2.2 Chain-Growth Polymerization

2.2.1 Free radical polymerization and copolymerization

Introduction to addition polymerization

- **activated (free radicals, cations, anions) by UV, heat, or a reaction initiator, and then polymerized**

- **three steps of addition polymerization:**

① **initiation step – radical (or ion) formation**

② **propagation step – $\overline{DP}n$ (mol. wt.) ↑**

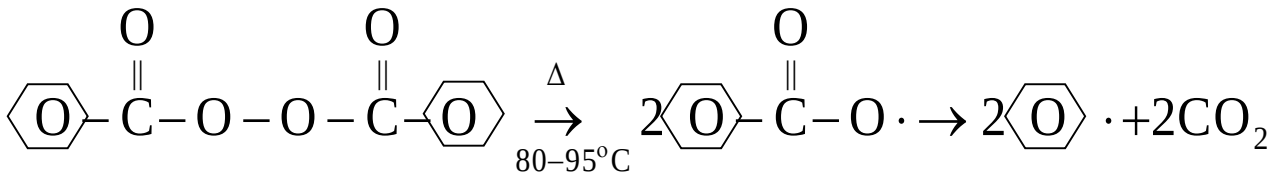
③ **termination step**

– **coupling: joining of 2 polymer radicals**
disproportionation:
→ dead polymer

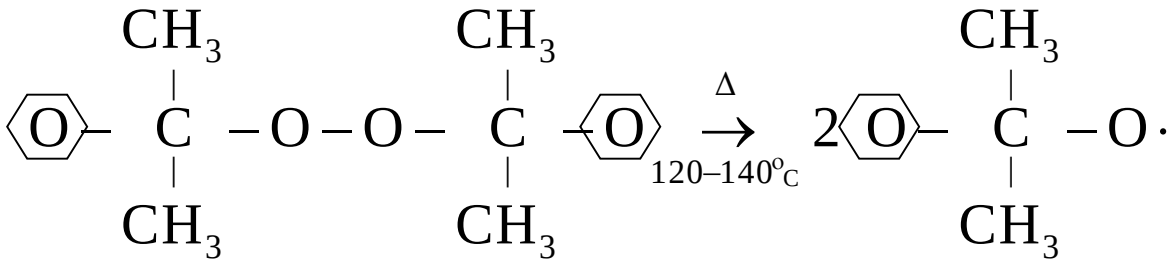
2 polymer radicals → 2 polymers

- **free radical initiators: small bond dissociation E (25 ~ 40 kcal/mol), compounds with O – O , S – S, N – O bonds**
main

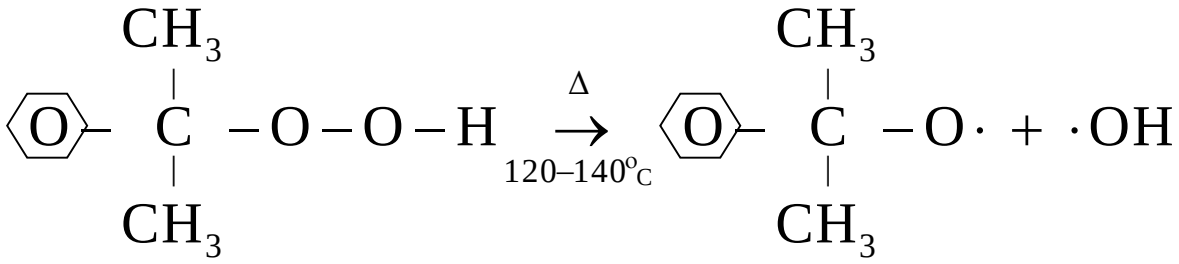
ex) ※ benzoyl peroxide: BPO



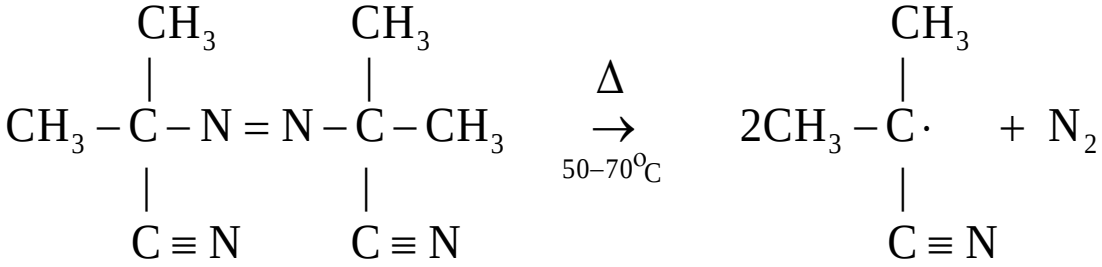
dicumyl peroxide: DCP



hydroxycumyl peroxide:



