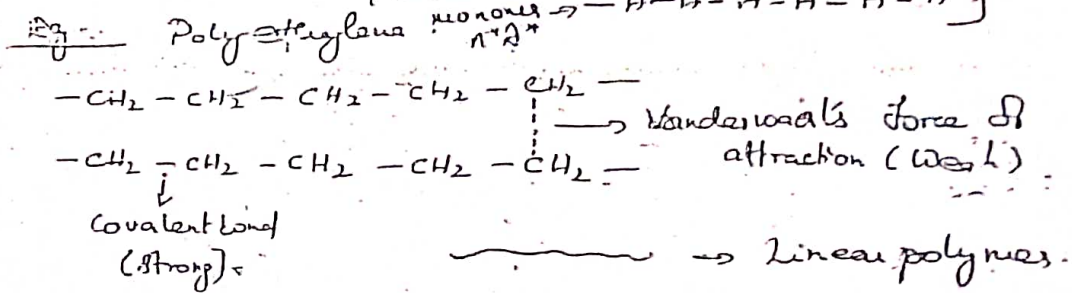
Mechanism & Kinetics

- i) Free radical
 - ii) Anionic
 - iii) Cationic
 - iv) Co-polymerization
- Reactions

(i) Linear polymer:

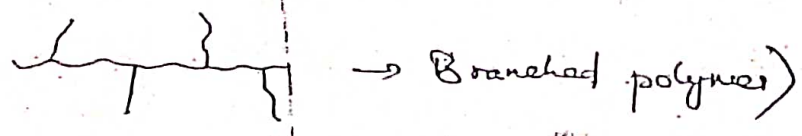
In a polymer, if the repeating units are joined together like links ^{like} in a chain, then it is called linear polymer. It is obtained ^{from} by the bidirectional monomers i.e., if the functionality of the monomer is two, only linear (or) straight chain polymer is formed. Each monomer in the linear chain are held together by strong covalent bonds. But the chains are held together by weak vanderwaal's force of attraction.

This is the reason for the mobility of the chains over one another { Bidirectional monomer $\rightarrow -A-A-A-A-A-A-$ }



(ii) Branched polymer:

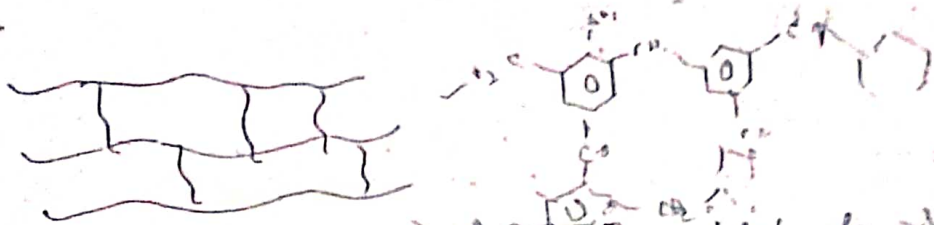
~~If the linear~~ In a polymer, if the linear chains are joined together by some other molecule, then it is called branched polymer. It is obtained by mixing bidirectional monomers with a small amount of trifunctional monomers. The mobility of branched polymer is less due to the presence of side chains.



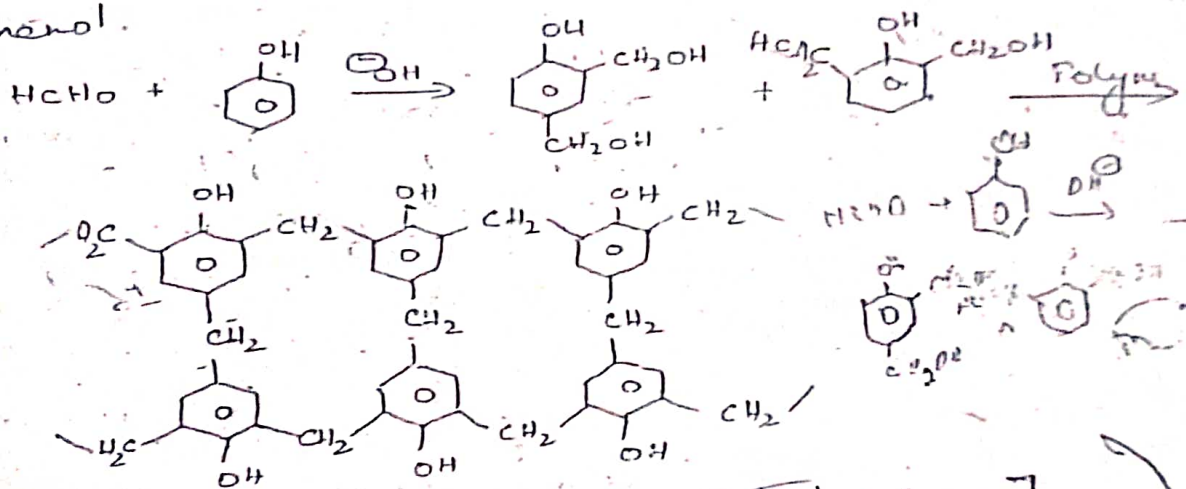
(iii) Crosslinked (or) network polymer.

If in a polymer, if the linear chains are joined together by cross links, it may lead to the formation of a three dimensional structure to the ~~these~~ these ~~types~~ types.

polymer molecule & they are called cross linked (or) network polymer. It is obtained from the trifunctional monomers & all the monomers in the polymer molecule are linked to each other by a strong covalent bond. So the strength of the polymer is very high.



Eg.: Bakelite - formed from formaldehyde & phenol.



Bakelite. [cross linked polymer].

Classification of polymer according to polymerisation mechanism.

According to the mechanisms involved in the polymerisation process, the polymerisation rxn is classified into 2 types

- i) Addition polymerisation
- ii) Condensation polymerisation
- iii) ~~Co-poly~~ ~~condensation~~ polymerisation.

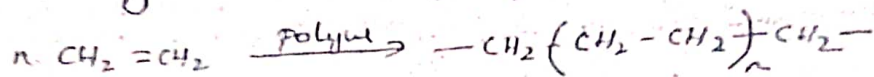
i) Addition polymerisation (or) Chain polymerisation

Addition polymerisation involves addition (or) union of monomers to one another to form a long polymer chains without forming any by products. The polymer product will be the exact multiple to that.

a) The original monomer & the product formed
 had the same elemental composition as that of
 monomer. \hookrightarrow Generally monomers containing
 double bonds [unsaturated compds] undergoes addition
 polymerisation & ^{here} the double bond provides bifunctionality
 to the monomer.

~~Ex:~~ Vinyl compd, Allyl compd, olefines & dienes
~~are~~ the monomers, that undergoes addition polymer.

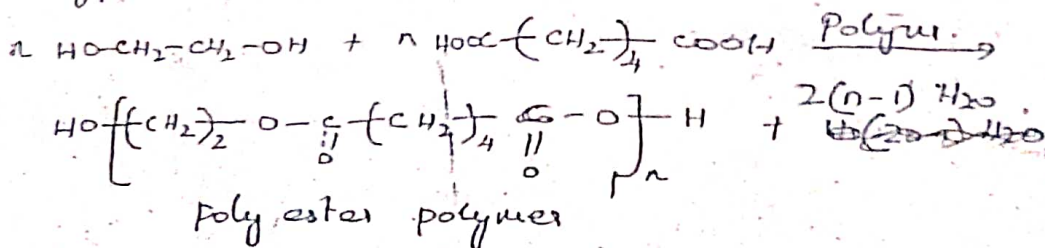
eg: n Ethylene $\xrightarrow{\text{polymer}}$ polyethylene.



ii) Condensation polymerisation \hookrightarrow step growth polymer

It involves the condensation of monomers
 with two or more ^{reactive} functional groups such as
 hydroxyl, carbonyl & amino group to give a polymer
 with elimination of small molecules as by products.
 Such as H_2O , CH_3OH , NH_3 , etc.

Eg: Condensation of ethylene glycol with
 adipic acid gives polyester & H_2O molecule as a
 byproduct.



