vinyl polymerisation

or

CHEMISTRY OF POLY

or

Addition polymerisation →

"Addition polymerisation is also known as chain polymerisation"

⇒ This type of polymerisation involve the self addition of normal unsaturated molecule without loss of any small molecule to give a single giant molecule.

∴ This polymerisation is also known as vinyl polymerisation.

These polymerisation pass through successive stage of Initiation, propagation, termination common to chain reactants.

free radical — Ionic — Co-ordinate

(1) FREE RADICAL ADDITION POLYMERISATION ⇒

Initiators: Initiators are thermally unstable compounds which on heating easily decompose into free radicals.

Exa: Peroxides, azocompound, ~~polyesters~~, H_2O_2

$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R$

Imp ⇒ Benzoyl peroxide is a commonly used initiator

$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5$ ⟶ Heat

$$2\,C_6H_5-\overset{O}{\overset{\|}{C}}-O^{\cdot} \downarrow$$

$$2\,C_6H_5^{\cdot} + 2CO_2$$

(Phenyl free radical)

gmp → Decomposition of H_2O_2 in the presence of Fe^{+2} ions to form OH^-, Fe^{+3}, $OH^{\cdot}$ ... such redox initiators are termed redox polymerisation.

$$H-O-O-H + Fe^{+2} \longrightarrow HO^{\cdot} + HO^- + Fe^{+3}$$

The free radical addition polymerisation involves process initiation, chain growth and chain termination.

(i) Initiation step → A free radical contains a lone or unpaired electron which always looks for another lone electron to couple with it, in order to get stabilised.

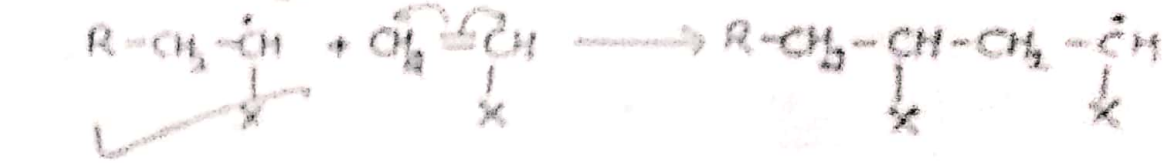
The free radical $R^{\cdot}$ attacks the double bond of the monomer molecules.

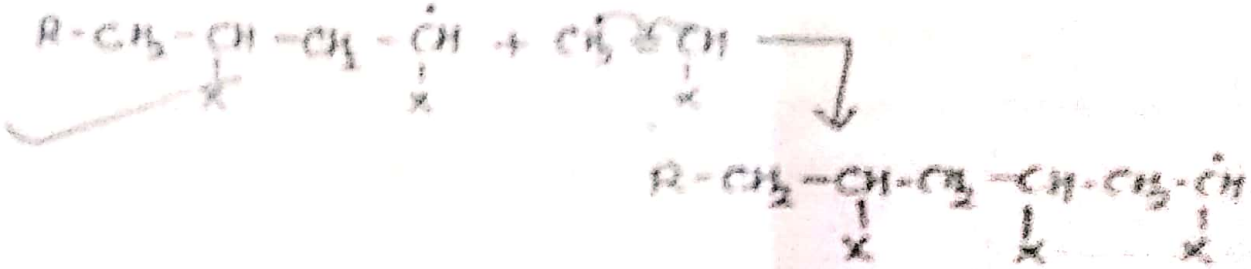
$$CH_2=CHX + R^{\cdot} \longrightarrow R-CH_2\dot{C}HX$$

The free radical attacks on the monomer, initiating polymerisation is an exothermic process and F.R. formation by initiator decomposition is an endothermic process.