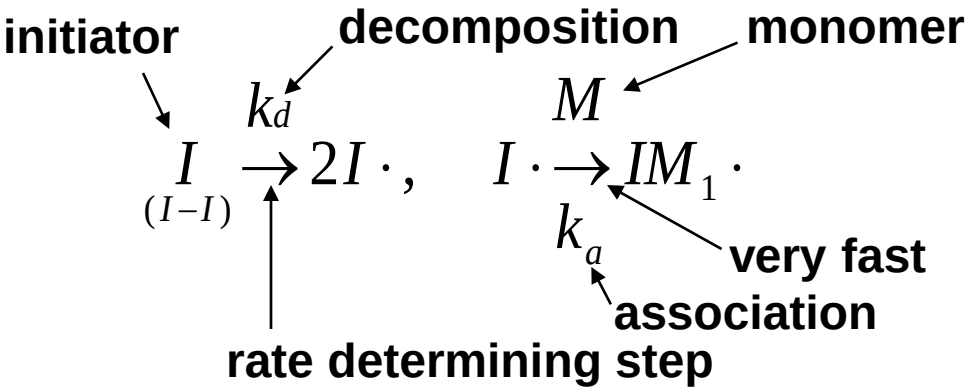
※ 2,2'-azobisisobutyronitrile: AIBN



Free-Radical Polymerization Kinetics

The Initiation Step (with a free radical initiator)

- **Initiation step**



k_d ~ initiator decomposition rate constant

k_a ~ initiation (association) rate constant

an initiator forms 2 radicals

$$R_i = 2 f k_d [I]$$

initiator efficiency: 0.3~0.8

$$\left(\frac{d[I\cdot]}{dt}\right) \equiv -\frac{d[M]}{dt}$$

$$k_d = \mathrm{A}\exp\left(\frac{-E_d}{RT}\right)$$; **Table 2-2**

$$k_d = \mathrm{A} \exp\left(\frac{-E_d}{RT}\right)$$

The Propagation Step

- **Propagation step**

$$IM_1\cdot + M \xrightarrow{k_p} IM_2\cdot$$

$$IM_2\cdot + M \xrightarrow{k_p} IM_3\cdot$$

M

$$IM_n\cdot + M \xrightarrow{k_p} IM_{n+1}\cdot$$

DP

k_p **~ propagation rate constant ; Table 2-3**

assumption: reactivity of each radical is not dependent on the size

→ the same *k_p* for all radicals

$$R_p = k_p[IM\cdot][M] \quad \left(\equiv -\frac{d[M]}{dt}\right)$$

= [IM_1·] + ⋯+[IM_n·]

(overall radical concentration)

$$k_p = \mathrm{A} \exp\left(\frac{-E_p}{RT}\right) \qquad k_t = \mathrm{A} \exp\left(\frac{-E_t}{RT}\right)$$

Termination

- **Termination step**

$$IM_n\cdot + IM_m\cdot \xrightarrow{k_{tc}} IM_{n+m}I \;:\; coupling$$

polymer radical

$$ex) -CH_2 + R\cdot \rightarrow -\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - R$$

$$IM_n\cdot + IM_m\cdot \xrightarrow{k_{td}} IM_n + IM_m \;:\; disproportionation$$

$$ex) -\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \dot{C}H_2 + \dot{C}H_2 - \underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \;\rightarrow\; -CH_2CH_3 + CH_2 = CH -$$

in general, $IM_n\cdot + IM_m\cdot \xrightarrow{k_t} dead\,(deactivated)\ polymer$

where, $k_t = k_{tc} + k_{td}$

Table 2-3

$$R_t = 2k_t[IM\cdot]^2 \quad \left(\equiv -\frac{d[IM\bullet]}{dt}\right)$$

2 radicals extinct by a reaction

- **extinction rate of monomers (≡ polymerization rate);**

no. of free radicals is limited, so very small amount of monomers is consumed in initiation step

$$-\frac{d[M]}{dt} = R_O = R_i + R_p \cong R_p = k_p[IM\cdot][M]$$

overall **initiation rate** **propagation rate** **all radicals**

Free-Radical Polymerization Kinetics

- **at steady state,** $\frac{d[IM\bullet]}{dt} = 0$ **: total radical concentration is constant**

2 radicals extinct by a reaction

$$R_i \equiv R_t = 2k_t[IM\bullet]^2 \rightarrow [IM\bullet] = \left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}$$

radical formation **radical extinction**

an initiator forms 2 radicals

$$R_O \equiv R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}, R_i = 2 f\ k_d[I]$$

$$\therefore R_O = k_p[M]\left(\frac{f\ k_d[I]}{k_t}\right)^{\frac{1}{2}}$$

initiator efficiency: 0.3~0.8
ratio of initiators participate in polymerization

overall rate of polymerization

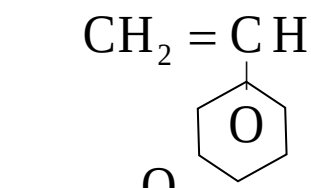
$$R_O = \frac{k_p}{k_t^{1/2}}[M]\sqrt{f\ k_d[I]} \quad \rightarrow \quad R_O \propto [M],\ [I]^{\frac{1}{2}}$$

