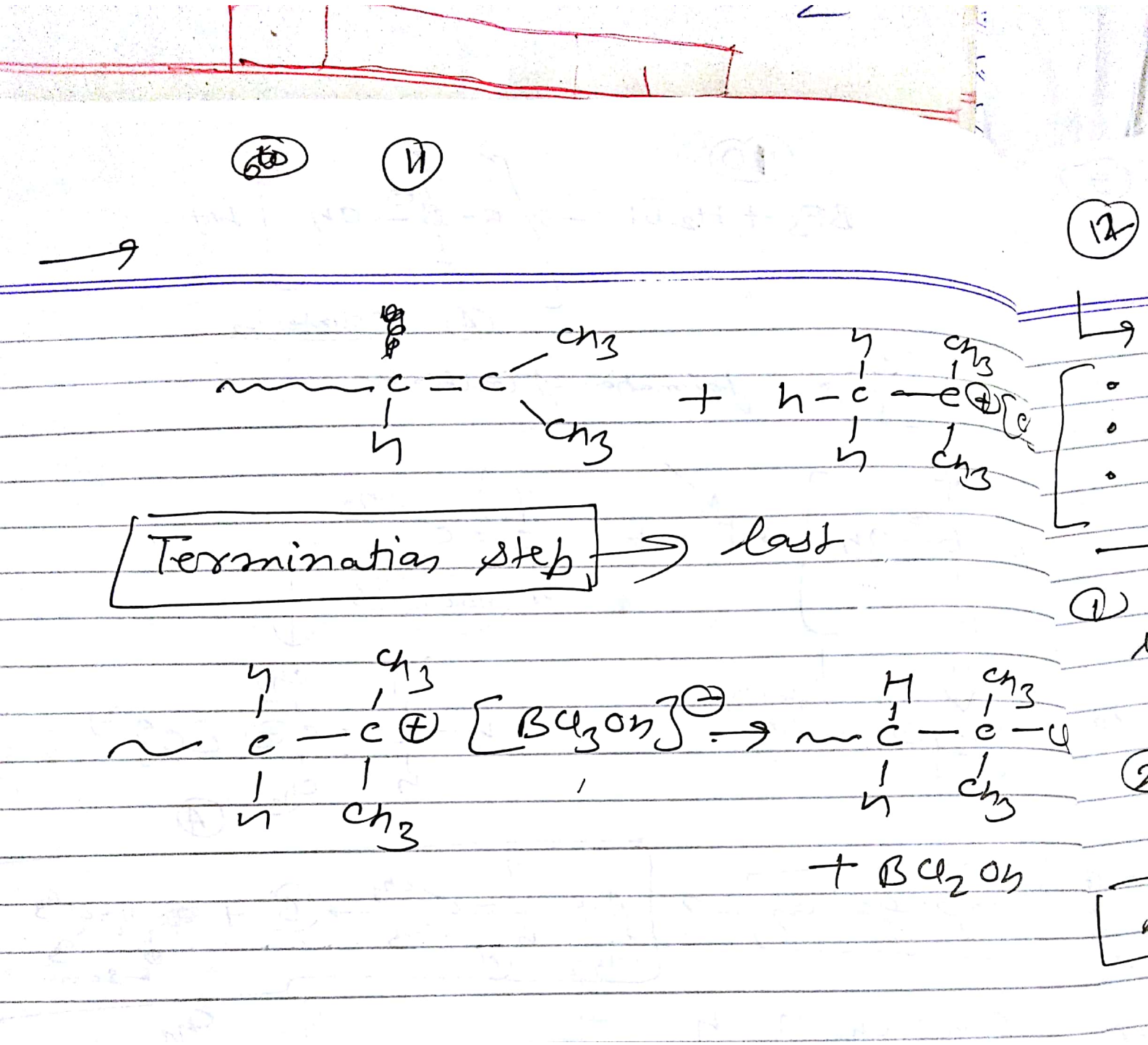


→ It is a form of chain growth polymerization

(12) **Anionic polymerization**

↳ Involve 3 step.

- Chain initiation step
- " propagation step
- " termination "

→ In this we need →

(1) An unsaturated compd like alkenes its derivative which contain e^- withdrawing gr attached to it (X).

(2) Need a initiator like $NaNH_2$ which is a strong base.

Step I → Chain initiation step →

attack of $NaNH_2$ on monomer having double bond & contain e^- withdrawing gr.

