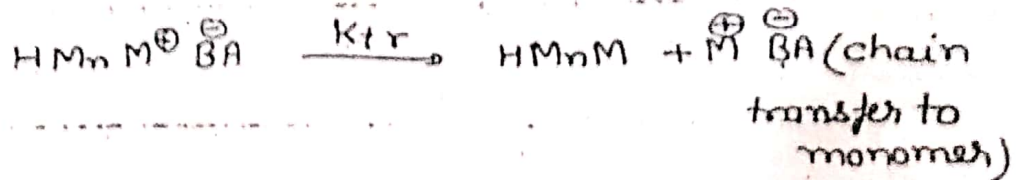
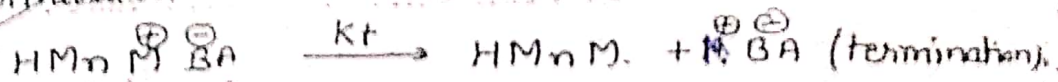


where the catalyst is given by a proton and propagates by dissociation is known as cation polymerisation. Example: Polymerisation of styrene

Termination



$$R_i = k_i (M)(H^{\oplus}) \quad - (1)$$

$$R_t = k_t (M^{\oplus}) \quad - (3)$$

$$R_p = k_p (M^{\oplus})(M) \quad - (2)$$

Acc. to steady state Rule

$$R_i = R_t$$

$$k_i (M)(H^{\oplus}) = k_t (M^{\oplus}) \quad - (4)$$

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

Rate of the propagation

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

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

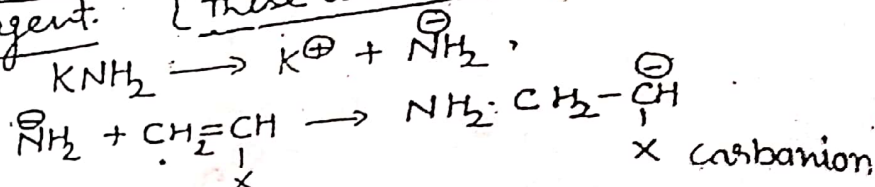
The overall polymerisation depends upon the square of monomer concentration.

(B) ANIONIC - POLYMERISATION $\Rightarrow$ 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.

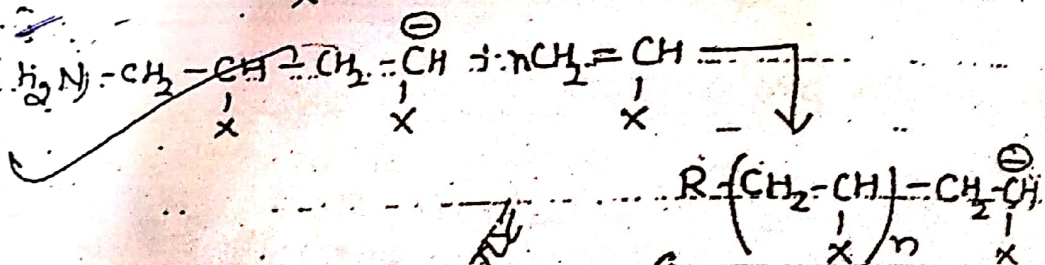
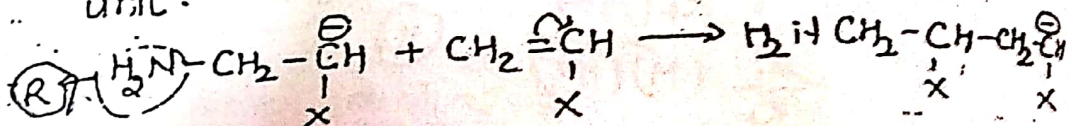


In Cationic polymerisation the movement of the active pair is in a direction opposite to that of the chain growth.

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



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



③ Termination $\Rightarrow$ 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.

Polymerisation produced by this tech are called "living polymers."

$\rightarrow$ 'Living polymerisation tech' is useful

for many application.
 e.g. Preparation of block copolymers.

of e-pair is in the characterisation
as that of chain growth.

KINETICS OF ANIONIC POLYMERISATION

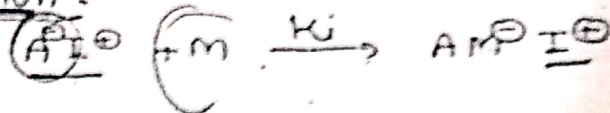


(Ion pair formation)

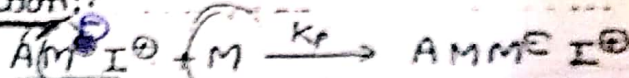
IA = Initiator

k_d = dissociation rate constant

(i) Initiation:



(ii) Propagation:



(iii) Termination:



where HA = protonating agent

k_i = Initiation rate constant

k_p = Propagation rate constant

k_t = Termination rate constant

$$R_i = k_i [M] [I^{\ominus} A^{\ominus}]$$

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

$$R_t = k_t [M^{\ominus}] [HA]$$

Acc to Steady State Law

$$R_i = R_t$$

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

$$M^{\ominus} = \frac{k_i [M] [I^{\ominus} A^{\ominus}]}{k_t [HA]}$$

Put this value in eqn (1)

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

$$R_p = k_p \frac{k_i}{k_t} \frac{(M)(A^\ominus)(M)}{(HA)}$$

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

Characteristic of Anionic polymerisation

① Rate of polymerisation depends on catalyst or conc.

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

③ In case of Heterogeneous mol. wt. distribution curve is broad.

④ In case of homogeneous mol. wt. distribution curve is narrow.

⑤ Monomers 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 bulk 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 active.

II

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.
- ✓ (5) monomers have double bonds. polymerisation takes place by ~~the~~ 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. feature of free radical polymerisation

- ✓ (1) Rate of polymerisation depends upon free radical initiator
- ✓ (2) Polymer has a broad mole. wt. distribution
- ✓ (3) monomers 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