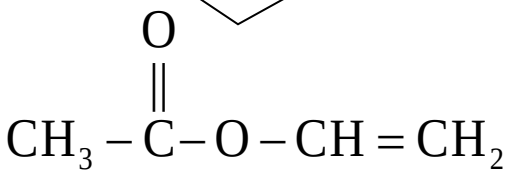
Figures in next slides

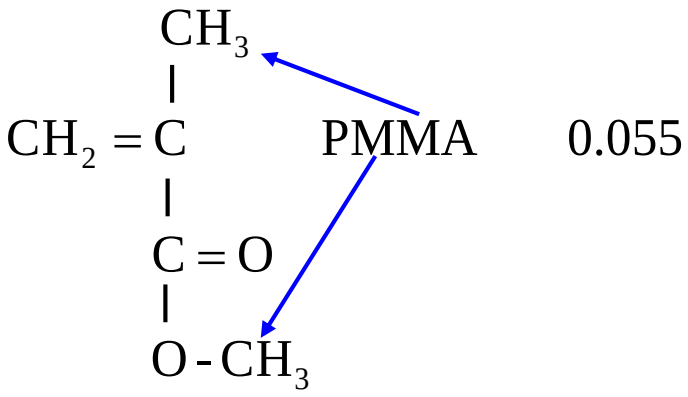
polymerizability (measure on how easily a system polymerizes)

Table 2-3 → **large: forms high mol. wt. polymers**

ex) monomer vs. polymerizability







$$R_O = R_p = k_p[M]\left(\frac{f\ k_d[I]}{k_t}\right)^{\frac{1}{2}}$$

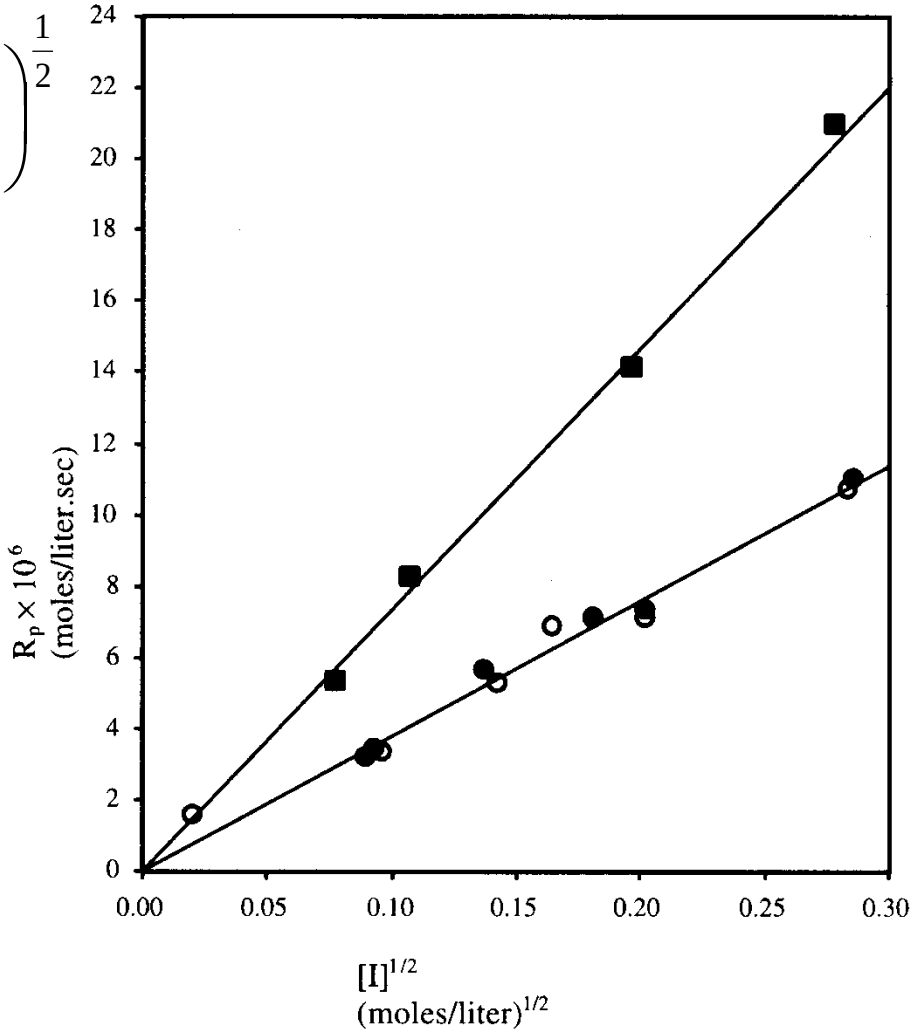


Figure Square-root dependence of the polymerization rate R_p on the initiator concentration [I]. ■: Methyl methacrylate, benzoyl peroxide, 50°C. After Schulz and Blaschke (1942) (by permission of Akademische Verlagsgesellschaft, Geest and Portig K.-G., Leipzig). ●, ○: Vinyl benzoate, azobisisobutyronitrile, 60°C. After Santee et al. (1964) and Vrancher and Smets (1959) (by permission of Huthig and Wepf Verlag, Basel).