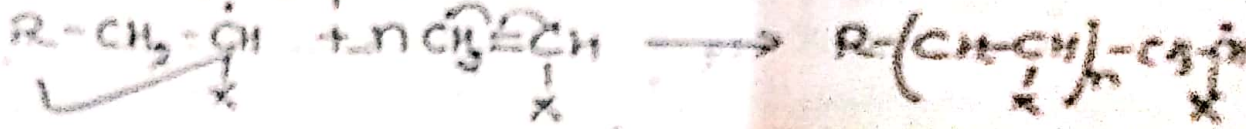
(ii) Propagation step ⇒ The new free radical so formed adds to another molecule of monomer to form another free radical, which further adds to another fresh molecule to form another free radical, ~~which~~

and so on.





overall propagation

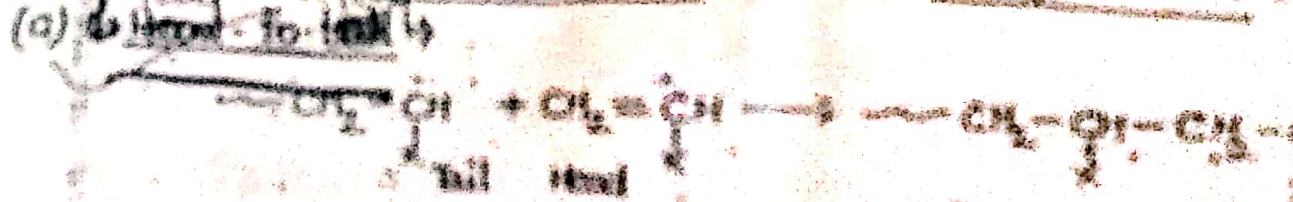


n is denoted the number of monomer units added up in the chain growth.

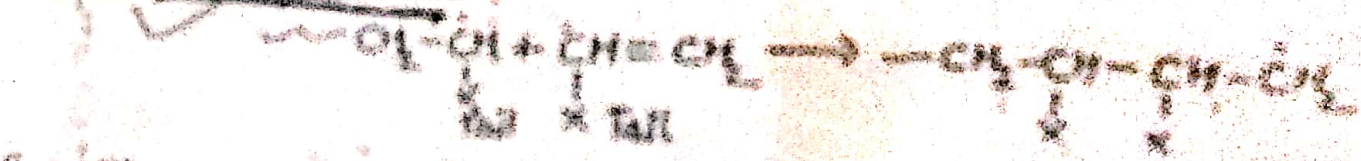
The mode of addition of the incoming monomer to the growing chain can be of the head-to-tail, tail to tail, head to head or tail to head type.

