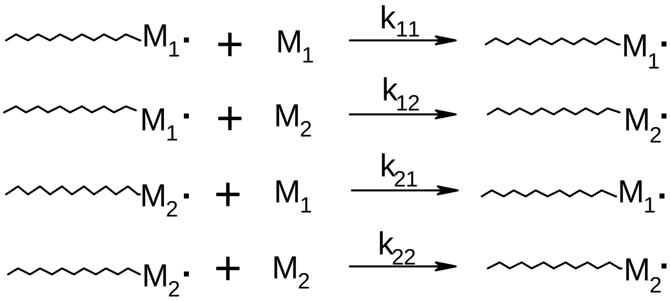
Chapter 12. Free Radical Copolymerization
(라디칼 공중합)

12.1 Introduction - Copolymer Eq.

Only Binary Case

Two Monomers; $M_1 + M_2$



$$\sim\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim\sim M_1\cdot$$

$$\sim\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim\sim M_2\cdot$$

$$\sim\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim\sim M_1\cdot$$

$$\sim\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim\sim M_2\cdot$$

Steady State Assumption

$$-\frac{d[M_1\cdot]}{dt} = -\frac{d[M_2\cdot]}{dt} = 0$$

$$k_{12}[M_1\cdot][M_2] = k_{21}[M_2\cdot][M_1]$$

$$\frac{[M_1\cdot]}{[M_2\cdot]} = \frac{k_{21}[M_1]}{k_{12}[M_2]} \quad \cdots\cdots①$$

and chain transfer & termination
small
compared w/ propagation

그리고

$$-\frac{d[M_1]}{dt} = k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1]$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2]$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\frac{k_{11}[M_1\cdot] + k_{21}[M_2\cdot][M_1]}{k_{12}[M_1\cdot] + k_{22}[M_2\cdot][M_2]} \quad \cdots\cdots②$$

$\uparrow$

Instantaneous ratio of monomers in copolymer

From ① and ②

$$\boxed{\frac{d[M_1]}{d[M_2]} = \frac{1 + r_1 \frac{[M_1]}{[M_2]}}{1 + r_2 \frac{[M_2]}{[M_1]}}} \quad \text{where} \quad r_1 = \frac{k_{11}}{k_{12}}, \; r_2 = \frac{k_{22}}{k_{21}} \longleftarrow \text{monomer reactivity ratio}$$

$\uparrow$

COPOLYMER EQ.

12.2 r 의 meaning

$r_1 > 1$ M$_1$*가 M$_1$ 에(M$_2$ 대신) 완전히 첨가

$r_1 < 1$ M$_1$*가 M$_2$ 에(M$_1$ 대신) 완전히 첨가

$r_1 = 0$ M$_1$ 이 HOMOPOLYMERIZATION 할 수 없을 때

12. 3 Define f$_1$, F$_1$

f_1, f_2 : mole fractions of monomers in feed

F_1, F_2 : mole fractions of monomers in polymer

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \cdots\cdots ③$$

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad \cdots\cdots ④$$

COPOLYMER EQ. ③과 ④로부터

$$\boxed{F_1 = \frac{r_1 f_1^{\,2} + f_1 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}}} \quad \cdots\cdots ⑤$$

how come? Homework!

12.4 Ideal Copolymerizaton (이상공중합)

$$r_1 \cdot r_2 = 1 \qquad \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}$$

$$r_2 = \frac{1}{r_1} \qquad\qquad = r_1 \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{r_1[M_1]+[M_2]}$$

$$= r_1 \frac{[M_1]}{[M_2]}$$

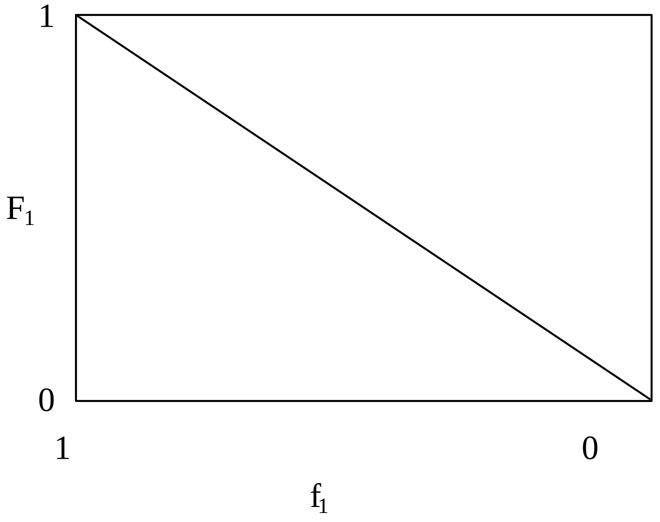
$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

$$\frac{k_{11}}{k_{12}} \cdot \frac{k_{22}}{k_{21}} = 1 \qquad \frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$$

결국 ratio of $\dfrac{1 \begin{smallmatrix}\nearrow 1 \\ \searrow 2\end{smallmatrix}}{2 \begin{smallmatrix}\nearrow 1 \\ \searrow 2\end{smallmatrix}}$ **가 같다**.