$$R_O = R_p = k_p[M]\left(\frac{f\ k_d[I]}{k_t}\right)^{\frac{1}{2}}$$

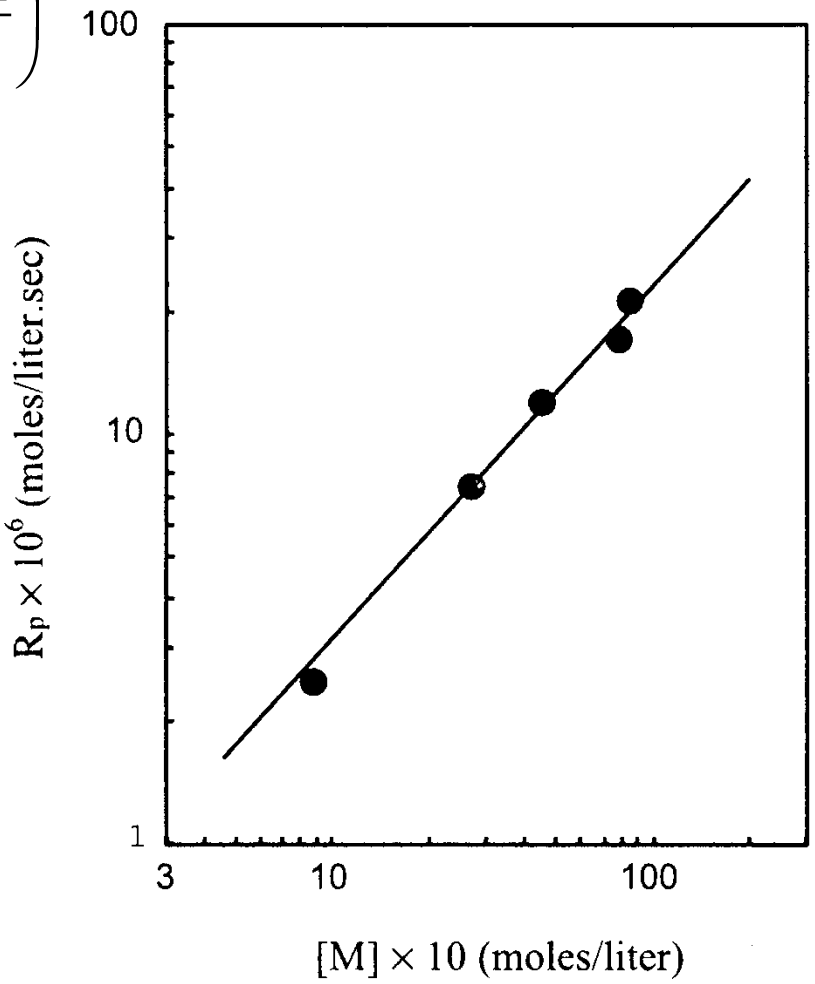


Figure First-order dependence of the polymerization rate R_p of methyl methacrylate on the monomer concentration [M]. The initiator is the *t*-butyl perbenzoate–diphenylthiourea redox system. After Sugimura and Minoura (1966) (by permission of Wiley-Interscience, New York).

Molecular weight (M_n) of polymers by free radical polymerization

- **kinetic chain length, (degree of polymerization of polymer radicals)**

$$\upsilon = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

$$\upsilon = \frac{k_p[M][IM\cdot]}{2\,k_t[IM\cdot]^2} = \frac{k_p[M]}{2\,k_t[IM\cdot]} = \frac{k_p{}^2[M]^2}{2\,k_t[IM\cdot]k_p[M]} = \frac{k_p{}^2[M]^2}{2\,k_t R_p}$$

$$= \frac{k_p[M]}{2(f\ k_d\,k_t[I])^{1/2}} \quad : \text{ in case of using initiators}$$

$$R_p = k_p[M]\left(\frac{f\ k_d[I]}{k_t}\right)^{\frac{1}{2}}$$

- **$\overline{\text{DPn}}$ of dead polymers:**

$$\overline{DPn} = 2\upsilon \quad \textbf{termination by coupling}$$

$$= \upsilon \quad \textbf{termination by disproportionation}$$

$$\overline{M_n} = M_o\ \overline{DP_n}$$

mol. wt. of a monomer

Chain transfer reaction (causes polymers with low mol. wt.) and $\overline{DPn}$

$$IM_n \cdot + SH \xrightarrow{k_{tr}} IM_n - H + S \cdot$$

monomer
initiator
solvent, etc.