Addition polymerisation	condensation polymerisation
1) Initiator is required for the polymerisation. 2) The same rate of initiation, propagation & termination $R_i = R_p = R_t$	1) No initiator is required. 2) Initiation, propagation & termination rate are different $R_p > R_i \approx R_t$

Difference between addition & condensation polymerisation

Addition polymerisation	Condensation polymerisation
1) Addition of monomers gives polymer & no by products	1) Monomers condensed to give polymer & H_2O , CH_3OH , HCl or NH_3 , etc as by products. (3)
2) Monomers must have at least one double or triple bond	2) Monomers must have two or more, identical or different functional groups.
3) It is a rapid chain growth reaction	3) It is a step-wise reaction.
4) Monomers can react, only when added to chain initiating species or growing chain species	4) Any two monomers or species can react with one another.
5) The <u>no</u> of monomer molecules decreases steadily throughout the rxn	5) The monomers disappear at the early stage of the rxn.
6) The polymer product is formed at once.	6) The polymer product is formed step-wise steadily.
7) The polymer product contains dead polymer chains	7) The polymer product contains active polymer chains or molecules.
8) Molecular weight of the polymer is a integral multiple of the molecular <u>wt</u> of the monomer	8) It is not applicable to all the cases.
9) The molecular weight of the polymer is roughly equal to the integral multiple of the molecular wt of the monomer.	9) The <u>molecular wt</u> of the polymer is always less than the integral multiple of the molecular wt of the monomer.
10) Mostly thermoplastic resins are obtained. The polymer formed can be reshaped or remoulded by applying heat or pressure. Repeated heating & cooling does not affect the chemical nature of the polymer. Eg: PVC, PAN ↓ polyacrylonitrile.	10) Mostly thermoset resins are obtained. The polymer formed cannot be reshaped or remoulded by applying heat or pressure. Eg: Bakelite, polyester, nylon.

Addition polymerisation (or) chain polymerisation

is characterised by a self addition of monomers to each other, very rapidly through a reaction, without elimination of by products. The product has same elemental composition as that of monomer. Usually monomers containing double bonds (unsaturated compounds) undergoes addition polymerisation. The bifunctionality is due to the double bonds.

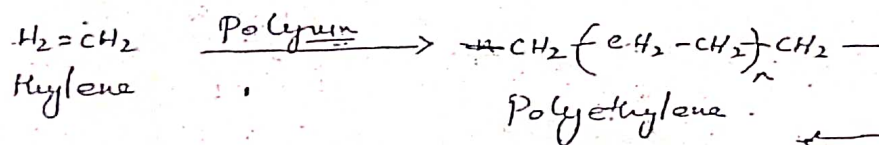
The monomers which undergoes chain polymerisation are

vinylic compounds Eg: $\text{CH}_2=\text{CH}-\text{CN}$ Acrylonitrile

allylic compounds Eg: $\text{CH}_2=\text{CHCH}_2-\text{Cl}$ Allyl chloride

olefines Eg: $\text{CH}_2=\text{CH}_2$ Ethylene

dienes Eg: $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ 1,3-Butadiene



Depending upon the mechanism of polymerisation, they are classified into 3 types

radical polymerisation:

Initiated by free radicals & free radical intermediate is formed.

ionic polymerisation:

It is classified into 2 types

anionic polymerisation:

Initiated by anions & anionic intermediate is formed

cationic polymerisation: Initiated by cations & cationic intermediate is formed.

Co-ordination polymer: Initiated by organometallic catalyst & co-ordinate complex intermediate is formed.

Mechanism

Chain polymerisation consists of 3 major steps

- i) Initiation ii) Propagation & iii) Termination.

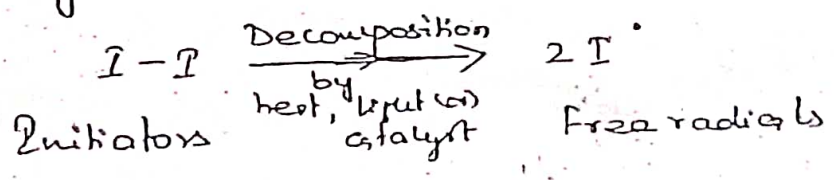
These process can be brought about by a free radical, ionic (or) co-ordination mechanism depending

Free-radical polymerisation:

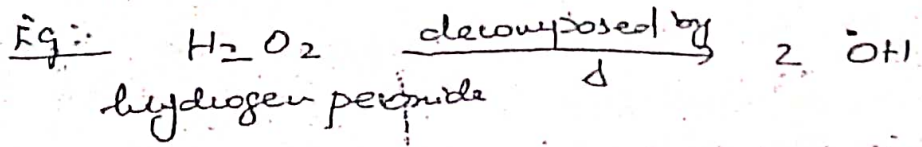
The monomer & the polymer chain growth is initiated by free radicals.

i) Initiation:

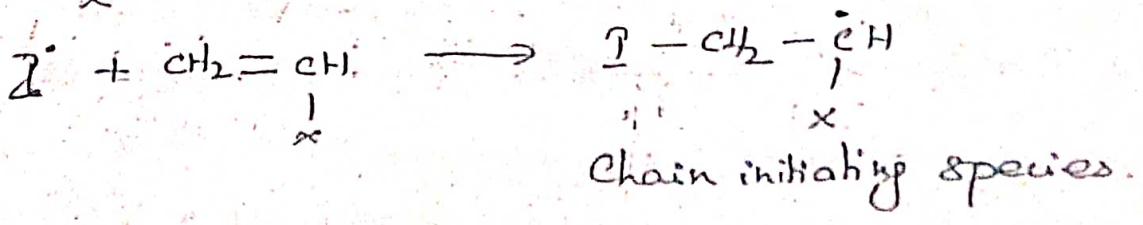
The monomer is initiated by free radicals. The initiator on decomposition gives free radicals. The decomposition is brought about by heat, light (or) catalyst.



Generally low molecular weight cpds peroxides, per acids, hydroperoxides, per esters & azo cpds are used as initiators

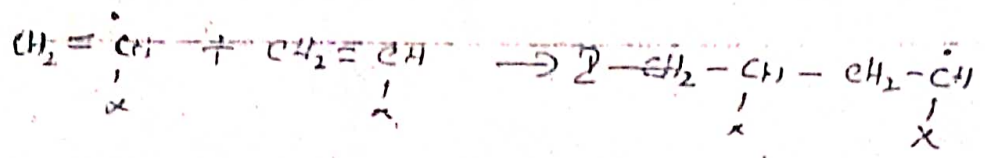


Let us assume that the monomer is $CH_2=CH$ & is initiated by free radical I^{\cdot}



propagation:

The initiated monomer propagates rapidly & forms chain growth polymer. Propagation may be a) Head to Head b) Head to tail c) Tail to head d) Tail to tail.



Propagating chain growth.

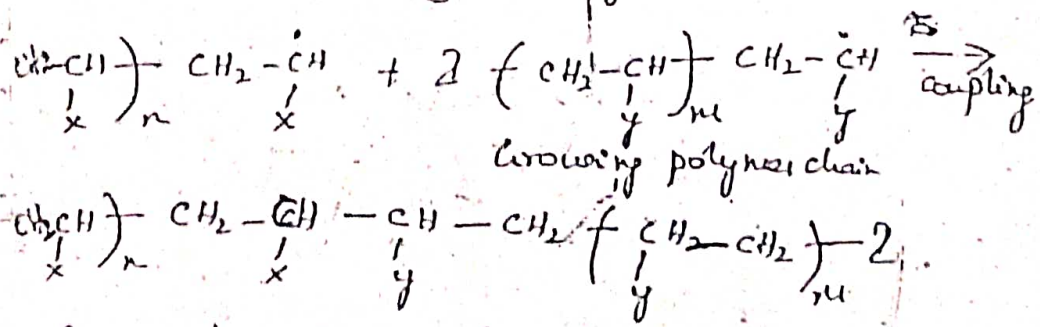
Termination:

The propagating chain undergoes termination a dead (or) inactive polymer. Termination brought about by

- 1) Termination by coupling
- 2) Termination by disproportionation (or)
- 3) Termination by chain transfer.

Termination by coupling:

Two growing polymer chains couple to form a polymer having strong covalent bond between the two growing polymer chain.

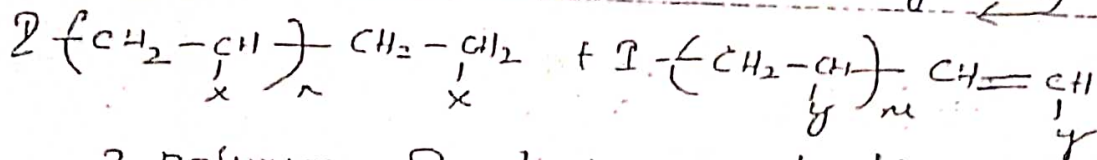
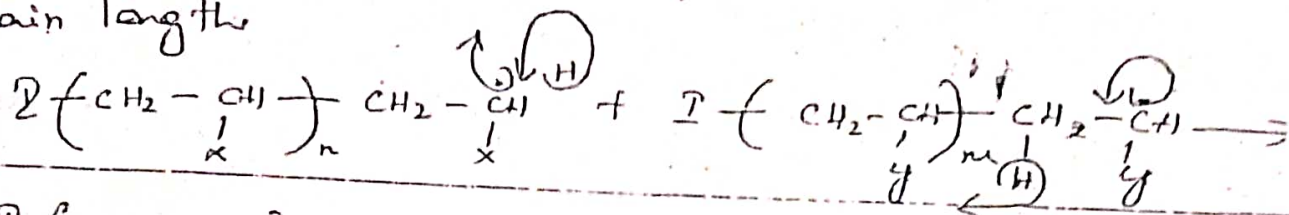


A dead polymer.