$R^- \text{ or } NaNH_2$ + $CH_2 = CH - X \rightarrow NH_2 - CH_2 - \overset{\ominus}{C}H - \overset{\oplus}{Na}$

strong base anion (initiator)

X = carbanion

Step II → **Chain propagation step**

monomer → double bond & the carbanion attack

$NH_2 - CH_2 - \overset{\ominus}{C}H - \overset{\oplus}{Na} + CH_2 = CH - X$

$NH_2 - CH_2 - CH - CH_2 - \overset{\ominus}{C}H - NH_2$

(3) Coupling

(12) (13)

(A) + $n\,CH_2=CH-X$

↓

$$NH_2-CH_2\left[CH-CH_2\right]_n CH-Na^{\oplus}$$
(with X on each CH)

carbanion polymer

(3) -chain termination step →

← addition of H^+

$$\bar{N}H_2-CH_2\left[CH-CH_2\right]_n CH-Na^{\oplus}$$
(with X on each CH)

↓ H^+

$$\bar{N}H_2-CH_2\left[CH-CH_2\right]_n CH_2$$
(with X on each CH)

Kine

$n\,CH_2$

Poly-

(D)

Kinetics of polymerization

Let consider polymerisation of (M)

$$M = CH_2 = CH - X$$

Step I $\quad I \xrightarrow[\text{Yields}]{K_1} R^{\cdot}$

The initiator molecule yields the free radical So,

Rate of formation of free radical $= K_1 [I]$

Chain propagation →

Step II → The free radical attack the monomer molecule to form another free radical.

$$R^{\cdot} + CH_2 = \underset{X}{CH} \xrightarrow{K_2} R - CH_2 - \overset{\cdot}{\underset{X}{CH}}$$

$$R - CH_2 - \overset{\cdot}{\underset{X}{CH}} + CH_2 = \underset{X}{CH} \xrightarrow{K_2} R - CH_2 - \underset{X}{CH} - CH_2 - \overset{\cdot}{\underset{X}{CH}}$$

$$\rightarrow\rightarrow R\left[CH_2-\underset{\underset{X}{|}}{CH}\right]_n$$

go for this →

// $R^{\cdot} + M \xrightarrow{K_2} (?)$ rate of reaction

Step II → Chain termination →

$$R\left[CH_2-\underset{\underset{X}{|}}{\dot{C}H}\right]_n + \left[\dot{C}H-\underset{\underset{X}{|}}{CH_2}\right]_n R \xrightarrow{K_3} R\left[CH_2-\underset{\underset{X}{|}}{CH}\right]_n\left[\underset{\underset{X}{|}}{CH}-CH_2\right]_n R$$

So Rate of disappearance of free radical $= K_3[R^{\cdot}]^2$

(OR)

// $R^{\cdot} + R^{\cdot} \xrightarrow{K_3} R-R$ Rate of disappear

Rate of reaction, $r = K_2[R^{\cdot}][M]$

on applying SSA on $[R^{\cdot}]$

Rate of formation $R^{\cdot}$ = Rate of disapp of $R^{\cdot}$

$$K_1[I] = K_3[R^\cdot]^2$$

$$[R^\cdot]^2 = \frac{K_1[I]}{K_3}$$

$$[R^\cdot] = \left[\frac{K_1}{K_3}\right]^{1/2} [I]^{1/2}$$

$$r = K_2\left[\frac{K_1}{K_3}\right]^{1/2} [I]^{1/2}[M]$$

order of reaction w.r.t

$I = 1/2$

$M = 1$

Overall $= \frac{1}{2} + 1 = 3/2$

Kinetic chain lenth :—

$$\frac{\frac{d}{dt}[Pdt]}{\frac{dl}{dt}\cdot\{\text{Initial step}\}}$$

Polymerization

- Addition
  - Free radical Polymerization
  - Ionic Polymerization
    - cationic
    - Anionic
  - complex coordination polymerization
- condensation

Addition polymers

Monomer molecule possessing double or triple bond.