} **a molecule with an abstractable H atom**

· **chain transfer reaction rate:** $R_{tr} = k_{tr}[IM \cdot][SH]$

· ***k_{tr}* >> *k_p* : $\overline{DPn} = 1 \sim 5$: telomers**

· **chain transfer agents for $\overline{DPn}$ control: prevent formation of too big polymers**

ex) R-SH (mercaptan)

$$\frac{R_p}{R_{tc}+R_{td}+R_{tr}} = \overline{DPn} = \frac{k_p[M][IM\cdot]}{R_t + k_{tr,M}[IM\cdot][M] + k_{tr,S}[IM\cdot][S] + k_{tr,I}[IM\cdot][I]}$$

$2k_t[IM\cdot]^2$

solvent initiator

chain transfer reaction rate constant by monomer

- **chain transfer constant**

$$let \quad C_M = \frac{k_{tr,M}}{k_p}, \quad C_S = \frac{k_{tr,S}}{k_p}, \quad C_I = \frac{k_{tr,I}}{k_p},$$

$$\frac{1}{\overline{DPn}} = \frac{2k_t R_p}{k_p{}^2[M]^2} + \underbrace{C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]}}_{\text{combine} \rightarrow \text{eq(2.30)}} \left(\equiv C_I\frac{k_t R_p{}^2}{k_p{}^2 f k_d [M]^3}\right)$$

$$= \frac{2k_t R_p}{k_p{}^2[M]^2} \left(= \frac{1}{(\overline{DPn})_0}\right) + C\frac{[SH]}{[M]}$$

$$\therefore \quad \frac{1}{\overline{DPn}} = \frac{1}{(\overline{DPn})_0} + C\frac{[SH]}{[M]} \quad \textbf{(2.30)}$$

Table 2-4

Thermodynamics of Free-Radical Polymerization

$\Delta G_p = \Delta H_p - T\Delta S_p$

ΔH_p : **heat(enthalpy change) of polymerization, (-)** **Table 2-5**

ΔS_p : **entropy change of polymerization, (-)**

ΔG_p : **Gibbs free energy of polymerization, (-) up to a certain T : thermodynamically favored**

$\Delta H_p = E_{dp} - E_p$ **from Figure 2-3**

E_p , E_{dp} : **activation energy for polymerization and depolymerization**

$\Delta G_p = 0$ **at ceiling temperature, T_c, (polymerization rate = depolymerization rate)**

Table 2-5

$$T_c = \frac{\Delta H_p}{\Delta S_p}$$

$$M_x\cdot + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{x+1}\cdot \qquad K = \frac{k_p}{k_{dp}} = \frac{[M_{x+1}\cdot]}{[M_x\cdot][M]} \approx \frac{1}{[M]}$$