Assuming $-CH_2$ part as head and $-CH$ part as tail

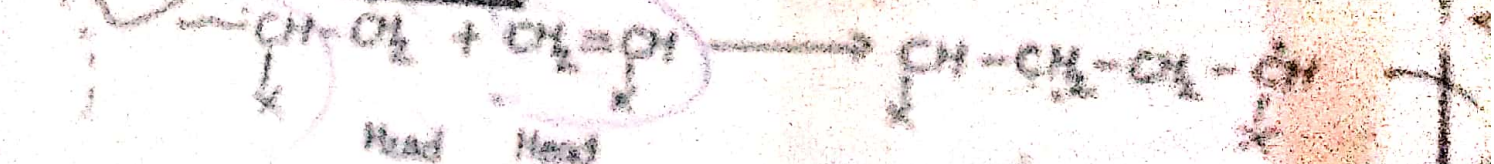
(a) Head-to-tail



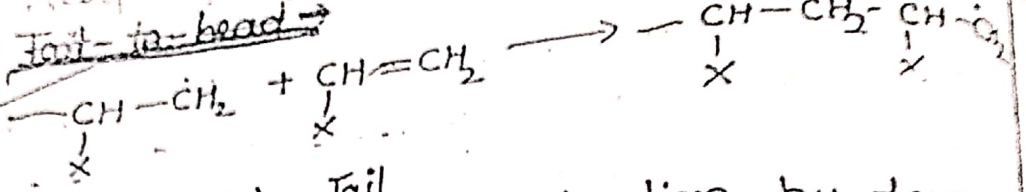
(b) Tail-to-tail



(c) Head-to-Head

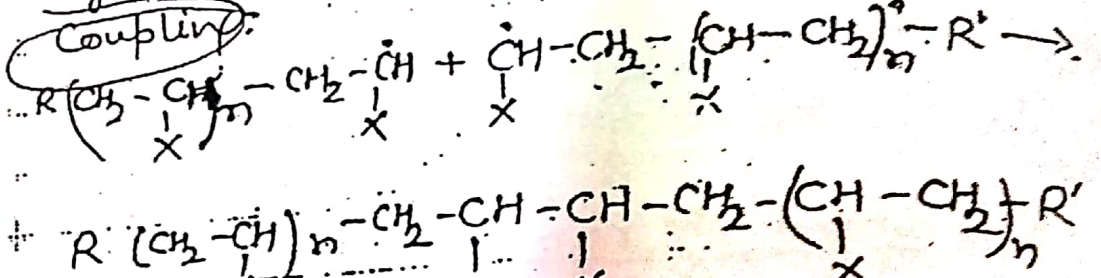


(a) Tail-to-head

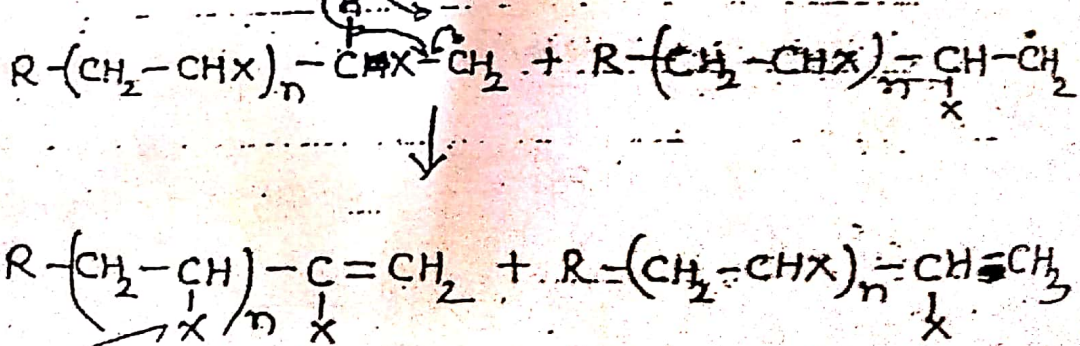


(iii) Termination step ⇒ Termination by four types:

(a) by coupling ⇒ The step in which two large growing chains come close and couple together to stop the chain reaction is called coupling.



(b) by disproportionation ⇒ The chain that loses hydrogen atom, stabilises itself by the formation of a double bond. This process is called disproportionation.



(c) by chain transfer ⇒ In the case of transfer reaction, while the growth of one polymer chain is stoped or arrested, forming a dead polymer, there is a simultaneous generation of a new free radical capable of initiating a fresh

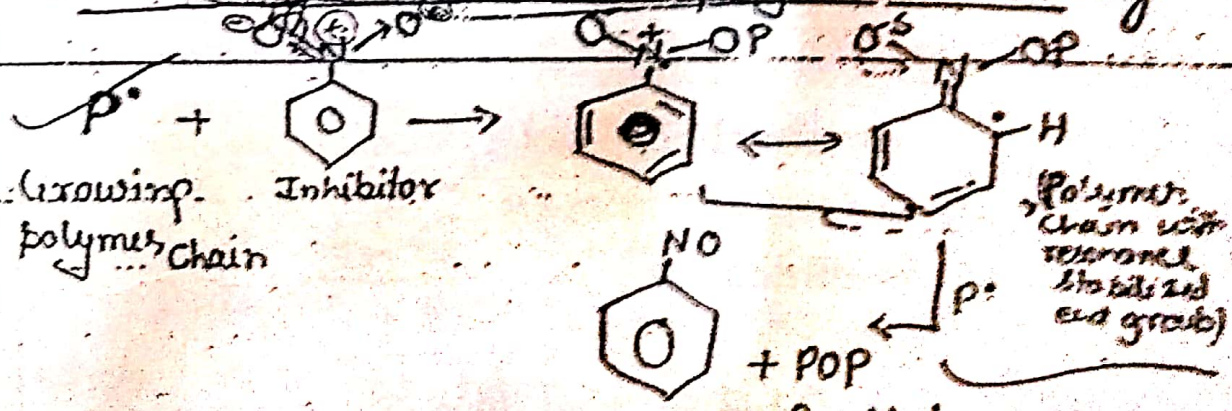
polymer chain growth. This reaction takes place by the abstraction of a hydrogen atom or some other atom from the initiator, monomer or polymer or from any other species present in the system, including the solvent.