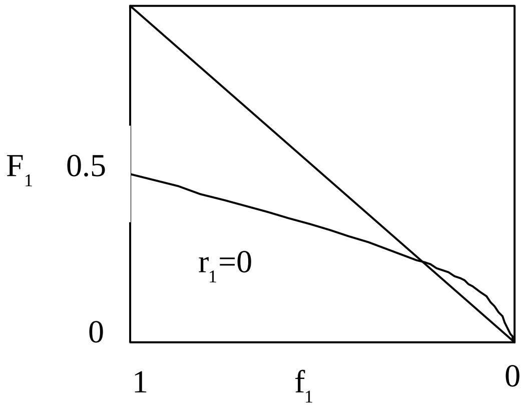
이 경우는 ionic(anionic or cationic) copolymerization**의 경우 잘 나타남**.

- **만약** $r_1 = 1 = r_2$ **인 경우는 두 모노머가 성장라디칼에 대해** equal reactivity **가 있음을 나타냄**. **그러니까 결국 고분자의 성장이** random **하게 이루어 진다는 뜻이다**.
- $r_1 > 1$ $r_2 < 1$ or $r_1 < 1$ $r_2 > 1$ **인 경우는 한쪽 모노모가 다른 쪽에 비해** reactivity **가 크다는 얘기이므로** copolymer **중에 반응성이 큰 모노머의** portion**이** random copolymer**중에 더 많이 산재해 있음을 의미함**.



12. 5 Alternating COPOLYMERIZATION (교대혼성 공중합)

$r_1 = r_2 = 0$



r_1, r_2 **가** 0 **에 가까울수록** alternating tendency **가 있음**.

$r_1 = r_2 = 0$ **이면** perfect alternation!

$$\frac{d[M_1]}{d[M_2]} = 1$$

$$F_1 = 0.5 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

$r_1 < 1,\ r_2 < 1$ **이면** F_1 vs. f_1 curve **에서** $F_1 = f_1$ **인 선을** cross **함**.

$r_1 = r_2 = \infty$ **이면** homopolymer

Cross-over Point 의 의미:

$$F_1 = f_1$$

공중합체의 조성이 공급액 조성과 같으며 공중합이 일어날 때 공급액 조성에 변화가 일어나지 않음. 이러한 공중합을 AZEOTROPIC COPOLYMZN(**공비공중합**) **이라 함**.

Azeotropic copolymeriztion **이 일어나는 조건은**

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \text{ 이고 } \frac{[M_1]}{[M_2]} = \frac{(r_2 - 1)}{(r_1 - 1)} \text{ 임.}$$

$$\because F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} = \frac{[M_1]}{[M_1] + [M_2]} = f_1$$

$$\frac{d[M_1]}{d[M_2]}=\frac{[M_1]}{[M_2]}\cdot\frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]}$$

$$r_1[M_1]+[M_2]=[M_1]+r_2[M_2]$$

$$r_1\frac{[M_1]}{[M_2]}+1=\frac{[M_1]}{[M_2]}+r_2$$

$$\frac{[M_1]}{[M_2]}=\frac{r_2-1}{r_1-1}$$

$$f_1=\frac{[M_1]}{[M_1]+[M_2]}$$

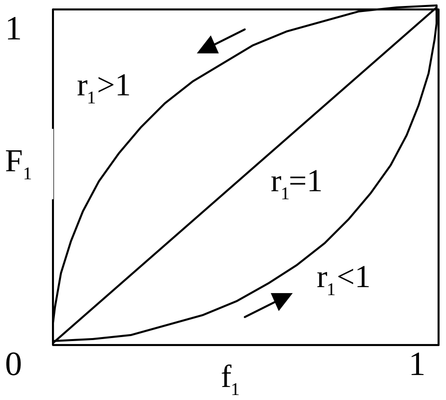
$$\frac{1}{f_1}=1+\frac{[M_2]}{[M_1]}=1+\frac{r_1-1}{r_2-1}=\frac{r_2+r_1-2}{r_2-1}$$