Block copolymers are obtained by this method.

b) Termination by disproportionation: (11)

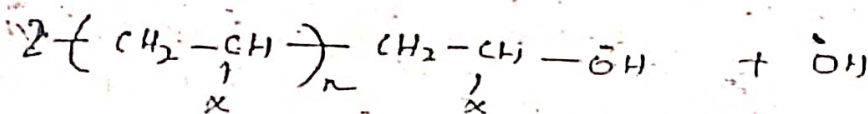
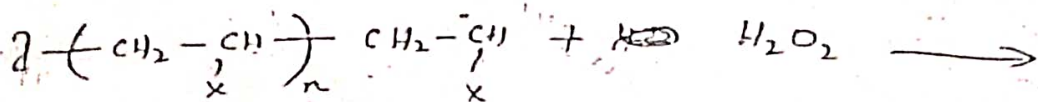
One growing polymer chain abstracts a hydrogen from another growing polymer chain, & forms 2 smaller polymer molecules of short chain length.



2 polymers of short chain length.

c) Termination by chain transfer:

Growing polymer chain abstracts hydrogen (or) some other atom from initiator, monomer, polymer molecule, solvent (or) impurities in the system, & so form a dead polymer, and newly generated free radicals x which initiates another growing polymer chain. Here one chain is terminated & other chain gets propagated, so it is called chain transfer termination.



Dead polymer

newly generated free radicals

↓
Initiates another growing polymer chain.

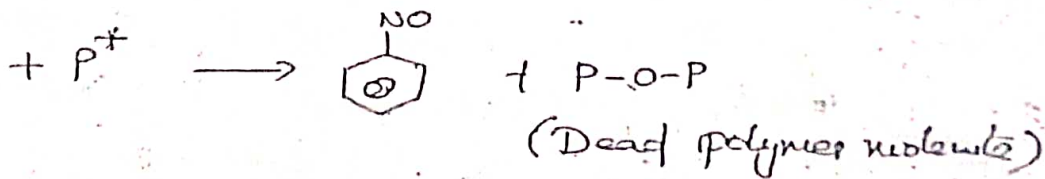
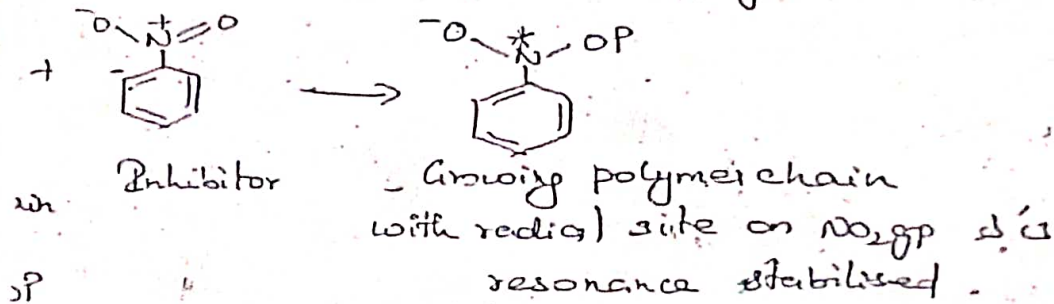
Inhibitors:

Inhibitors are the chemical substances capable of inhibiting (or) killing the chain growth. They terminate the growing polymer chain by combining with the active free radicals and

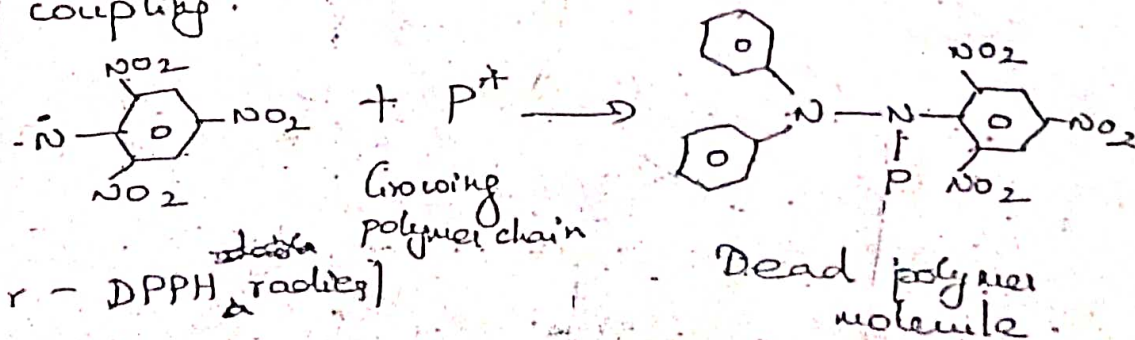
other stable products (dead polymer molecules) are free-radicals.

nitrobenzene, dinitrobenzene, trinitrobenzene, quinone, benzothiazine, diphenyl picryl & [DPPH], and oxygen are the inhibitors used in polymer industry.

Mode of inhibition:
 Inhibitors like nitrobenzene attacks the polymer chain P^* & forms a polymer with a radical site on the $-NO_2$ group. It is not active enough to attack a fresh radical & hence chain propagation does not take place. But it attacks the another growing chain & forms a dead polymer.

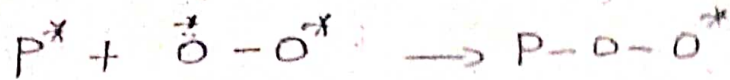


exists in the form of a stable free radical which can stop the chain growth by coupling:



Atmospheric oxygen acts as an inhibitor due to its biradical nature. The inhibiting

action is



(13)



Uses:

Generally inhibitor is mainly used in the preservation of monomers during production & storage. The monomers produced are stored by using ~~very little~~ using small amount of inhibitors. Without inhibitors, the monomers cannot be transported from one place to another. Before using, the monomer is freed from inhibitors by distilling or washing with aq. soln of NaOH (or) KOH. As a result the inhibitor is destroyed & removed by aqueous phase.

It is also used in polymer industries to arrest polymerisation for ~~active~~ getting uniform or product to avoid cross-linking of the polymer. It is added towards the end of the polymerisation to kill all the active radicals & thus arrest the polym. rxn.



Ionic polymerisation

Depending upon the nature of ions used for the initiation, ^{& nature of substituents in the monomer,} ~~the~~ polymerisation ionic polymerisation is classified into 2 types

i) Cationic polymerisation:

Cations (or) positively charged ions are used ~~for~~ for initiation. The monomers used should contain electron releasing ^{groups} substituents.

ii) Anionic polymerisation:

Anions (or) negatively charged ions are used for initiation. The monomers used should

electron attracting groups. (14)

Cationic polymerisation:

presence of e^- donating (or) releasing groups in the monomer, favours cationic polymerisation. The formation of carbonium ion (or) carbocation intermediate as an active species.

Cationic polymerisation.

presence of e^- donating (or) releasing groups in monomer molecule favours cationic polymerisation. Carbonium ion (or) carbocation intermediate is active species. The e^- donating groups are methyl, ethyl, etc.

Generally vinyl epds containing e^- releasing groups act as a monomer. The monomer undergoes heterolytic cleavage & forms a carbocation intermediate with a positively charged ion.

Initiation:

Initiation is brought about by initiators.

Initiators acts as a catalyst used are acids like $AlCl_3$, BF_3 , $SiCl_4$, $TiCl_4$, H_2SO_4 , etc.

presence of co-catalyst H_2O .

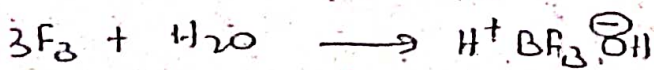
A catalyst may be

acidic eg: HCl , H_2SO_4 , etc.

basic eg: BF_3 , $AlCl_3$, etc.

transition metal salt eg: $Al(C_2H_5)_3 Cl^-$, etc.

