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:

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

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

$$RMMM^{\bullet} + Mn \xrightarrow{Kp} RMn+2 M^{\bullet} \quad -(9)$$

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.

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

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

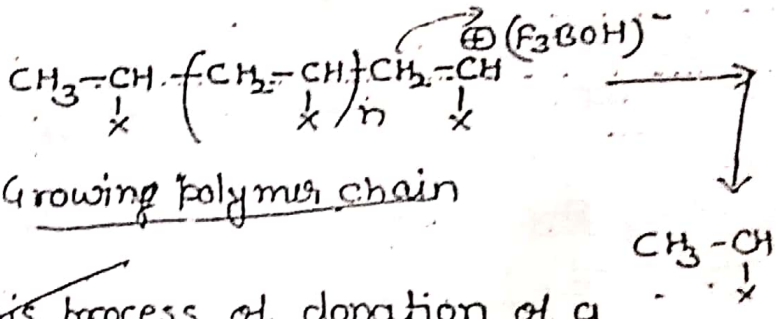
$$\downarrow n\,CH_2=\underset{X}{CH}$$

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

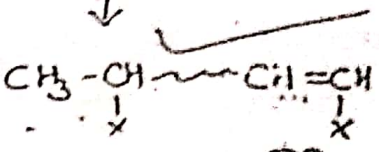
the chain growth and the counter-ion all the time, moves along with the ct ion like a "watch dog".]

(iii) Termination ⇒ two types.

(a) Donation of proton to counter-ion.

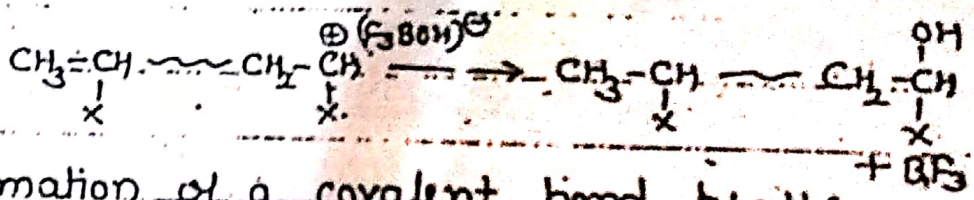


Growing polymer chain



* 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