$$\therefore\ f_1=\frac{r_2-1}{r_2+r_1-2}=\frac{1-r_2}{2-r_1-r_2}$$

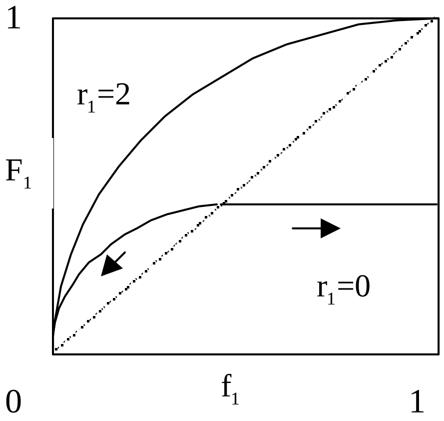
$\underline{r_1 >> r_2}$ (**특히** $r_1 >> 1$ and $r_1 << 1$)

이때는 모너머 M_1 **이 모두 소비될 때까지** HOMOPOLYMERIZE **함**. **그 다음에** M_2 **가 부수적으로 중합함**.

축을 바꾸어서



결국 $r_1r_2=1$ ideal or random



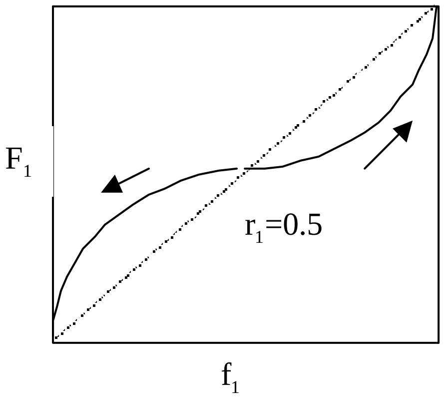
fix r_2=0.5

$r_1 = 0 = \frac{k_{11}}{k_{12}}$ 모노머 A와 A*가 첨가

copolymer를 만들지 못함.

0.5까지는 alternating 으로 가다가

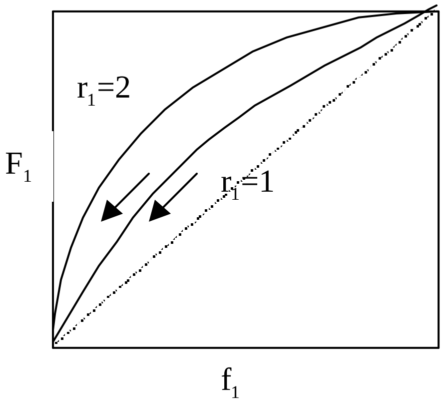
0.5 이상에서는 copolymer가 안됨.



r_2=0.5

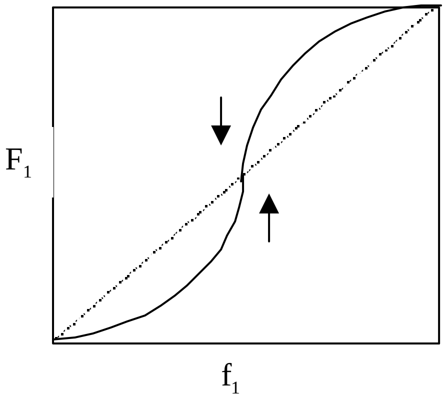
azeotropic comp

alternating



r_2=0.5

r_1=1 no azeotrope



$r_1, r_2 > 1$ 인 경우

copolymerization의 끝이 여기에 이름

tend to be a block copolymzn

Drift: ↙ $r_1, r_2 > 1$ block azeotrope

↗

↗

↙ $r_1, r_2 < 1$ alternating

$r_1 > 1$, $r_2 > 1$ 즉 $r_1 r_2 > 1$ ⟶▶Block COPOLYMERIZATION

HW #6.

Solve S.S. expression for a monomer concentration and substitute into the original composition equation which contains the active center. You can get eq. in terms of active center concentrations and if necessary define new kind of new reactivity ratio in eq.

12.6 Experimental Determination of r_1 & r_2

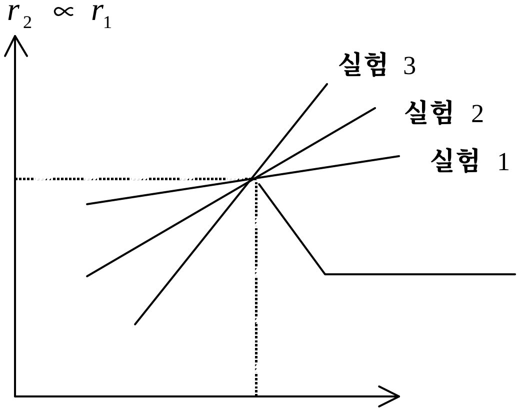
12.6.1 Mayo and Lewis 의 방법

rearrange copolymer eq. and can get

$$r_2 = \frac{[M_1]}{[M_2]} \cdot \left\{ \frac{d[M_2]}{d[M_1]} \left[1 + \frac{r_1[M_1]}{[M_2]} \right] - 1 \right\}$$

