Where the initiation is done by a proton and propagation by carbocation is known as cation polymerisation. Ex: Polymerisation of ...

termination

$$HM_n\overset{\oplus}{M}\,\overset{\ominus}{BA} \xrightarrow{K_t} HM_nM. + \overset{\oplus}{H}\,\overset{\ominus}{BA} \text{ (termination).}$$

$$HM_nM^{\oplus}\,\overset{\ominus}{BA} \xrightarrow{K_{tr}} HM_nM + \overset{\oplus}{M}\,\overset{\ominus}{BA} \text{ (chain transfer to monomer)}$$

$R_i = k_i\,(M)\,(H^{\oplus})$ — ①

$R_t = k_t\,(M^{\oplus})$ — ③

$R_p = k_p\,(M^{\oplus})\,(M)$ — ②

Acc. to steady state Rule

$R_i = R_t$

$k_i\,(M)\,(H^+) = k_t\,(M^{\oplus})$ — ④

$M^{\oplus} = \frac{k_i}{k_t}\,(M)\,(H^+)$

Rate of the propagation

$$R_p = -\frac{d(M)}{dt} = k_p\,(M)\,(M^{\oplus})$$

$$\boxed{R_p = k_p\,\frac{k_i}{k_t}\,(M)^2\;H^{\oplus}}$$

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.

$$R^- + CH_2 = \underset{\underset{X}{|}}{CH} \longrightarrow R - CH_2 - \underset{|}{\overset{\ominus}{C}H}$$

III Cationic poly... the movement of the electron pair is in a direction opposite that of the chain growth.

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

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

$$\overset{\ominus}{N}H_2 + CH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow NH_2{\cdot}CH_2-\underset{X}{\underset{|}{\overset{\ominus}{C}H}} \text{ carbanion}$$

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

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

$$H_2N-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\overset{\ominus}{C}H}} + nCH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow R{-}\left(CH_2-\underset{X}{\underset{|}{CH}}\right)_n-CH_2-\underset{X}{\underset{|}{\overset{\ominus}{C}H}}$$

③ **Termination** ⇒ Do not occur spontaneously. All monomers are consumed in the anionic polymerisation, leaving active end behinds. 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.

Ex: 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.