Eg → formation of polythene from ethene & polypropene from propene

The addition polymers formed by the polymerization of a single monomeric species are known as homopolymers e.g polythene

$$n\,CH_2=CH_2 \longrightarrow -(CH_2-CH_2)-_n$$

ethene → polythene (Homopolymer)

The polymers made by addition polymerisation from 2 different monomers are called as copolymers eg Buna-S, Buna-N etc

$$n\,CH_2=CH-CH=CH_2 + n\,C_6H_5CH=CH_2$$

1,3-Butadiene + Styrene

$$\downarrow$$

$$-(CH_2-CH=CH-CH_2-CH_2-\underset{C_6H_5}{CH})-_n$$

Butadiene-styrene copolymer

Buna-S

(b) condensation polymers → These polymers are formed by repeated condensation reaction b/w two different bi-functional or tri-functional monomeric units. In these polymerization reaction the elimination of small molecules such as H_2O, HCl, CH_3OH etc. take place.

(Ex) → terylene (dacron), nylon 6,6 nylon-6 etc.

(Ex) फीनॉल

↳ (Polymerization) → The joining together of many small molecules to form very large molecules. The simple compounds from which polymers are made are called monomers. Polymers are formed in two general ways—

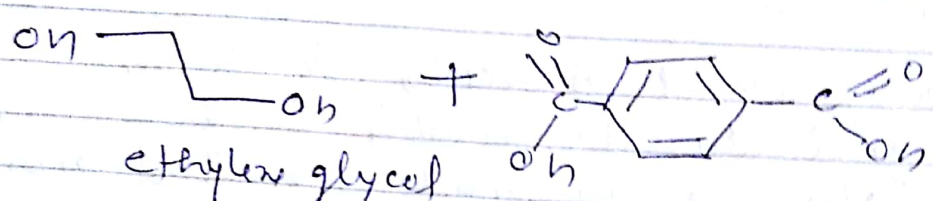
(a) Chain reaction polymerization → In this there is a series of reactions each of which consumes a reactive particle & produces another similar particle, each individual reaction thus depends on the previous one. The reactive particle can be free radicals, cations or anions. A typical ex is the polymerization of ethylene. Here the chain carrying particles are free radicals, each of which adds to a monomer molecule to form a new, bigger free radicals.

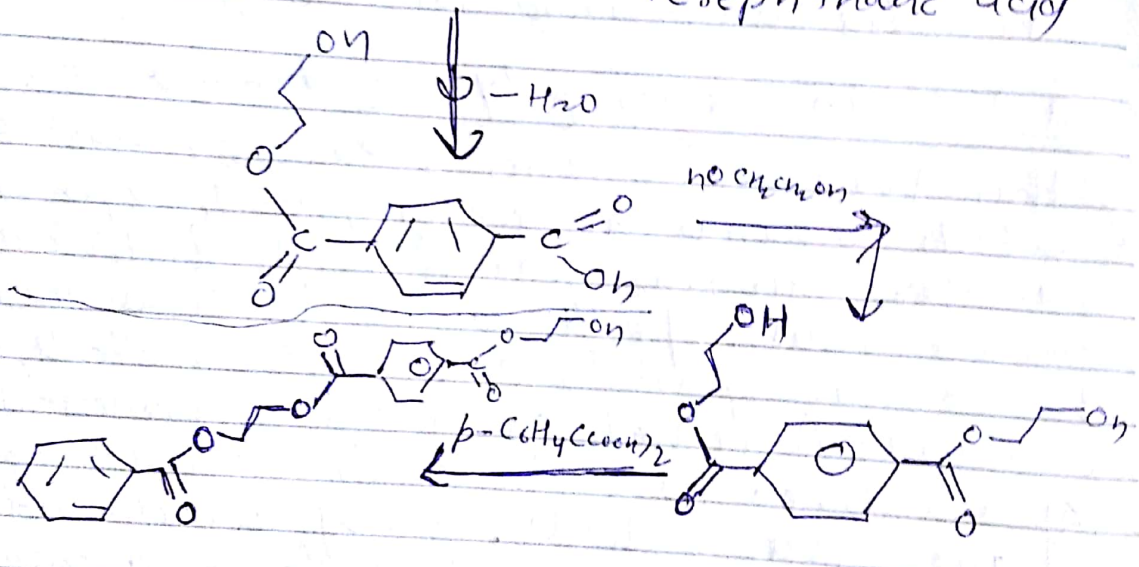
$$Rad. + CH_2=CH_2 \rightarrow Rad\,CH_2CH_2^{\bullet} \xrightarrow{CH_2=CH_2} \text{etc.} \leftarrow Rad\,CH_2CH_2CH_2CH_2^{\bullet}$$

(b) Step reaction polymerization →

In this there is a series of reactions each of

which is essentially independent of the preceding one, a polymer is formed simply because the monomer happens to undergo reaction at more than one functional group.
ex. a diol reacts with a dicarboxylic acid to form an ester, but each moiety of the simple ester still contains a group that can react to generate another ester linkage & hence a larger molecule, which itself can react further, & so on.