monomer comp.	copolymer comp.
$[M_1]/[M_2]$	$d[M_1]/d[M_2]$
⋮	⋮
⋮	⋮

then vary r_1 value (put) and iterate



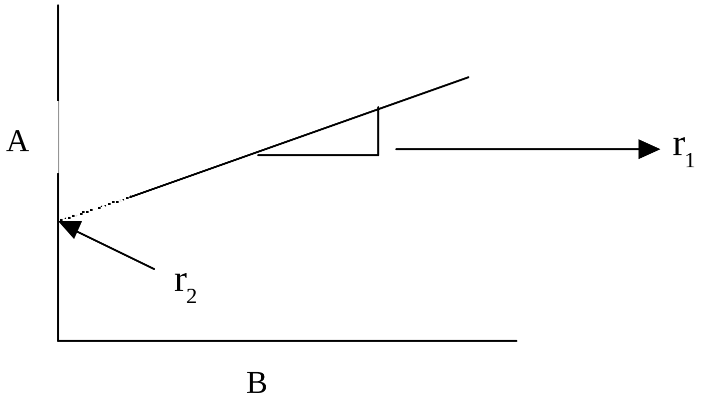
이 삼각형(Ä)이 작을수록 정확한 r_1, r_2값을 구할 수 있음.

12.6.2 Finemann and Ross 의 방법

Recall $F_1 = \dfrac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$

$$\underbrace{\frac{f_1(1-2F_1)}{F_1(1-f_1)}}_{A} = r_2 + \underbrace{\frac{f_1^{\,2}(F_1-1)}{F_1(1-f_1)^2}}_{B}\cdot r_1$$

at low conversion



12.7 Relationship Between ξ and F_1, f_1

Material Balance for M_1

$-d([M]f_1) = -d[M]F_1$ where [M] = total # of moles of monomers

$\uparrow$

decrease of M_1 monomer

$+d([M]f_1) = \{d[M]\}\cdot F_1 = f_1 d[M] + [M]df_1$

$(F_1 - f_1)d[M] = [M]df_1$

$$\frac{d[M]}{[M]} = \frac{df_1}{F_1 - f_1}$$

$$\lim \frac{[M]}{[M_0]} = \int_{f_{1,0}}^{f} \frac{df_1}{F_1 - f_1}$$

$$x = 1 - \frac{[M]}{[M]_0} = 1 - e^{\int_{f_{1,0}}^{f} \frac{df_1}{F_1 - f_1}}$$

12.8 Structure and Reactivity

13 Resonance Stabilization

14 Polar Effects

15 Steric Effects

12.8.1 Resonance Stabilization

- 라디칼 안정화가 공명 안정성을 지배하는 경향
- 라디칼이 그에 상응하는 모노머보다 더 공명안정화하는 경향

Substituent on Double Bond	Relative Reactivity of Monomer	Stabilization Energy, kcal/mole	
		Olefine	Radical
-H, $-OCH_3$	1	0	0
-OAc, $-CH_3$	1.5-5	2.5	4
-Cl	3-20	-	6
-COO, -COOH	20-60	2.5	-
-CN, -COR	30-60	0	-
$-C_2H_3$, $-C_6H_5$	50-100	3-4	25

* Walling' s "Free Radicals in Solution"

Define

r_A, r_B : monomer reactivity ratios

R_A, R_B : active center reactivity ratios

$$r_A = \frac{k_{AA}}{k_{AB}} \qquad r_B = \frac{k_{BB}}{k_{BA}}$$

$$R_A = \frac{k_{AA}}{k_{BA}} \qquad R_B = \frac{k_{BB}}{k_{AB}}$$

$$R_A = \frac{k_{AA}}{k_{BB}} \cdot r_B = \frac{k_{AA}}{k_{BB}} \frac{k_{BB}}{k_{BA}}$$

$$R_B = \frac{k_{BB}}{k_{AA}} \cdot r_A$$

TABLE I. Propagation Rate Constants, Monomer Reactivity Ratios, and Active Center Reactivity Ratios for Radical Chain-Growth Polymerizations[1]