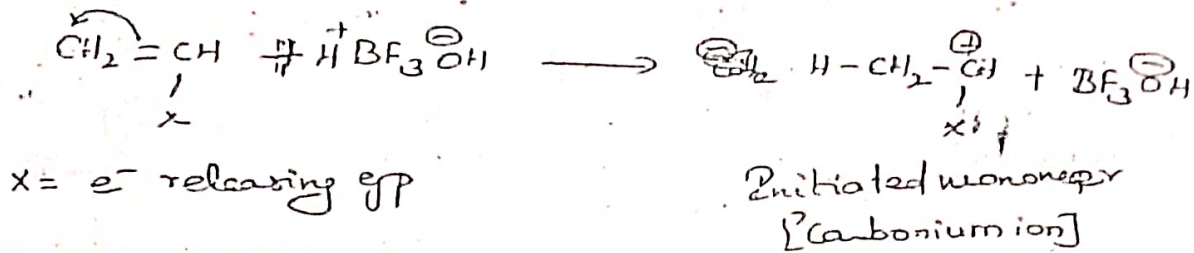
Initiator is catalyst + co-catalyst.



catalyst co-catalyst Initiator.

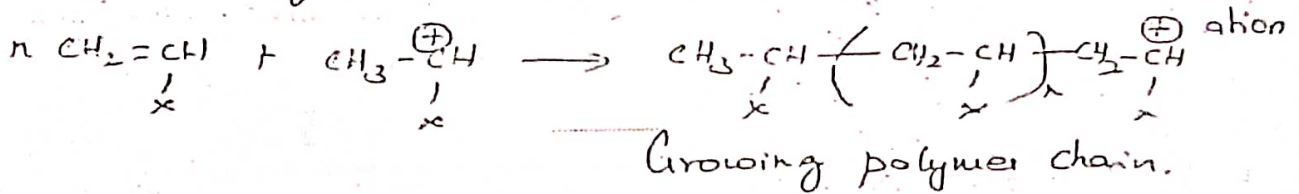
The monomer undergoes heterolytic cleavage in the presence of e^- releasing groups & forms

intermediate with both positive & negatively charged ions. Then the initiator attacks the monomer containing the & -vely charged ions.



Propagation:

The initiated monomer (or) carbonium ion combines with n no of monomer molecules & forms a growing polymer chain.

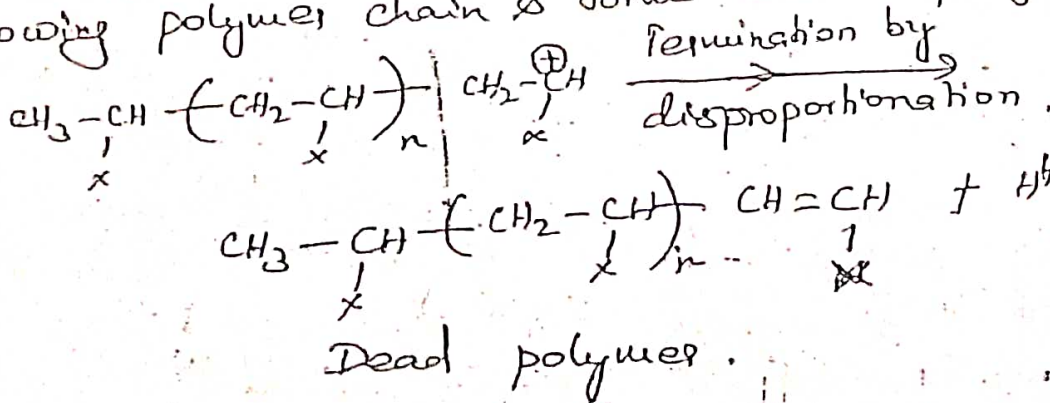


Termination:

The growing polymer chain undergoes termination in 3 diff ways to form a dead polymer molecule.

i) Termination by disproportionation:

Usually termination is brought about by disproportionation. By ~~abstraction~~ ^{elimination} or ^{removal} of hydrogen ion from the adjacent carbon atom of growing polymer chain & forms a dead polymer.

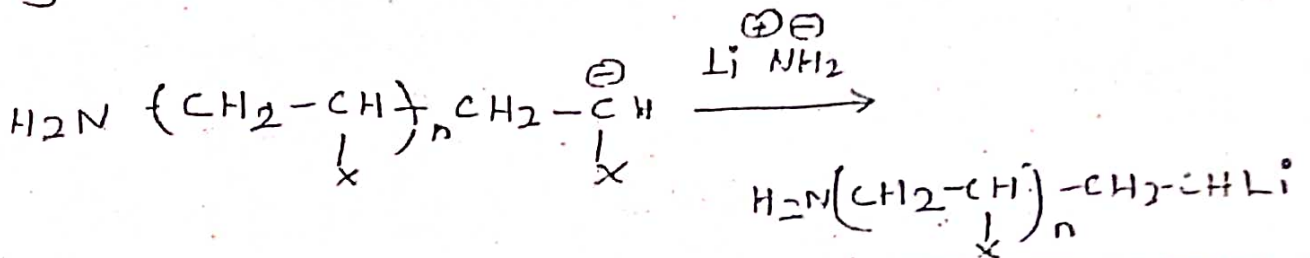


ii) Termination by combination with base:

Termination is brought about by combination of growing polymer chain with conjugate base B[⊖]

anionic polymerisation

1) By chain transfer:



+[⊖]
NH₂

initiator
monomer

It forms a dead polymer.

(17)

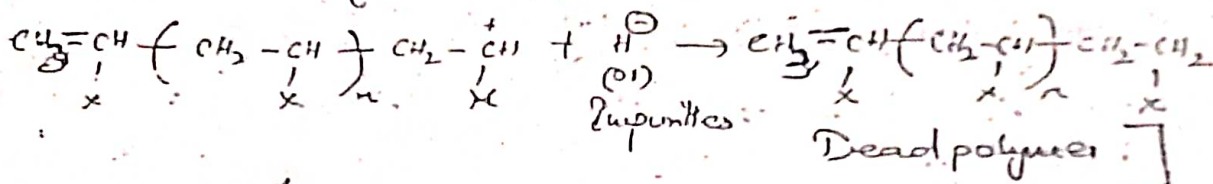


Dead polymer

$\text{B} = \text{BF}_3 \text{OEt}^-$. This type of termination occurs rarely.

(ii) Termination by chain-transfer:

The macro-carbonium ion transfers its positive charge by interaction with other molecules in the reaction medium. These molecules may be monomer, solvent or impurities. The resulting polymer have low molecular weight.



Anionic polymerisation

Presence of electron withdrawing groups in the monomer molecule favours anionic polymerisation.

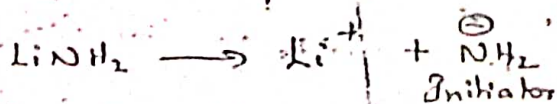
It forms carbanion or anionic intermediate as an active species. The e^- withdrawing groups are Cl , Br , I , $-\text{CN}$, $-\text{COOH}$, etc.

Initiation:

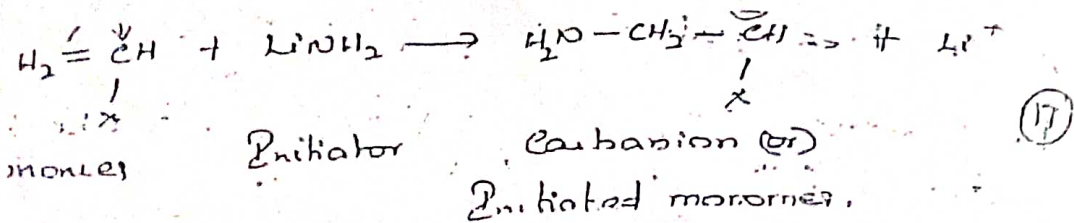
Initiation is brought about by initiators.

The initiators are organo metallic compounds and

Lewis bases. Eg: LiNH_2 , NaNH_2 , KNH_2 & NH_3

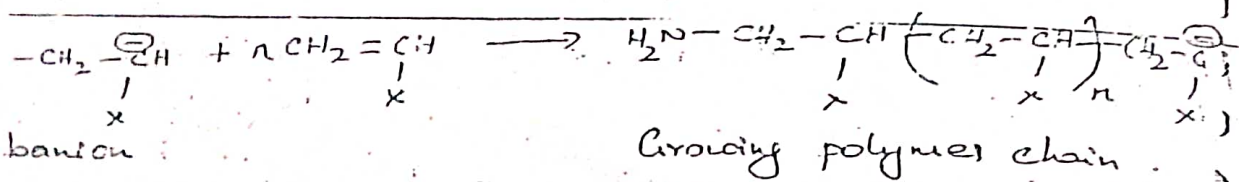


Generally, the monomers used are styrene, acrylic acid, butadiene, etc. The monomer undergoes heterolytic cleavage due to the presence of e^- withdrawing groups & forms intermediate with both positive & negatively charged ions. Then the initiator attacks the monomer containing +ve & -vely charged ions.