$$R-(CH_2-\underset{X}{CH})_n-CH_2-\dot{\underset{X}{C}}H + R'H \longrightarrow R-(CH_2-\underset{X}{CH})_n-CH_2-\underset{X}{CH_2} + R'^{\bullet}$$

free radical

(d) Inhibitors: Inhibitors are chemicals substances capable of inhibiting or killing the chain growth by combining with the active free-radicals and forming either stable products or inactive free radicals.

Exa: Hydroquinone, nitrobenzene, dinitrobenzene, benzothiazine are some of the inhibitors customarily used in the polymer industry.



⇒ Inhibitors are used to arrest the polymerisation at some specific point in order to get a uniform product and to avoid cross linking. When used for this purpose inhibitors are called "short stops".

By coupling or disproportionation or Inhibitors, the products formed are dead or non reactive - but ⇒ by chain transfer the product formed are not dead polymers.

KINETICS OF FREE-RADICALS POLYMERISATION

$I \xrightarrow{Kd} 2R^{\cdot}$ (Homolytic cleavage)

Here Kd = Initiator decomposition rate const

$R^{\cdot}$ = free radical

$$\frac{-d(I)}{dt} = Rd = 2Kd(I) \quad -(2)$$

A factor of 2 is used in eq(2) as a pair of radicals is produced by decomposing one molecule of initiator

We know that the rate constant is related to temp as follows.

$$Kd = Ae^{-Ea/RT} \quad -(3)$$

A = is constant called frequency factor

E = is activation Energy

R = Gas constant.

T = Temp.

Substituting kd from equation (3). equation (2) can be written as

$$Rd = 2Ae^{-Ea/RT}(I) \quad -(4)$$

Rate of decomposition $\propto I \propto T$

Initiation:

The free radicals generated by the decomposition of the initiator, can attack the monomer to give a new free radicals.

$$R^{\bullet} + M \xrightarrow{Ki} RM^{\bullet} \quad -(5)$$

where M is monomer

Ki = Initiator rate constant

The rate of Initiation

$$-\frac{d(M)}{dt} = Ri = Ki (R^{\bullet}) (M), \quad -(6)$$

From eq (2) we

$$Ri = 2 f Ka (I) \quad -(7) \qquad Ri = Rd$$

$$Ri = d f Ka (I) \quad -(8)$$

* The value of f 0.1 to 1

f is fraction of free radicals.

Propagation:

$$RM^{\bullet} + M \xrightarrow{Kp} RMM^{\bullet}$$

$$RMM^{\bullet} + M \xrightarrow{Kp} RMMM^{\bullet}$$

$$RMMM^{\bullet} + Mn \xrightarrow{Kp} RMn+3M^{\bullet} \quad -(9)$$

Kp = Propagation rate constant

The value of propagation Rp is represented by

$$-\frac{d(M)}{dt} = Rp = Kp (M^{\bullet}) (M) \quad -(10)$$

termination

The final step in polymerisation is termination.

$$RMn(M)^{\bullet} + RMn(M)^{\bullet} \xrightarrow{Kt} RMn, MMMn_2R \quad -(11)$$

where Kt is the termination rate constant

$$-\frac{d(M^{\bullet})}{dt} = Rt = 2 Kt (M^{\bullet})^2 \quad -(12)$$

The rate of Initiation is equal to Rate of termination.