Mon A[2]	Mon B[2]	$K_{AA}x10^{-3}$	$K_{BB}x10^{-3}$	r_A	r_B	R_A	R_B
AN	MA	1.96	2.09	1.26	0.67	$6.28x10^{-1}$	$1.34\ x10^{0}$
AN	MMA	1.96	0.515	0.15	1.20	$4.57x10^{0}$	$3.94\ x10^{-2}$
AN	STY	1.96	0.165	0.04	0.40	$4.8\ x10^{0}$	$3.4\ x10^{-3}$
AN	VA	1.96	2.30	5.4	0.050	$4.3\ x10^{-2}$	$6.3\ x10^{0}$
MA	MMA	2.09	0.515	0.25	3.22	$1.31x10^{1}$	$6.16\ x10^{-2}$
MA	STY	2.09	0.165	0.20	0.75	$9.5\ x10^{0}$	$1.6\ x10^{-2}$

MA	VA	2.09	2.30	9.	0.1	9. x10^{-2}	1. x10^{1}
MMA	STY	0.515	0.165	0.46	0.52	1.6 x10^{0}	1.5 x10^{-1}
MMA	VA	0.515	2.30	20	0.015	3.4 x10^{-3}	8.9 x10^{1}
STY	VA	0.515	2.30	55	0.01	7. x10^{-4}	8. x10^{2}

[1] All values are based on data collected at 60℃

[2] AN=acrylonitrile; MA=methylacrylate; MMA=methylmetacrylate; STY=styrene; VA=vinyl acetate

Active Center Reactivity Ratios vs. Monomer Reactivity Ratios

$$\frac{d[A]}{d[B]}=\frac{[A^*]}{[B^*]}\left(\frac{R_A[A^*]+[B^*]}{[A^*]+R_B[B^*]}\right)$$

$$R_A=\frac{k_{AA}}{k_{BA}} \qquad R_B=\frac{k_{BB}}{k_{AB}}$$

when $R_A > R_B$ then $r_A < r_B$

$$\frac{R_A}{R_B}>\frac{r_B}{r_A} \quad \text{when} \quad R_A > R_B$$

따라서 모노머의 비반응성(relative reactivity)**에 영향을 미치는 것은** active center **의 비반응성에 더 강한 영향을 미치는 것을 알 수 있다**.

모노머 반응성은 active center **반응성과 반대로 영향을 받는다**.

Odian Table 6-3. Relative Reactivities(1/r) of Monomers

Monomer	Polymer Radical						
	Butadiene	Sty	VAc	VC	MMA	MA	AN
Butadiene		1.7		29	4	20	50
Styrene	0.7		100	50	2.2	5.0	25
Methyl Metacrylate	1.3	1.9	67	10		2	6.7
Methyl Vinyl Ketones		3.4	20	10			1.7
Acrylonitrile	3.3	2.5	20	25	0.82	1.2	
Methyl Acrylate	1.3	1.3	10	17	0.52		0.67
Vinylidene Chloride		0.54	10		0.39		1.1
Vinyl Chloride	0.11	0.059	4.4		0.10	0.25	0.37
Vinyl Acetate		0.019		0.59	0.05	0.11	0.24

치환기 효과(Substituent Effects)

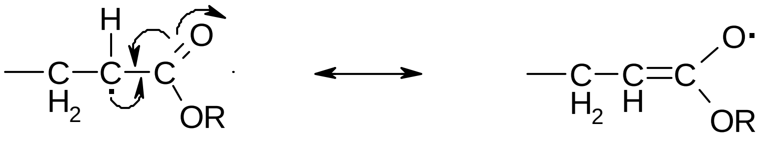
Φ, CH_2=CH- > -C≡N, -COR > -COOH, -COOR > -Cl > -O-COR, -R > -OR, -H

치환기들은 공명안정화로 인해 모노머의 상대반응성을 증가
모노머의 공명안정성은 모노머의 반응성을 증가시킴.
라디칼의 공명안정성은 라디칼의 반응성이 약화됨.

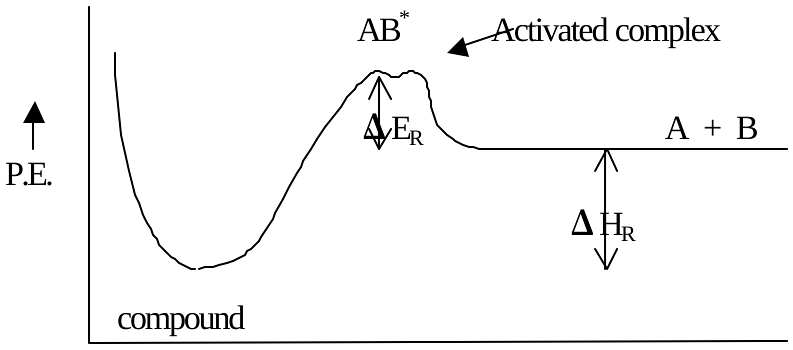
Table 6-4 Rate Constant(k_{12}) for Radical-Monomer Reactions