Propagation:

The initiated monomer (or) Carbanion combines with n no of monomer molecules & forms a growing polymer chain.

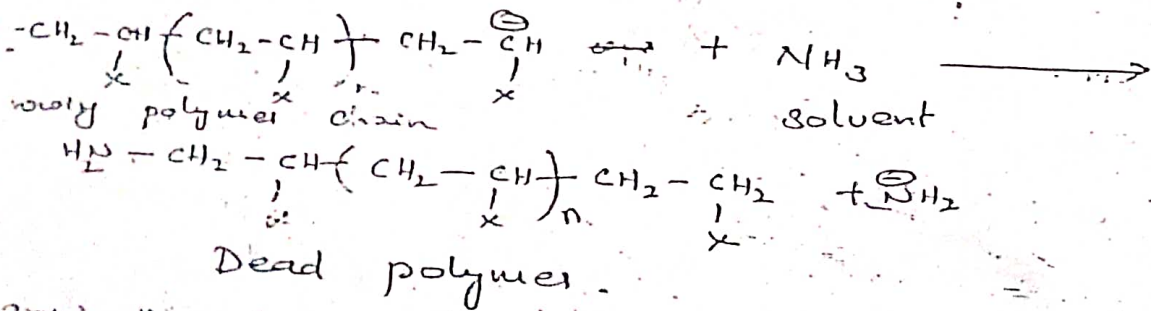


Termination:

The growing polymer chain undergoes termination in diff ways to form a dead polymer.

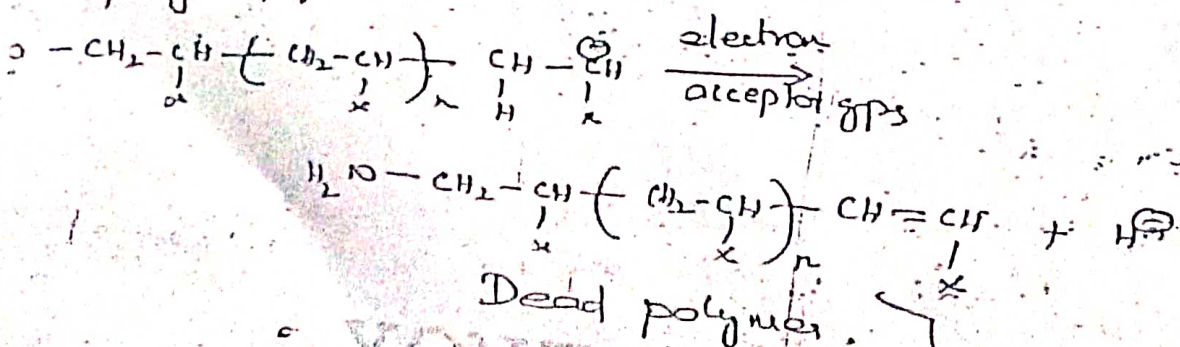
Termination by abstraction of a proton:

In anionic polymer, usually this termination is by abstraction (or) transfer of proton from a solvent molecule & it forms a dead polymer.



Termination by disproportionation:

The growing polymer chain reacts with any electron acceptor groups (or) species & loses one H^{\ominus} at the adjacent carbon atom & forms a dead polymer.



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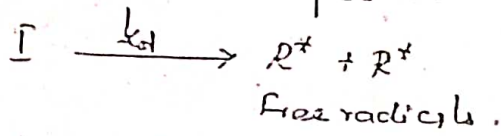
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Kinetics of Free-radical polymerisation:

(Free radical polymerisation is brought about by 3 steps i) Initiation ii) Propagation & iii) Termination.

Initiators on homolytic decomposition produces (i) Free radicals. (ii) Compare benzene

Initiator $\xrightarrow{\text{homolytic decomposition}}$ Free radicals



k_d = Rate constant for the decomposition of the initiator.

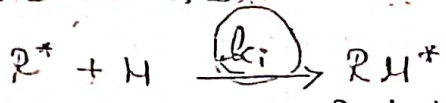
The rate of decomposition $[R^*]$ is related to the initiator $[I]$ is related to the concentration of the initiator (I) by the eqn as

$$R_d = 2k_d [I] \rightarrow (1)$$

The value '2' refers to pair of radicals produced by decomposing one molecule of the initiator.

Initiation Free radicals

The FR attacks the monomer & form new free radicals.



M: Monomer

Initiated monomer

$$R_i = [R^*][M] \rightarrow (2)$$

k_i = Initiator rate constant.

Then the rate of initiation R_i can be denoted by

$$R_i = k_i [R^*][M] \rightarrow (2)$$

The rate of formation of Free radicals in eqn (1) equal to the rate of disappearance of free radicals in eqn (2)

$$R_i = R_d$$

Applying the Condition

$$R_i = 2k_d[I]$$

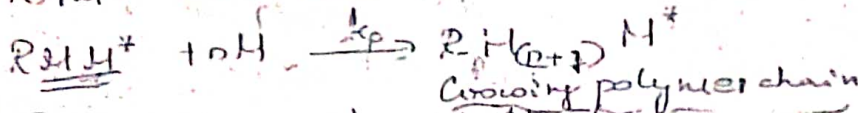
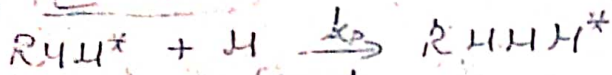
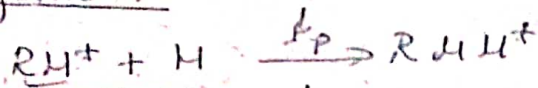
$$R_i = R_d$$

The free radicals thus formed may be effective & effective. The less effective less (or) not effective. The less effective free radicals lost as by pdts, effective free radicals initiate the chain growth. 'f' be the fraction of free effective free radical placed in initiating the chain growth, then

$$R_i = 2f k_d [I] \rightarrow (2)$$

$$R_i = 2f k_d [I]$$

Propagation:



k_p Propagation rate constant

Rate of propagation R_p is denoted by

$$R_p = k_p [M^*][M] \rightarrow (3)$$

$$R_p = k_p [M^*][M]$$

$$[M^*] = \frac{R_p}{k_p [M]} \rightarrow (5)$$

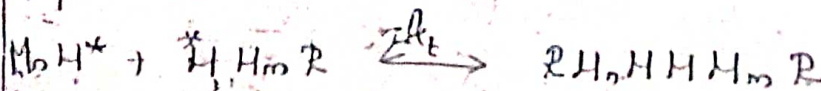
$$[M^*] = \frac{R_p}{k_p [M]}$$

$[M^*]$ = concentration of free radical sites

$[M]$ concentration of the monomer.

Termination:

The two growing polymer chains undergoes termination, the coupling rxn to form a dead polymer. It can be represented as



growing polymer chain $R_1M_nM^* + ^*M_mR$ Dead polymer.

k_t Termination rate constant.

Rate of termination R_t is denoted by

$$R_t = 2k_t [M^*]^2 \rightarrow (6)$$

At steady state approximation, the rate of initiation is equal to the rate of termination.

$$\therefore R_i = R_t$$

From eqn's (3) & (6), we can write

$$2k_d[I] = 2k_t[M^*]^2$$

$$k_d[I] = k_t[M^*]^2$$

$$[M^*]^2 = \frac{k_d}{k_t} [I]$$

$$\therefore [M^*] = \left[\frac{k_d}{k_t} [I] \right]^{1/2} \rightarrow (7)$$

Substitute the value of $[M^*]$ in the eqn (5)

$$[I^*] = \frac{R_p}{k_p [M]} \quad ; \quad \text{[Already known from eqn (5)]}$$

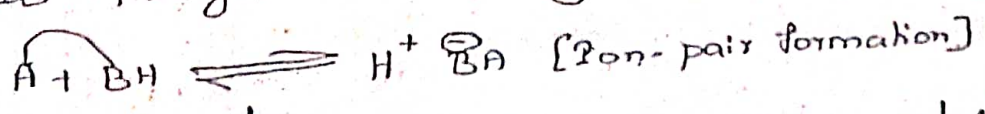
$$\frac{R_p}{k_p [M]} = \left[\frac{k_d}{k_t} [I] \right]^{1/2}$$

$$\therefore R_p = k_p \frac{k_d^{1/2}}{k_t^{1/2}} [I]^{1/2} [M]$$

This equation states that the rate of polymer formation is proportional to the first power of the monomer conc and also to the square root of the initiator concentration.