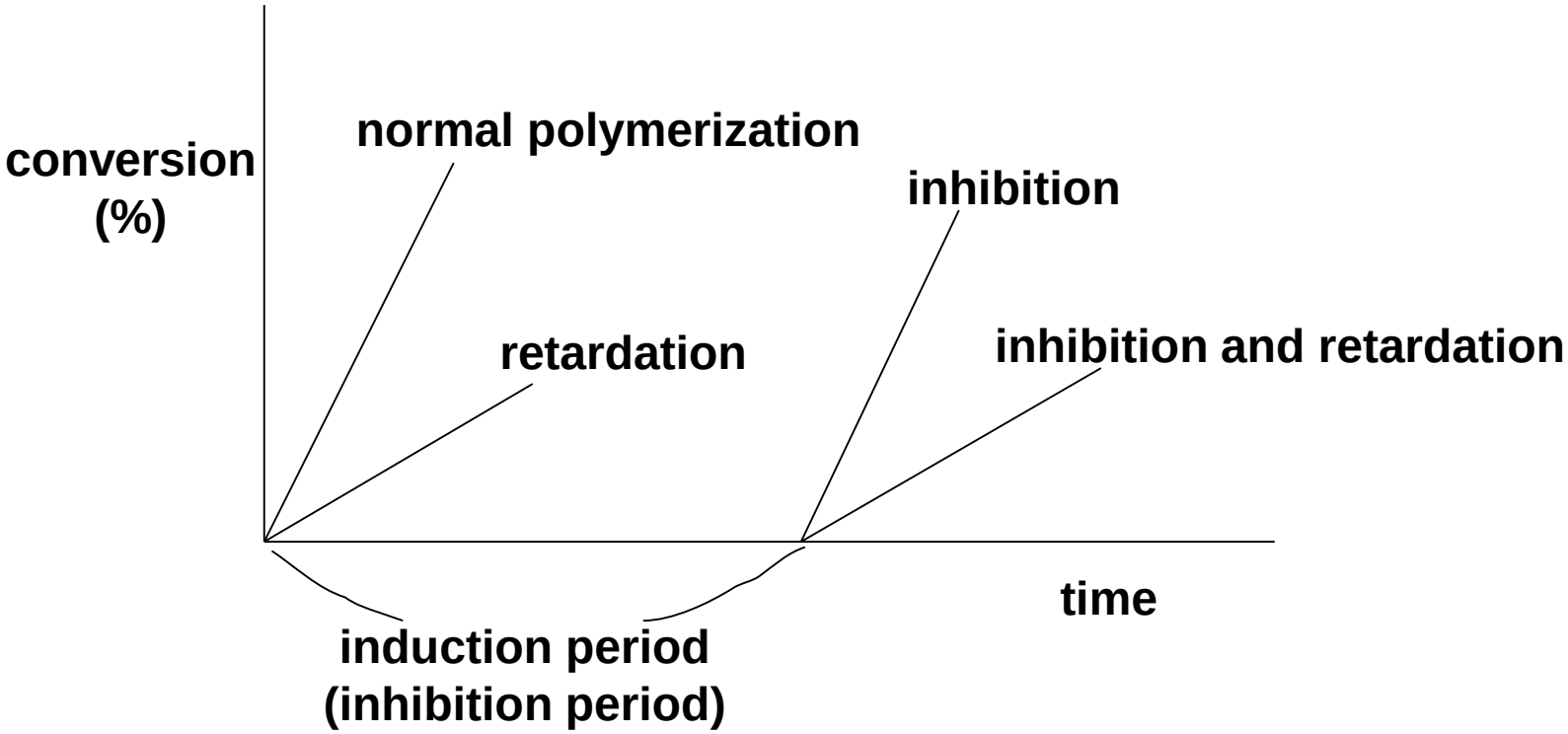
standard state, [M]=1 mol/l; ln[M]=0

at equilibrium, $\Delta G_p^o = 0 = \Delta H_p^o - T_c\Delta S_p^o = -RT_c \ln K = RT_c \ln[M]_c$

$$\boxed{T_c = \frac{\Delta H_p^o}{\Delta S_p^o + R\ln[M]_c}} \qquad = \frac{\Delta H_p^o}{\Delta S_p^o}$$

Retardation and inhibition of polymerization

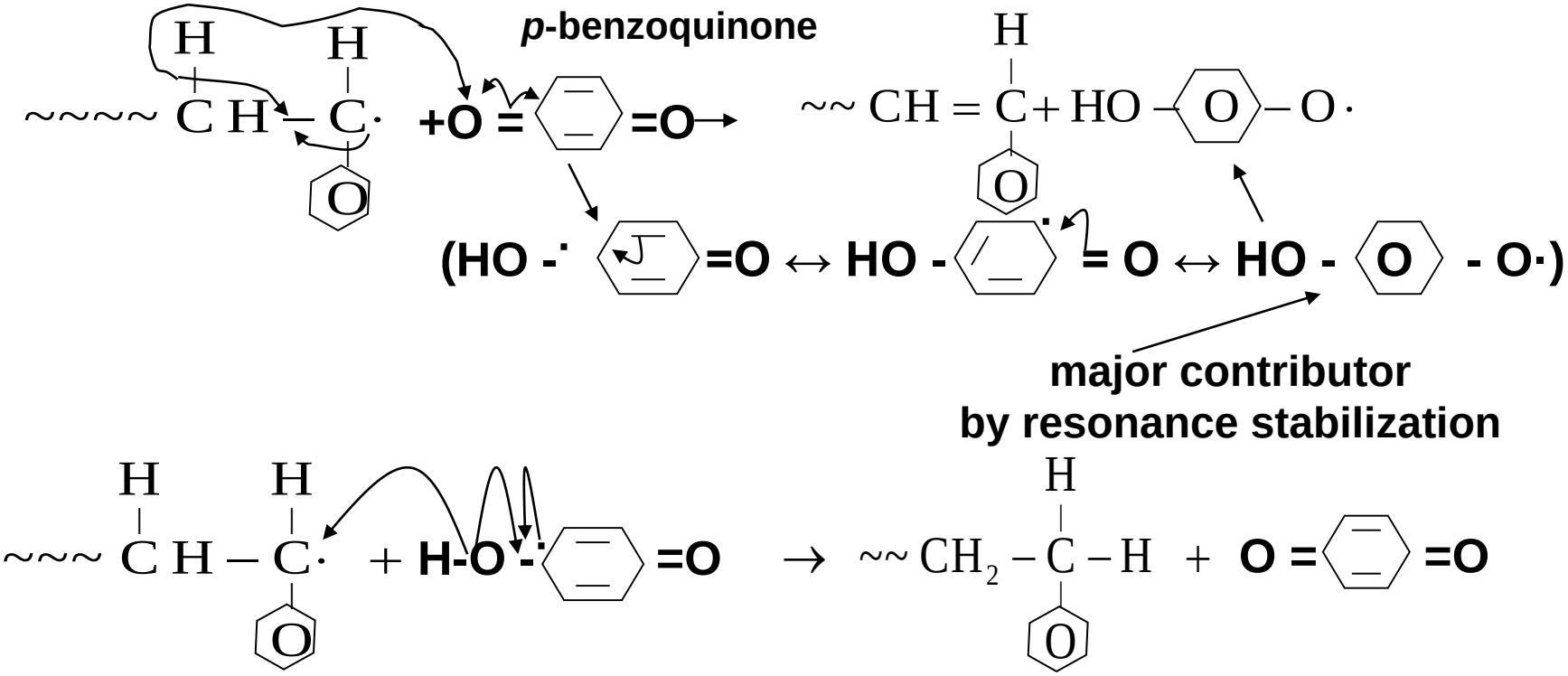
- retardation: polymerization rate is very slow
- inhibition: polymerization rate = 0 (during induction period)
  - inhibition to prevent premature thermal polymerization during storage and shipment
  - → to polymerize, remove inhibition agents or add excess initiators