	Polymer Radical								
Monomer(M_1)	Buta-diene	Sty-rene	Methyl Metacrylate	Acrylo-nirile	Methyl Acrylate	Vinyl Acetate	Vinyl Chloride	Q_1	e_1
Butadiene	100	280	2,060	98,000	41,800		319,000	2.39	-1.05
Styrene	70	165	1,130	49,000	10,045	230,000	550,000	1.00	-0.80
Methyl methacrylate	130	314	515	13,100	4,180	154,000	110,000	0.74	0.40
Acrylonitrile	330	413	422	1,960	2,510	46,000	225,000	0.60	1.20
Methyl acrylate	130	215	268	1,310	2,090	23,000	187,000	0.42	0.60
Vinyl chloride	11	9.7	52	720	520	10,100	11,000	0.044	0.20
Vinyl acetate		3.4	26	230	530	2,300	6,490	0.026	-0.22

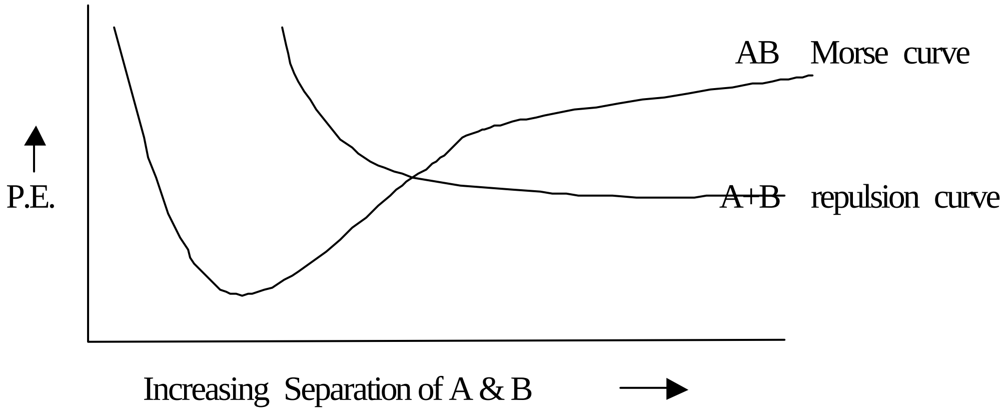
Resonance stabilization of Active Center

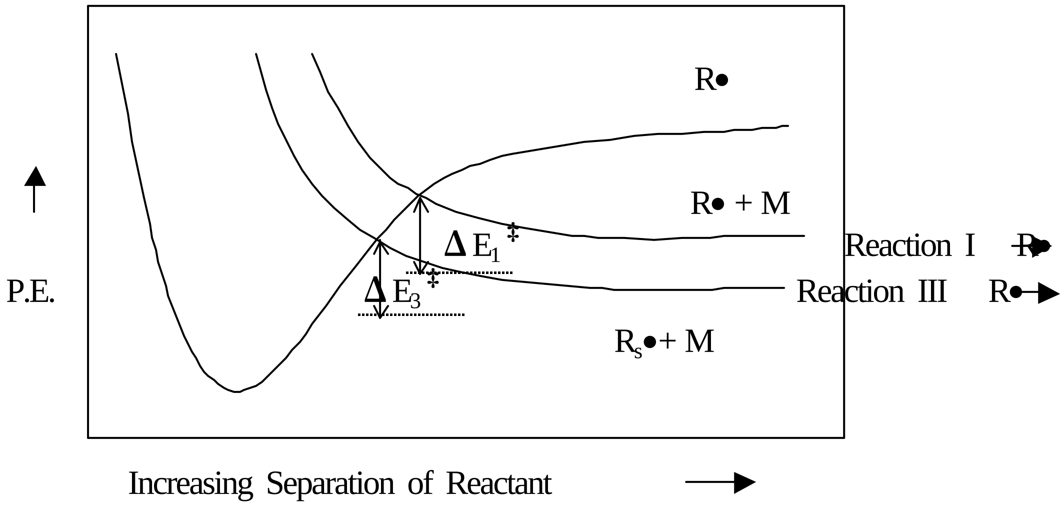


Transition State Theory



Increasing Separation of A & B →





$\Delta E_3^{\ddagger} > \Delta E_1^{\ddagger}$ then Rexn III is less stable than Rexn I