Kinetics of cationic polymerisation: (5)(ii)

The general cationic polymerisation proceeds through the following steps



$H^+ \cdot BA \xrightarrow{k_i} \dots$ A = Catalyst ; BH = co-catalyst

The initiator is formed in the combination of catalyst with co-catalyst.

Initiation:

The initiator attacks the monomer in this step.



= Initiator rate constant.

so the rate of initiation is given by

$$R_i = k_i [H^+] [M] \longrightarrow \textcircled{1}$$

Propagation:



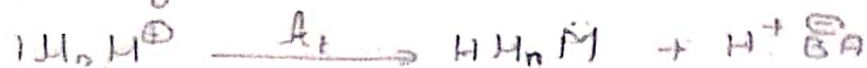
k_p = Propagation rate constant.
 growing polymer chain

so the rate of propagation is given by

$$R_p = k_p [H^+] [M] \longrightarrow \textcircled{2}$$

Termination:

By removing a proton $[H^+]$ from growing chain, the termination rxn occurs & forms a polymer chain.



H^+ is removed combined with BA & forms complex $H^+ BA^{\ominus}$

= Termination rate constant.

Then the rate of termination is given by

$$R_t = k_t [H^+] \longrightarrow \textcircled{3}$$

steady state approximation: the rate of initiation is equal to the rate of termination.

$$R_i = R_t$$

$$k_i [H^+] [M] = k_t [H^+]$$

$$[H^+] = \frac{k_i [H^+] [M]}{k_t} \longrightarrow \textcircled{4}$$

(22)

Substitute the value of $[M^+]$ in the eqn (2)

$$R_p = k_p [M^+] [M]$$

$$R_p = \frac{k_p k_i [M] [M^+] [M]}{k_t}$$

$$\therefore R_p = \frac{k_p k_i}{k_t} [M^+] [M]^2$$

This states that the rate of propagation of the ~~polymer~~ cationic polymerisation ~~is~~ depends upon is second order with respect to monomer concentration

(or) Square of the monomer concentration.

The degree of polymerisation is given by

$$D_p = \frac{R_p}{R_t} = \frac{k_p [M] [M^+]}{k_t [M^+]}$$

$$\therefore D_p = \frac{k_p [M]}{k_t}$$

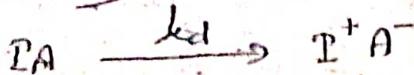
This indicates that degree of polymerisation depends upon the monomer concentration & independent of initiator concentration

Kinetics of Anionic polymerisation:

(Generally Anionic polymer proceeds through the following steps.

Initiator on decomposition produces ion pairs

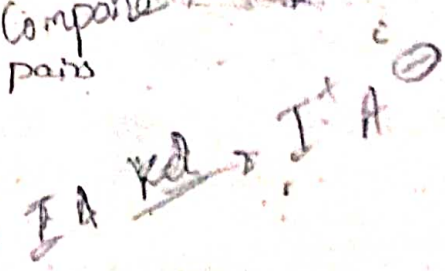
Which initiate the monomer



Initiator Ion pair formation

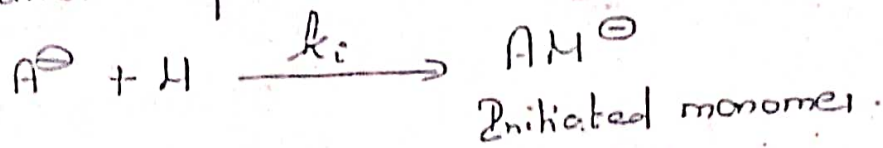
k_d = Rate constant for initiator decomposition.

(5) (ii) Compare ~~terose~~ (i)



Initiation:

The initiator attacks the monomer in the initiation step.

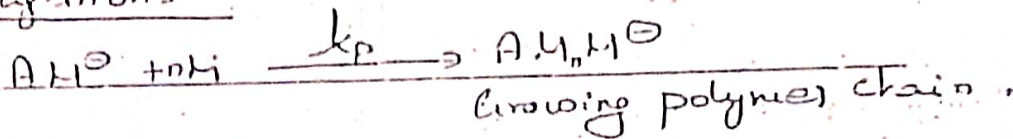


$$R_i = k_i [M] [A^\ominus]$$

k_i = Rate constant for initiation
Then the rate of initiation is given by

$$R_i = k_i [M] [A^\ominus] \quad \text{--- (1)}$$

Propagation:

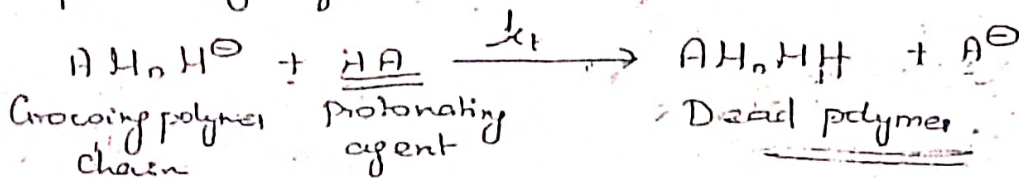


k_p = Rate constant for propagation.
Then the rate of propagation is given by

$$R_p = k_p [M^\ominus] [M] \quad \text{--- (2)}$$

Termination:

The growing polymer chain abstracts a proton from the protonating agent & forms a dead polymer chain.



k_t = Rate constant for termination.

Then the rate of termination is given by

$$R_t = k_t [M^\ominus] [HA] \quad \text{--- (3)}$$

At steady state approximation, the rate of initiation is equal to the rate of termination.

$$R_i = R_t$$

$$k_i [M] [A^\ominus] = k_t [M^\ominus] [HA]$$

$$[M^\ominus] = \frac{k_i [M] [A^\ominus]}{k_t [HA]} \quad \text{--- (4)}$$

Substitute the value of $[M^\ominus]$ in the eqn (2), then

$$R_p = k_p [M^\ominus] [M]$$

$$R_p = k_p [M] \cdot \frac{k_i [M] [A^\ominus]}{k_t [HA]}$$

$$\therefore R_p = \frac{k_p k_i [A^\ominus] [M]^2}{k_t [HA]}$$

This states that the rate of propagation of the anionic polymerisation is second order with respect to the monomer concentration (or) square of the monomer conc.

The degree of polymerisation is given by

$$D_p = \frac{R_p}{R_t} = \frac{k_p [M] [M^\ominus]}{k_t [M] [HA]}$$

~~$$D_p = \frac{k_p [M] [M^\ominus]}{k_t [M] [HA]}$$~~

$$\therefore D_p = \frac{k_p [M]}{k_t [HA]}$$

This indicates that degree of polymerisation depends upon the monomer concentration and independent of initiator concentration.

Condensation polymerisation:

When monomers having 2 or more ^{reactive} functional groups brought together, they ^{undergo} condensation rxn to form a polymer with small byproducts.

(i) Monomers having only 2 ^{reactive} functional gps. - condensed together, to form linear polymer is obtained.

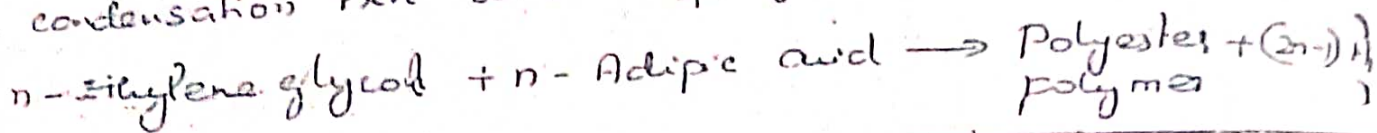
(ii) when monomers having 3 ^{reactive} functional gps condensed together, then cross-linked, network (or) branched polymer is obtained.

Condensation polymerisation is otherwise called step-growth (or) step-wise polymerisation.