- inhibition and retardation agents ~ mainly quinones

ex) benzoquinone – inhibition agent for styrene, vinyl acetate, etc.

in the case of styrene:



$$M_n\cdot + Z \xrightarrow{k_z} M_n + Z\cdot$$

inhibition agent

inhibition constant: $Z = \frac{k_z}{k_p}$

ex) *p*-benzoquinone:

- **acrylonitrile (50 °C) - Z = 0.91**
- **methylmethacrylate (60 °C) - Z = 4.5**
- **styrene (50 °C) - Z = 518**

Free-Radical Copolymerization

- **polymerization of 2 (or more than 2) monomers → copolymer**
- **composition and structure of a copolymer determine physical and chemical properties of the copolymer**

ex) SBR - styrene butadiene rubber
NBR – acrylonitrile butadiene rubber
ABS – acrylonitrile butadiene styrene

⊙ **reaction kinetics of radical copolymerization:**

$$\sim\sim\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim\sim M_1\cdot \qquad R_{11} = k_{11}[M_1\cdot][M_1]$$

$$\sim\sim\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim\sim M_2\cdot \qquad R_{12} = k_{12}[M_1\cdot][M_2]$$

$$\sim\sim\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim\sim M_1\cdot \qquad R_{21} = k_{21}[M_2\cdot][M_1]$$

$$\sim\sim\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim\sim M_2\cdot \qquad R_{22} = k_{22}[M_2\cdot][M_2]$$

- at steady state, *[M_1·] + [M_2 ·]* = constant : total radical conc. is constant

radical forming rate = radical extinction rate

$$\frac{d([M_1\cdot]+[M_2\cdot])}{dt}=0 \quad \Rightarrow \quad \underbrace{k_{21}[M_2\cdot][M_1]}_{\text{M}_1\cdot\text{ forming rate}} \quad = \quad \underbrace{k_{12}[M_1\cdot][M_2]}_{\text{M}_1\cdot\text{ extinction rate}}$$

(M_2 · extinction rate) **(M_2 · forming rate)**

- extinction rates of each monomer M_1 and M_2,

$$-\frac{d[M_1]}{dt}=R_{11}+R_{21} \quad =k_{11}[M_1\cdot][M_1]+k_{21}[M_2\cdot][M_1] \qquad \textbf{(2.37)}$$

$$-\frac{d[M_2]}{dt}=R_{12}+R_{22} \quad =k_{12}[M_1\cdot][M_2]+k_{22}[M_2\cdot][M_2] \qquad \textbf{(2.38)}$$

$$\frac{d[M_1]}{d[M_2]}=\frac{[M_1]}{[M_2]}\left(\frac{k_{11}[M_1\cdot]+k_{21}[M_2\cdot]}{k_{12}[M_1\cdot]+k_{22}[M_2\cdot]}\right)$$: **instantaneous copolymerization equation**

⊙ **copolymer equation : (derive the equation: homework)**

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]}\right)$$: **copolymer composition**

where, $r_1 = \frac{k_{11}}{k_{12}}$, $r_2 = \frac{k_{22}}{k_{21}}$ **Table 2-6**

Case1, $r_1 >> 1, r_2 >> 1 \Rightarrow$ **homopolymerization**

Case2, $r_1 << 1, r_2 << 1$

a growing radical prefers other monomer

$\Rightarrow$ **alternating copolymer (**$r_1 \rightarrow 0, r_2 \rightarrow 0$ **: perfect alternating)**

Case3, $r_1 > 1, r_2 > 1 \Rightarrow$ **block copolymer**

a growing radical prefers the same monomer

Case 4, $r_1 \cong 1, r_2 \cong 1, r_1 r_2 \cong 1 \Rightarrow$ **random copolymer**

theoretically ideal (not practical meaning) copolymer system

theoretically most successful copolymer system

⊙ **copolymer composition:** $$F_1 = \frac{\frac{d[M_1]}{dt}}{\frac{d[M_1]}{dt} + \frac{d[M_2]}{dt}}$$