$\Delta H_{R3}^{\ddagger} < \Delta H_{R1}^{\ddagger}$

Active Center **의 공명안정화가** primary factor **임**

Monomer **의 공명안정화가** secondary factor **임**

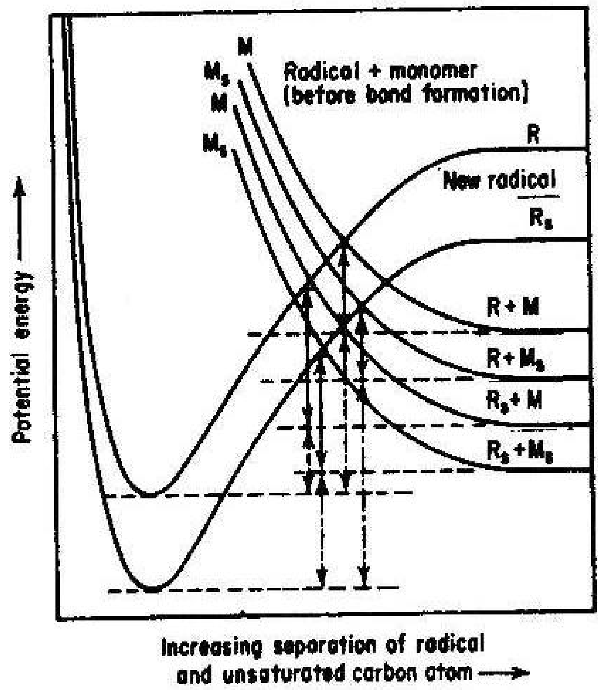


Fig. 6-12 Reaction coordination diagram for the reaction of a polymer radical with a monomer. The dependence of the potential energy of the system (radical + monomer) on the separation between the radical and the unsaturated carbon atom of the monomer is shown. The subscript *s* indicates the presence of a substituent that is capable of resonance stabilization. Activation energies are represented by the solid-line arrows; heats of reaction by the broken-line arrows. After Walling [1957] (by permission of Wiley, New York).

	$-\Delta H$	$\Delta E^{\ddagger}$
$R\cdot + M_S \rightarrow R_S\cdot$	1.20	0.40
$R\cdot + M \rightarrow R\cdot$	0.95	0.50
$R_S\cdot + M_S \rightarrow R_S\cdot$	0.70	0.70
$R_S\cdot + M \rightarrow R\cdot$	0.40	0.80

$|-\Delta H|$ ① > ② > ③ > ④
$\Delta E^{\ddagger}$ ④ > ③ > ② > ①

Rule of Thumb

- 공명안정화된 모노머는 안정성을 증가시키나 그것의 라디칼의 반응성은 낮춘다.
- 모노머가 공명안정화될수록 반응성은 다른 모노머들과 비교하여 높다.
- 공명안정화된 모노머가 라디칼이 되면 그 모노머보다 더욱 안정화되며 다른 active center 들 보다 더욱 안정화된다.

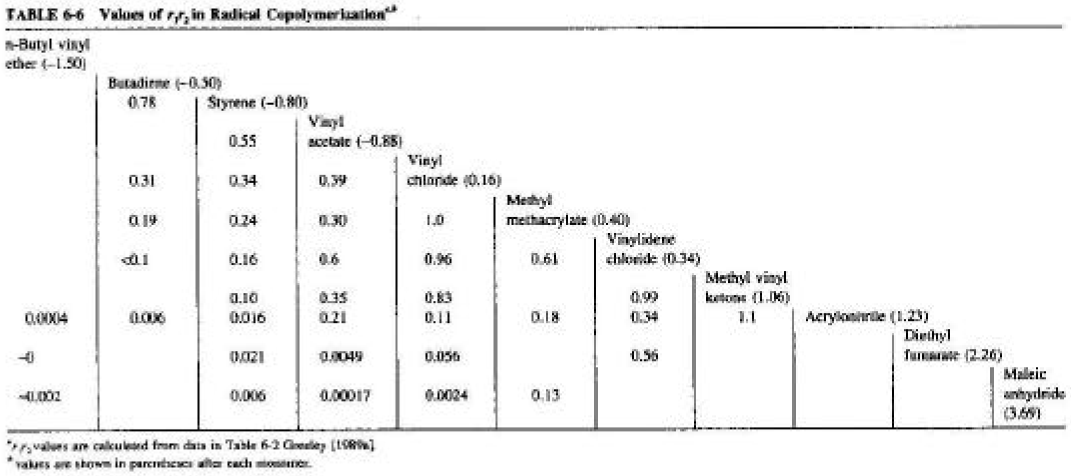
Example) Styrene $r_S = 55$ Vinyl Acetate $r_V = 0.01$

① $X_S = 0.02$
$X_V = 0.98$
VAc · 로 끝나면 sty. 붙음
Sty · 로 끝나면 unreactive
VAc monomer 면 unreactive
Sty. monomer 면 reactive
Styrene → retarder in this case
Reaction slows down until
styrene is consumed