↳ condensation type

↳ In step growth polymerization or Step reaction polymerization →

all molecules as polymer, oligomer & monomer + any another molecule

→ Chain reaction polymerization (addition type)
only monomer + active site (radical or cation or anion)

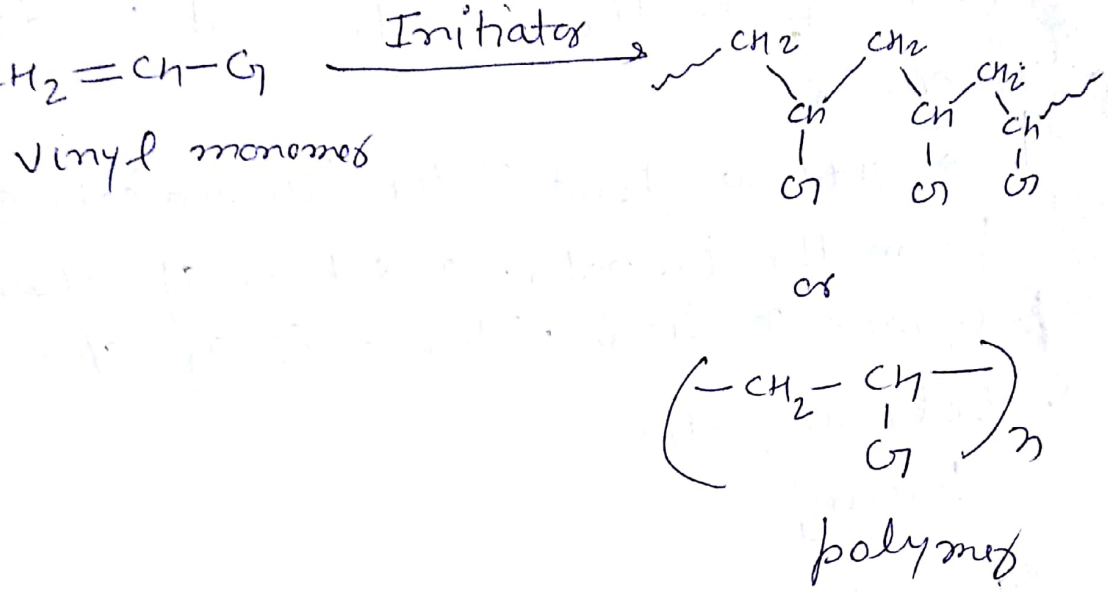
(14)

Free radical addition polymerisation

It is a method of polymerization by which a polymer forms by the successive adding of free radical building blocks. Free radicals can be formed by a number of different mechanism, usually involving separate initiator molecules.

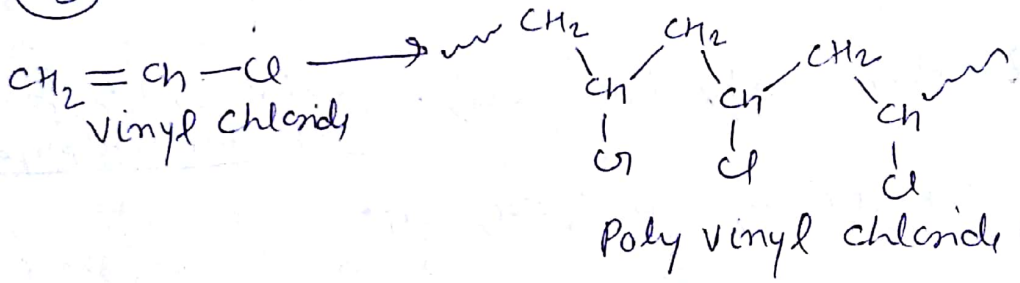
(21)

⇒ Free radical vinyl polymerization



at the doubly bonded carbons – the vinyl gr – so it is called vinyl polymerization. A wide variety of unsaturated monomer may be used to give polymers with different pendant group (Gr) attached to the polymer back bone.

(as)



$CH_2=CH-CN$ ⟶ Polyacrylonitrile (Orlon)
acrylonitrile

Styrene ⟶ Polystyrene