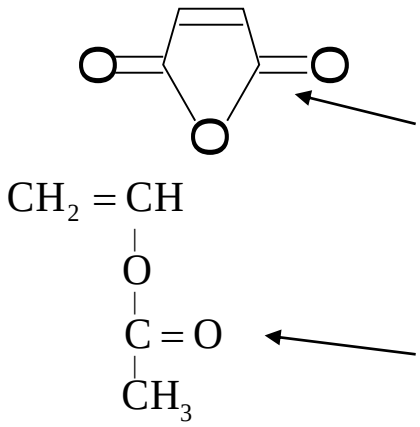
⊙ **feed composition:** $$f_1 = \frac{[M_1]}{[M_1]+[M_2]} \quad , \quad f_2 = 1 - f_1$$

- using the copolymer equation, *F_1* and *F_2* can be derived (homework)

$$F_1 = \frac{r_1 f_1^{\,2} + f_1 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}} \quad , \quad F_2 = 1 - F_1$$

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$



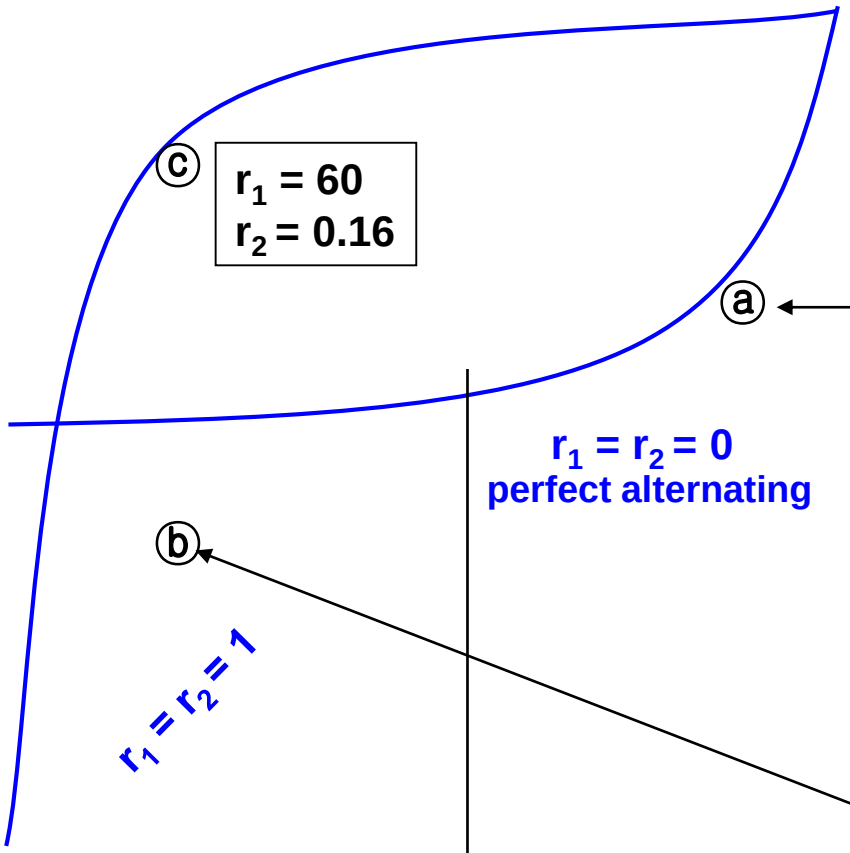
ⓐ

ⓑ

ⓒ

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$



ⓐ 시스템에서 $f_1 \rightarrow 0$인 경우
M_1 양이 적으므로 (M_2M_1)이
교대인 상태로 중합종결;
$M_2M_1M_2M_1$~~~
M_1 fraction in polymer, $F_1 = 0.5$

ⓑ 시스템에서 f_1이 작은 경우
M_1이 M_2를 만날 확률이
상대적으로 높으므로 M_1이 더
많이 반응되어 중합됨
$\rightarrow F_1 > f_1$ (위로 볼록)
f_1이 큰 경우는 반대

Q-e equation (by Price-Alfrey)

- represents quantitatively relationships between structure and reactivity of radicals and monomers

$k_{11} = P_1 Q_1 \exp(-e_1 e_1)$
$k_{12} = P_1 Q_2 \exp(-e_1 e_2)$
$k_{21} = P_2 Q_1 \exp(-e_2 e_1)$
$k_{22} = P_2 Q_2 \exp(-e_2 e_2)$

P_1 , P_2 : measures of resonance stabilization of $M_1\cdot$ and $M_2\cdot$ radicals respectively, proportional constant

Q_1 , Q_2 : measures of resonance stabilization of M_1 and M_2 monomers respectively, reactivity

e_1 , e_2 : polarity of M_1 ($M_1\cdot$) and M_2 ($M_2\cdot$) respectively

measures on reactivity

$$\therefore r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2}\exp[-e_1(e_1 - e_2)]$$

$$\therefore r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1}\exp[-e_2(e_2 - e_1)]$$

$$\therefore r_1 r_2 = \exp[-(e_1 - e_2)^2]$$

- give Q and e values of monomers → predicting structure and composition of a copolymer is possible, Table 2-7