Chapter 10. Free radical polymerization (or Chain-growth polymerizaion)

(1) Initiation : Free radicals must be introduced into the system to start the reaction

$$I \xrightarrow{k_d} 2R\bullet$$

Where I : initiator

R : primary radical

k_d : the specific rate constant : $10^{-4} \sim 10^{-6} sec^{-1}$

The rate of radical production is

$d[R\bullet]/dt = 2k_d[I]$

The rate of initiation $R_i\bullet$ is

$R_i = 2 f k_d [I]$

where f = initiator efficiency ≤ 1.0

- the fraction of all radicals generated that are captured by monomers

Initiation reaction :

$$R\bullet + CH_2{=}C(H)(Cl) \longrightarrow R{-}CH_2{-}C\bullet(H)(Cl)$$

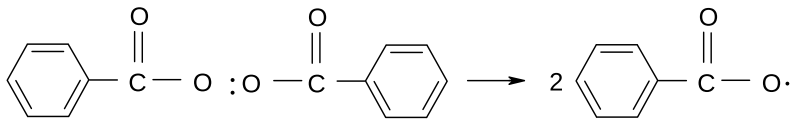
$$R\bullet + M \xrightarrow{K_i} M_i\bullet$$

(2) Propagation : products are formed, and the site of the reactive center changes but the number of active centers is not changed

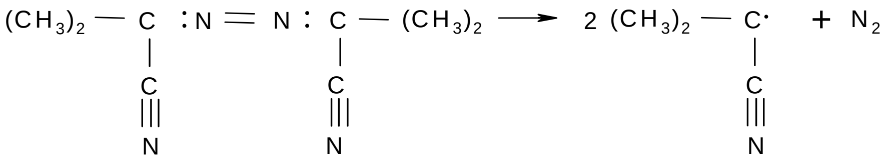
(a) Addition Reactions

$$R\bullet + M \xrightarrow{ki} M1\bullet$$

(ex) Benzoyl Peroxide:



Azobisiobutyronitrile (ALBN)



$M1\bullet + M = M2\bullet$

$M2\bullet + M = M3\bullet$

$Mi\bullet + M = Mi+1\bullet$

Assume : molecular size 에 관계없이 같은 rate constant, kp 를 갖는다.

∴ $R_p = K_p [M\bullet][M]$: Rate of Propagation

Kp : 2^{nd}-oder rate constant : $[conc, time]^{-1}$

$\rightarrow 10^2 - 10^4$ (L/mol.s)

where [M•] is the sum of the concentrations of all monomer-ended radicals in the system.

(b) Atom Transfer Reactions (Chain Transfer Reaction)

(ex) chlorination

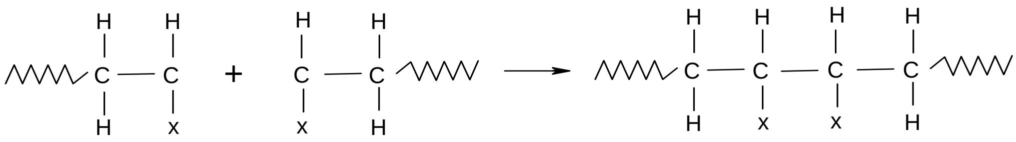
$Cl_2 \xrightarrow{200} 2Cl\bullet$

$Cl\bullet + CH_4 \rightarrow HCl + \bullet CH_3$

$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

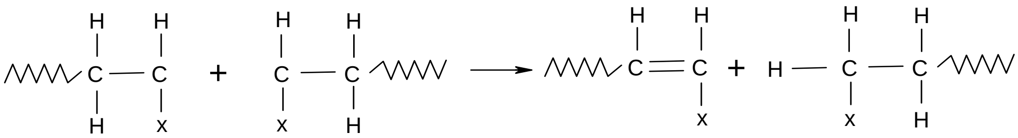
(3) Termination : the squence of monomer additions is terminated by the mutual annihilation of two radicals.

(ex)



$$Mn\bullet + Mm\bullet \xrightarrow{Ktc} M_{n+m}$$

(ex)



$$Mn\bullet + Mm\bullet \xrightarrow{Ktd} Mm + Mn$$

Ktd: disproportionation rate constant.

◦ Termination may also occur a mixture of disproportionation and combination.

$$Mn\bullet + Mm \xrightarrow{Ktd} \text{dead polymer}$$

Kt = Ktc + Ktd (overall rate constant)
$Rtc = 2\ Ktc[M\bullet]^2$
$Rtd = 2\ Ktd[M\bullet]^2$
$Rt = 2\ Kt[M\bullet]^2$ ($Kt = 10^6 - 10^8$ L/mol.sec)

(4) Rate of polymerization

◦ the rate of radical generation = the rate at which radicals undergo mutual annihilation.
◦ the concentration of radicals in the system will reach a steady value.

We assume that
$Ri = Rt$ at steady state
$d[M\bullet]/dt = 0$ at steady state

$$2fKd[I] = 2\ Kt\ [M\bullet]^2 \qquad (6\text{-}26)$$
$$[M\bullet] = [fKd[I]/Kt]^{1/2} \qquad (6\text{-}27)$$

° The rate of polymerization is take to be the rate of disappearance of monomer, which is d[M]/dt.

- $d[M]/dt = Ri + Rp$
- $d[M]/dt = Rp = kp[M][M\bullet] = (kp/kt^{½})[M](fkd[I])^{½} \quad (6\text{-}29)$

  $= (kp/kt^{½})[M]$ (rate of formation of monomer -ended radials)^{½}

- The rate of propagation is proportional to the concentration of the monomer and the square root of the concentration of the initiator.
- The rate of termination is proportional to the concentration of the initiator.