$$Ri = Rt$$

from eq. ① & ② we can write

$$Kd\,f(I) = Kt\,(M^\cdot)^2$$

$$(M^\cdot)^2 = \frac{Kd\,f(I)}{Kt}$$

$$M^\cdot = \left(\frac{Kd\,f(I)}{kt}\right)^{1/2}$$

from eq. ⑤, we get the value of $M^\cdot$ as

$$M^\cdot = \frac{Rp}{Kp(M)}$$

on substituting value of

$$\frac{Rp}{Kp(M)} = \left(\frac{Kd}{Kt}\,f(I)\right)^{1/2}$$

$$\therefore Rp = Kp\left(\frac{Kd}{Kt}\right)^{1/2} f[I]^{1/2}\,(M) \quad \text{(M}_1\text{)}$$

Rate of polymer formation is proportional to the ~~list~~ first power of the monomer concentration and square Root of the initiator concentration.

② Ionic polymerisation ⇒ The ionic mechanism of chain polymerisation also involves an attack on the π electron pair of monomer.

There are of two types

(A) CATIONIC – POLYMERISATION ⇒ In this polymerisation proton pulls the π e's of monomer molecule towards it and the positive charge of the proton is transferred to the farthest end of the second monomer molecule, forming

a carbenium ion.

$H^{\oplus} + CH_2=CHX \rightleftharpoons CH_3-\overset{\oplus}{C}HX$

Initiation ⇒ Initiation is carried out by proton donation by acids & co-catalysts.

Catalyst = BF_3, $AlCl_3$, $SnCl_4$, $FeCl_3$, $TiCl_4$ (Initiators)
Co-catalyst = Methanol, H_2O

$$F-\underset{F}{\overset{F}{B}} + HOH \longrightarrow \left[F-\underset{F}{\overset{F}{B}}-OH\right]^{\ominus\oplus}\cdots H \quad \text{or} \quad [F_3B{:}OH]^{\ominus}\cdots H^{\oplus}$$

ion-pair; counter ion

Here $H^{\oplus}$ is initiating species and $(F_3B.OH)^-$ counter ion

$$H^+(BF_4)^- + CH_2=\underset{X}{CH} \longrightarrow CH_3-\overset{\oplus}{\underset{X}{C}}H\,[F_3BOH]^{\ominus}$$

There is no loss of e/- only shifting of electron occurs.

Propagation ⇒ The propagation reaction involves further adding up of the monomer units and simultaneous transfer of the charge to the newly added monomer units.

$$CH_3-\overset{\oplus}{\underset{X}{C}}H\,[F_3BOH]^{\ominus} + CH_2=\underset{X}{CH} \longrightarrow CH_3-\underset{X}{CH}-CH_2-\overset{\oplus}{\underset{X}{C}}H\,[F_3BOH]^-$$

$$CH_3-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\overset{\oplus}{\underset{X}{C}}H\,[F_3BOH]^{\ominus} \xleftarrow{} CH_2=\underset{X}{CH}$$

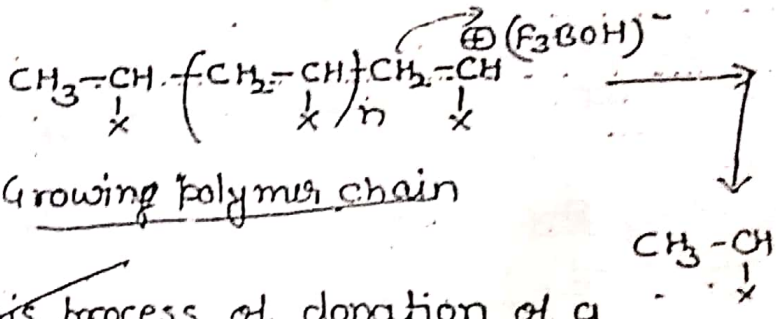
$$\downarrow n\,CH_2=\underset{X}{CH}$$

$$CH_3-\underset{X}{CH}-\left(CH_2-\underset{X}{CH}\right)_n-CH_2-\overset{\oplus}{\underset{X}{C}}H\,[F_3BOH]^-$$

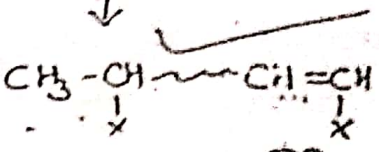
the chain growth and the counter-ion all the time, moves along with the ct ion like a "watch dog".]