As the monomer adds to the another

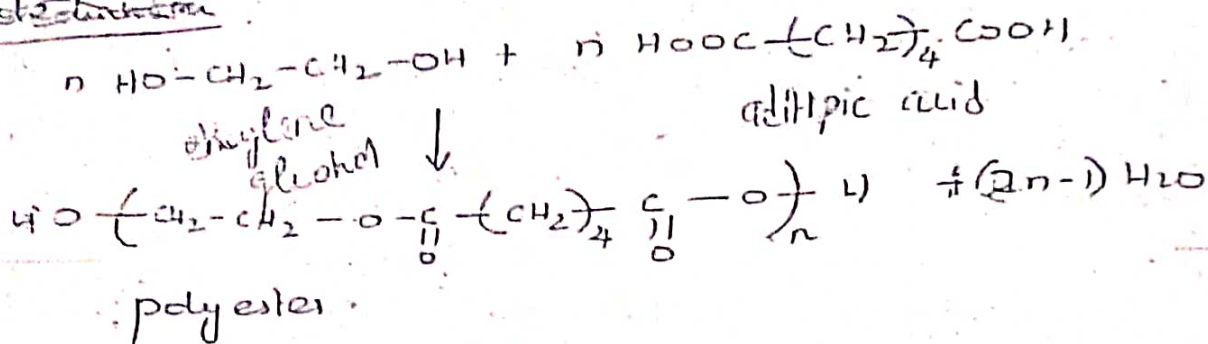
monomers. (ii) growing polymer chain in a step wise manner. So the polymer chain grows slowly in a step-wise manner.

Eg: ~~n molecules~~ n number of ethylene glycol monomers reacts with n number of adipic acid monomers, undergoes a condensation rxn to form polyester polymer.

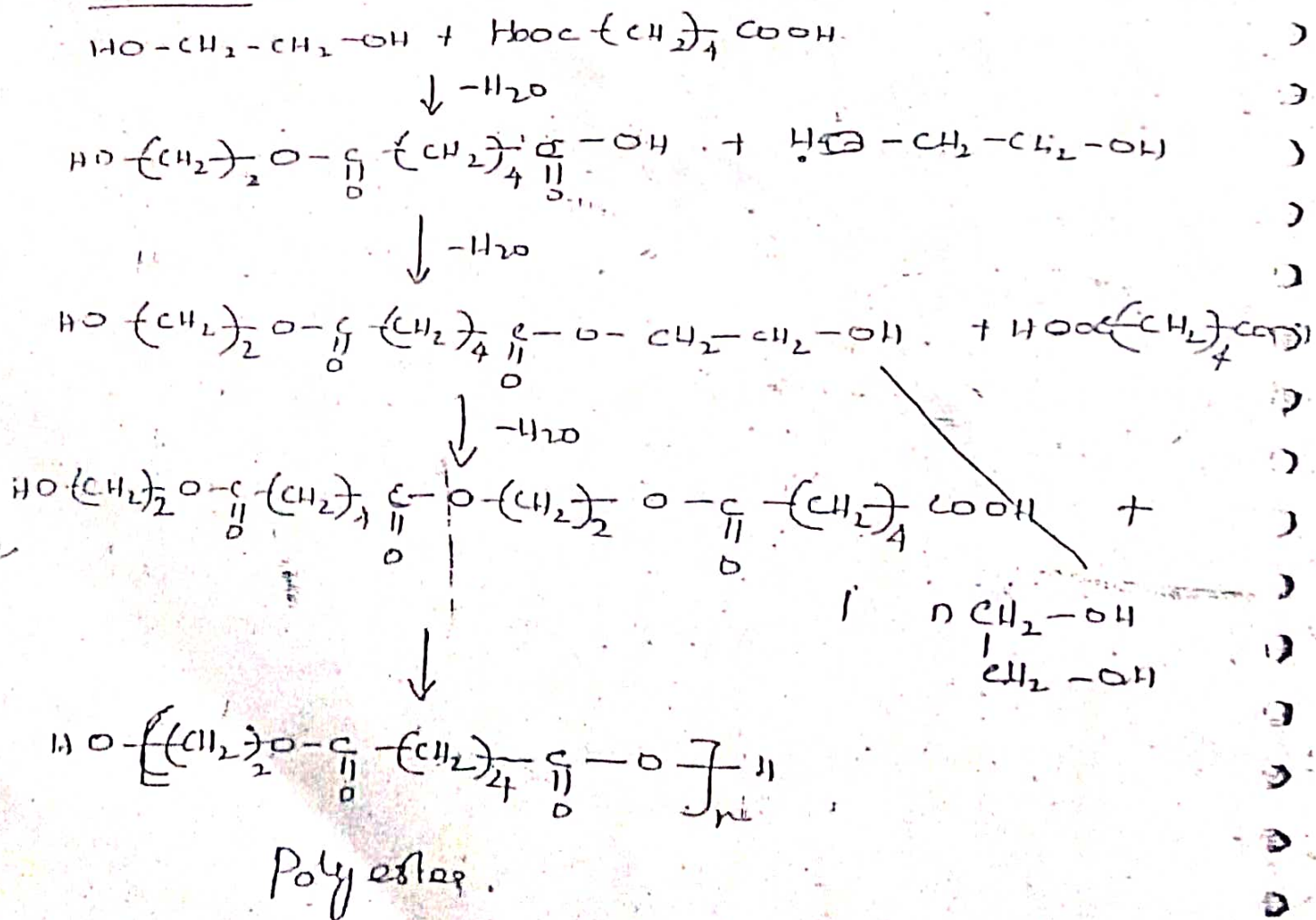


Here water molecule removed as a byproduct.

Structure



Mechanism:



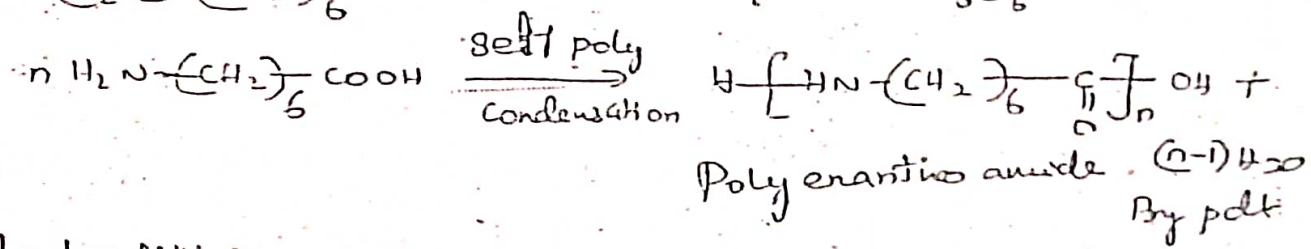
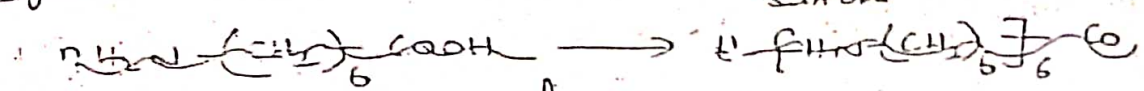
In condensation polymer, the ^{final} polymer chain formed is active and not dead polymer as in chain polymer. It is the only type of rxn where the 2 reactive functional grps involved in polymer formation.

Self poly condensation:

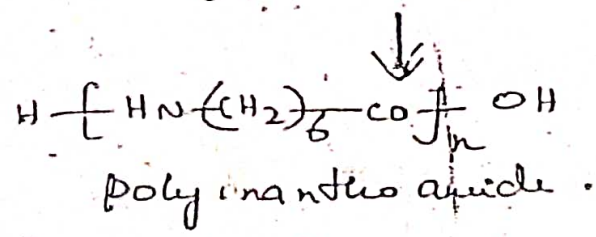
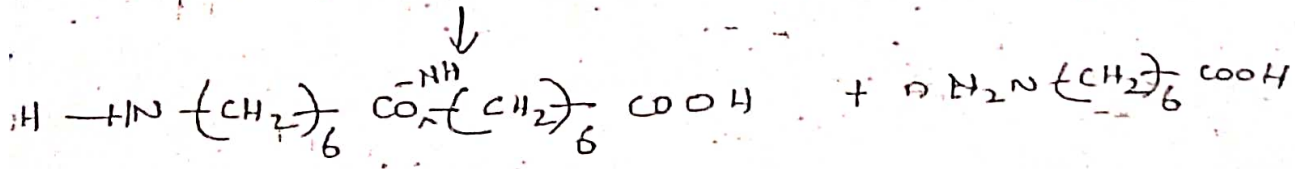
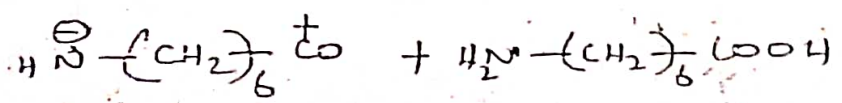
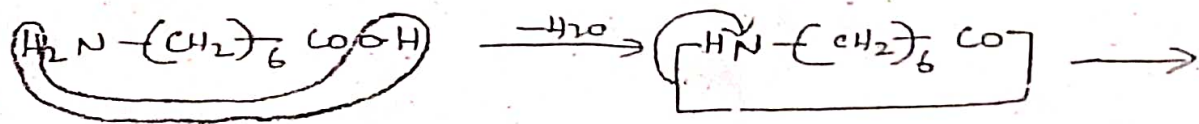
~~It is 2 reactive functional grps present on~~

the same monomer molecule, a self poly condensation rxn occurs & forms a polymer molecule.