(iii) Termination ⇒ two types.

(a) Donation of proton to counter-ion.

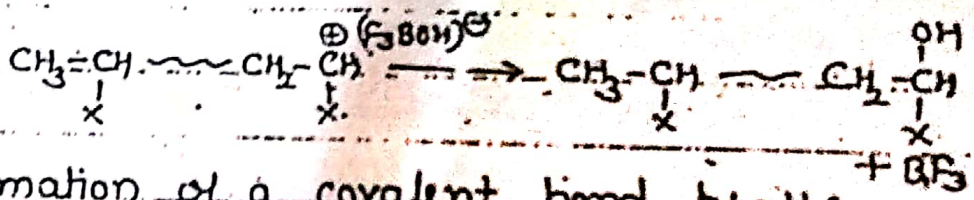


Growing polymer chain



* This process of donation of a proton and the re-formation of the BF_3 hydrate is called "ion-pair precipitation".

(b) By Simple coupling ⇒



formation of a covalent bond b/w the Carbonium ion and the counter-ion.

* See page on Top

Kinetics of Cationic polymerisation ⇒

$$A + BH \rightleftharpoons H^{\oplus} BA^{\ominus}$$

('Catalyst) (Co-Catalyst) (ion-pair formation)

Initiation ⇒

$$H^{\oplus} BA^{\ominus} + M \xrightarrow{K_i} HM^{\oplus} BA^{\ominus}$$ initiation

Propagation ⇒

$$HM^{\oplus} BA^{\ominus} + M \xrightarrow{K_p} HMM^{\oplus} BA^{\ominus}$$ Propagation

$$HMM^{\oplus} BA^{\ominus} + nM \xrightarrow{K_p} HMM_nM^{\oplus} BA^{\ominus}$$ Propagation

cation polymerisation. Eg: Polymerisation of [illegible]

termination

$HMn\overset{\oplus}{M}\overset{\ominus}{BA} \xrightarrow{Kt} HMnM. + \overset{\oplus}{M}\overset{\ominus}{BA}$ (termination)

$HMn\,M^{\oplus}\overset{\ominus}{BA} \xrightarrow{Ktr} HMnM + \overset{\oplus}{M}\overset{\ominus}{BA}$ (chain transfer to monomer)

$Ri = ki\,(M)(H^{\oplus})$ — ①

$Rt = Kt\,(M^{\oplus})$ — ③

$Rp = kp\,(M^{\oplus})(M)$ — ②

Acc. to steady state Rule

$Ri = Rt$

$ki\,(M)(H^{+}) = Kt(M^{\oplus})$

$M^{\oplus} = \frac{ki}{Kt}(M)(H^{+})$ — ④

Rate of the propagation

$$Rp = -\frac{d(M)}{dt} = kp(M)(M^{\oplus})$$

$$\boxed{Rp = kp\frac{ki}{Kt}(M)^2\ H^{\oplus}}$$

The overall polymerisation depends upon the square of monomer concentration.

(B) ANIONIC - POLYMERISATION ⇒ In anionic polymerisation, π e's of the monomers are attacked by negatively charged ion (an anion). So the anionic polymerisation is initiated by a negative ion or anion.

$$R^{-} + CH_2=\underset{X}{CH} \longrightarrow R-CH_2-\underset{}{CH}^{-}$$

In Cationic poly... movement of the ... pair is in a ... tion opposite ... of the chain ...

① Initiation ⇒ Initiation is carried out by strong bases such as alkali metal amides, alkali metal alkyls and Grignard reagent. [These are initiators]

$$KNH_2 \longrightarrow K^{\oplus} + \overset{\ominus}{N}H_2$$

$$\overset{\ominus}{N}H_2 + CH_2{=}\underset{X}{CH} \longrightarrow NH_2{:}CH_2{-}\overset{\ominus}{\underset{X}{CH}}$$

X carbanion

② Propagation ⇒ The carbanion formed in initiation step propagates the chain growth by attacking the second monomer unit.

$$H_2N{-}CH_2{-}\overset{\ominus}{\underset{X}{CH}} + CH_2{=}\underset{X}{CH} \longrightarrow H_2N{-}CH_2{-}\underset{X}{CH}{-}CH_2{-}\overset{\ominus}{\underset{X}{CH}}$$

$$H_2N{-}CH_2{-}\underset{X}{CH}{-}CH_2{-}\overset{\ominus}{\underset{X}{CH}} + n\,CH_2{=}\underset{X}{CH} \longrightarrow$$

$$R{-}\left(CH_2{-}\underset{X}{CH}\right)_n{-}CH_2{-}\overset{\ominus}{\underset{X}{CH}}$$

(Living polymer)

③ Termination ⇒ Do not occur spontaneously. All monomer are consumed in the anionic polymerisation, leaving active end behind. If fresh quantity of monomer is added then polymerisation again starts. Polymers produced by this tech are called "living polymers".

→ Living polymerisation tech is useful for many application. Eg: Preparation of Block copolymers.

of e pair is in the rearrangement as that of chain growth

II KINETICS OF ANIONIC POLYMERISATION

$$IA \xrightarrow{K_d} I^{\oplus} A^{\ominus}$$

(Ion pairs formation)

IA = Initiator

K_d = is dissociation rate constant

(i) Initiation :

$$A^{\ominus} I^{\oplus} + M \xrightarrow{K_i} A M^{\ominus} I^{\oplus}$$

(ii) Propagation:

$$A M^{\ominus} I^{\oplus} + M \xrightarrow{K_p} A M M^{\ominus} I^{\oplus}$$

$$A M_n^{\ominus} I^{\oplus} + nM \xrightarrow{K_p} A M_n M^{\ominus} I^{\oplus}$$

(iii) Termination

$$A M_n M^{\ominus} I^{\oplus} + H A \xrightarrow{K_t} A M_n M H + A^{\ominus} I^{\oplus}$$

where HA = protective agent

K_i = Initiation rate constant

K_p = Propagation rate constant

K_t = Termination rate constant

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

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

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

Acc to steady state law

$$R_i = R_t$$

$$K_i (M)(A^{\ominus}) = K_t (M^{\ominus})(HA)$$

$$M^{\ominus} = \frac{K_i (M)(A^{\ominus})}{K_t (HA)}$$

Put this value in eq: ①

$$R_p = k_p (M^{\ominus})(M)$$

$$R_p = k_p \frac{K_i}{K_t} \frac{(M)(A^{\ominus})(M)}{(HA)}$$

$$R_p = \frac{K_i k_p}{K_t} \frac{(M)^2 [A^{\ominus}]}{(HA)}$$

II

Characteristic of Anionic polymerisation

① Rate of polymerisation depend on catalyst conc.,

② There is no termination in absence of impurities which gives concept of living polymer.

③ In case of Heterogeneous kinetics curve is broad.

④ In case of homogeneous kinetics curve is narrow.

⑤ Monomer have double bonds (Polymerisation takes place by the attack of an anion or carbanion on the π electrons of the double bond.

⑥ The process is suitable for solution technique.

⑦ It is not suitable for suspension and emulsion polymerisation because reaction is sensitive to moisture and other ionic impurities.

⑧ The polymer formed is generally atactic.

Characteristic of Cationic polymerisation

(1) very high rate of Reaction.
(2) very high molecular wt polymer.
(3) No activation energy is required.
(4) Polymer formed has a medium mol. wt distribution. Generally
(5) monomer have double bond. polymerisation takes place by an attack of cation or Carbonium ion on the π electrons of the double bond.
(6) Same as Anionic
(7) Same as Anionic
(8) Same as Anionic

Imp. feauture of free radical polymerisation

(1) Rate of polymerisation depends upon free radical initiator
(2) Polymer has a broad mole. wt. distribution
(3) Monomer have double bond. polymerisation takes place by an attack of free radical on the π e's of the double bond.
(4) This type of polymerisation is suitable for bulk, suspension and emulsion tech.
(5) It is most widely used in industry because reaction is simple.