Eg: n Amino enanthic acid $\xrightarrow[\text{polycondensation}]{\text{self}}$ Poly enanthoamide.

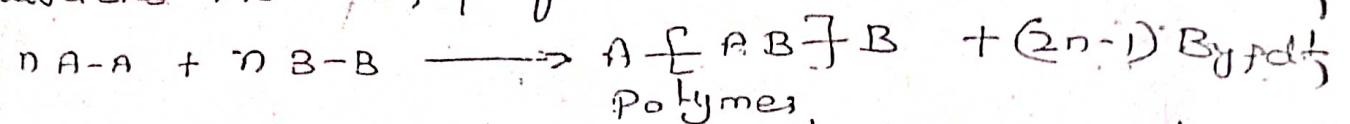


Mechanism:

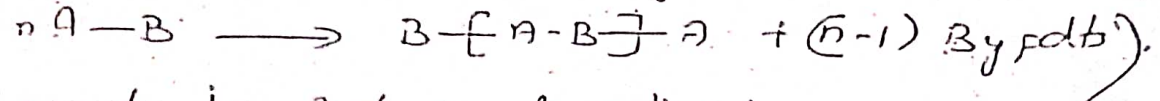


In addition to amino acids, lydiony acids, alkylene chloroaldehydes also undergoes self poly condensation.

If two reactive functional groups present on two different monomers, polycondensation rxn occurs



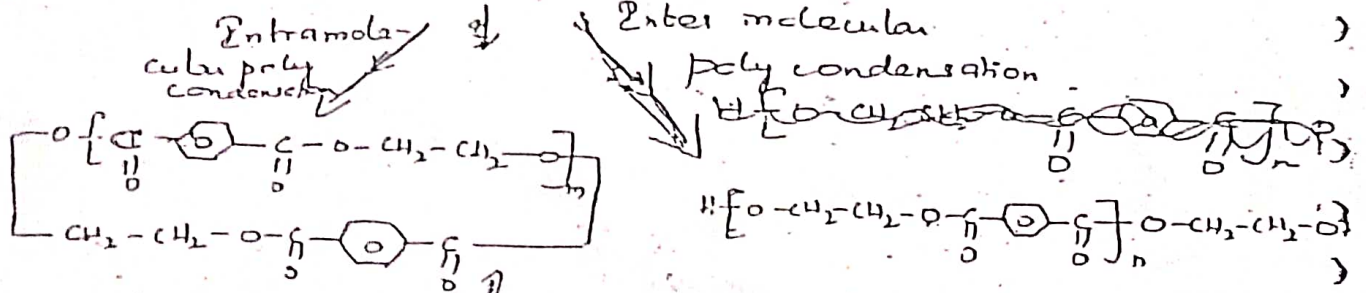
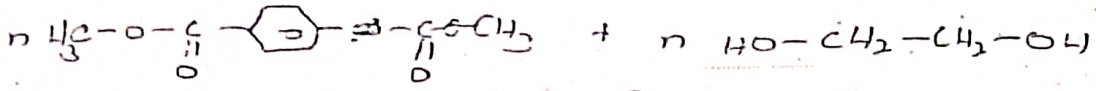
If the two reactive functional groups present on the same monomer, self polycondensation rxn occurs



Intramolecular polycondensation:

If AA-BB & A-B type of monomers reacts, in addition to intermolecular condensation, intramolecular condensation rxn also occurs & forms a cyclic poly

Ex: Rxn between dimethyl terephthalate & Ethylene glycol



n = 2, 3, 4

Kinetics of condensation polymerisation:

Condensation polymer can be brought about by

- (i) by using catalyst & (ii) By non-catalysed
- (i) Without catalyst & (ii) With catalyst.

Kinetics of non-catalysed polycondensation:

(i) Considers the synthesis of a polyester from a dicarboxylic acid and diol. It is a type of esterification rxn. Usually the esterification rxns carried out in the are catalysed by acids.

But here the dicarboxylic acid used is very strong, so this is carried out in the absence of catalyst. Also, the dicarboxylic acid acts as a catalyst.

ence in polyesterification

∴, the rate of the rxn is proportional to the square of the concentration of the -COOH gp & 1st power conc. of the -OH gp:

The rate of rxn is given by the eqn as

$$-\frac{d[\text{OH}]}{dt} = k[\text{COOH}]^2 [\text{OH}] \quad \rightarrow \textcircled{1} \quad \frac{d[\text{COOH}]}{dt} = k[\text{COOH}]^2 [\text{OH}]$$

~~A - Esterification rate constant~~

When the concentration of -OH & -COOH gps are equal, i.e., when we take stoichiometric (or eqm) quantities of the functional gps $[\text{FC}]$, we can represent that at a given time 't':

$$[\text{COOH}] = [\text{OH}] = [\text{FC}]$$

Then the eqn $\textcircled{1}$ can be written as

$$-\frac{d[\text{FC}]}{dt} = k[\text{FC}]^2 [\text{FC}]$$

$$-\frac{d[\text{FC}]}{dt} = k[\text{FC}]^3$$

In Bringing the $[\text{FC}]$ terms on one side

$$\frac{-d[\text{FC}]}{[\text{FC}]^3} = k dt$$

On integrating the above eqn, we get the value as

$$\frac{1}{2[\text{FC}]^2} = kt + c \quad \rightarrow \textcircled{2}$$

At initial conc $[\text{FC}] = [\text{FC}_0]$, and $t = 0$.

$$\frac{1}{2[\text{FC}_0]^2} = c \quad \rightarrow \textcircled{3}$$

Substitute the 'c' value in the eqn $\textcircled{2}$, we get

$$\frac{1}{2[\text{FC}]^2} = kt + \frac{1}{2[\text{FC}_0]^2}$$

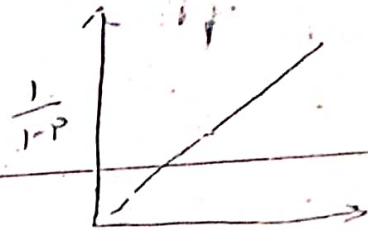
We know that $D_p = \frac{1}{1-P}$

where D_p = Degree of polymerisation.

$$\therefore D_p = k_2 [M]_0 t + 1$$

By plotting $\frac{1}{1-P}$ vs time 't', a

a linear straight line is obtained.



The above eqn. states that the

Degree of polymer D_p appears as the 1st power of

the time 't' also as the 1st power. \therefore the molecular weight of the polymer increases rapidly.

Polymerisation conditions:

To produce the polymer of a required molecular weight, molecular weight distribution & degree of branching, various factors have to be taken in consideration.

The factors are i) Nature of the monomer,

ii) Type of polymerisation mechanism chosen,

iii) Required physical form of the polymer,

iv) Usability of the process for industrial production.

The polymerisation reaction may be carried out

in the i) solid phase, ii) liquid phase & iii) gas phase.

The most of the commercial polymers are prepared in

the liquid phase & more recently the solid phase polymerisation

has also been used.

The liquid phase polymerisation may be further

subdivided into 4 categories, depending on the nature of the physical system.

i) Bulk polymerisation ii) Solution polymerisation

iii) Suspension polymerisation & iv) Emulsion polymerisation.

Bulk polymerisation: [Homogeneous system]

It is the simplest process & widely used for the synthesis of condensation polymer. The system is homogeneous which consists of monomers (or) polymer in the liq. state. The monomer, initiator and chain transfer agent are heated (or) exposed to radiation source in the reactor vessel for initiating polymerisation.

The reactor is kept under agitation for proper mass and heat transfer. The chain transfer agent is added to control the molecular weight of the polymer. As the polymerisation proceeds, the viscosity of the medium increases & heat transfer ^{and mixing} becomes difficult. This leads to the products with very broad molecular weight distribution.

Advantages:

It is a simple process & the product obtained has a high purity, b'cos except the initiator & the chain transfer agent ^{there is} no other additive to contaminate the product.

Disadvantages:

- i) As polymer formation proceeds, the medium becomes viscous and heat transfer becomes difficult.
- ii) If polymerisation is exothermic, ^{heat} control becomes more difficult and sometimes it may lead to explosions.
- iii) Due to the difficulties in transferring heat, the local and accumulation of heat occurs in the particular spot area of the product & this leads to degradation and decolouration of polymer.

Ex: This technique is used in free radical polymerisation of methyl methacrylate or styrene.