② $X_S = 0.6$
$X_V = 0.4$
nearly pure homo PS
Sty. consumed at a rapid ratio
$r_1 \cdot r_2 = 0.55$
to random
copolymer
slight tendency
to alternate
rather than Blocky

12.8.2 Polar Effects

TABLE 6-6 Values of r_1r_2 in Radical Copolymerization[a,b]



	n-Butyl vinyl ether (−1.50)	Butadiene (−0.50)	Styrene (−0.80)	Vinyl acetate (−0.88)	Vinyl chloride (0.16)	Methyl methacrylate (0.40)	Vinylidene chloride (0.34)	Methyl vinyl ketone (1.06)	Acrylonitrile (1.23)	Diethyl fumarate (2.26)
Butadiene (−0.50)										
Styrene (−0.80)		0.78								
Vinyl acetate (−0.88)			0.55							
Vinyl chloride (0.16)		0.31	0.34	0.39						
Methyl methacrylate (0.40)		0.19	0.24	0.30	1.0					
Vinylidene chloride (0.34)		<0.1	0.16	0.6	0.96	0.61				
Methyl vinyl ketone (1.06)			0.10	0.35	0.83		0.99			
Acrylonitrile (1.23)	0.0004	0.006	0.016	0.21	0.11	0.18	0.34	1.1		
Diethyl fumarate (2.26)	~0		0.021	0.0049	0.056		0.56			
Maleic anhydride (3.69)	~0.002		0.006	0.00017	0.0024	0.13				

[a] r_1r_2 values are calculated from data in Table 6-2 Greenley [1989a].
[b] e values are shown in parentheses after each monomer.

Tend to cause alternation in a copolymerization

i.e. $r_A \cdot r_B < 1$ for polar effects

e : tendency to give monomer a polar effects (Polarity Values)
Alfrey-Price Q,e scheme

Δe 가 큰 값과 small reactivity ratio 곱 사이에 어떤 연관이 있다.
결국 polarity 또는 polarization of monomer 와 active center 로 alternating effect 설명

Alfred-Price 의 Q-e scheme

r_A, r_B 는 공중합체중 randomness 를 예측.

polar, resonance effect 를 알면 r 을 예측 가능.
Guidance to chemists.

$$k_{ij} = P_i Q_j \exp(-e_i e_j)$$

where P : active center reactivity
Q : monomer reactivity
i, j : active center, monomer, respectively

$$r_i = \frac{k_{ii}}{k_{ij}} = \frac{P_i Q_i \exp(-e_i e_i)}{P_i Q_j \exp(-e_i e_j)}$$

$$\boxed{r_i = \frac{Q_i}{Q_j}\exp[-e_i(e_i - e_j)]}$$

따라서 이식으로 r_i를 예측 가능.

styrene 을 base 로 사용 : $Q = 1$
(arbitrary)
$e = -0.8$ (처음에는 -)

fair results, but not absolute in predicting r using Q-e scheme.

$$r_j = \frac{k_{jj}}{k_{ji}} = \frac{P_j Q_j \exp(-e_j e_j)}{P_j Q_i \exp(-e_j e_i)} = \frac{Q_j}{Q_i}\exp[-e_j(e_j - e_i)]$$

$$r_i \cdot r_j = \frac{\exp[-e_i(e_i - e_j)]}{\exp[-e_j(e_j - e_i)]} = \exp[-(e_i - e_j)^2]$$

$$r_i \cdot r_j = \exp[-(e_i - e_j)^2] < 1$$

$$-(e_i - e_j)^2 < 0 \Rightarrow (e_i - e_j)^2 > 0$$

∴ alternating tendency is correct

Active Center Reacting Ratios

$$\frac{d[A]}{d[B]} = \frac{[A^*]}{[B^*]} \cdot \frac{R_A[A^*]+[B^*]}{[A^*]+R_B[B^*]}$$

P-e scheme

$$R_i = \frac{P_iQ_i\exp(-e_ie_i)}{P_jQ_i\exp(-e_je_i)} = \frac{k_{ii}}{k_{ji}}$$

$$R_i = \frac{P_i}{P_j}\exp[-e_i(e_i-e_j)]$$

	P	e	Q	e
St	1	-0.8	1	-0.8
AN	58.23	1.233	0.4	1.2
MA	21.03	0.577	0.42	1.2
MMA	2.413	0.397	0.24	0.4
VAc	751.3	-0.027	0.024	-0.22

Q-e scheme 에 대한 비난

1. Reference state arbitrarily set.
2. Alternating effect 가 fixed charges 때문에 나오며 induced dipole 때문이 아니다.

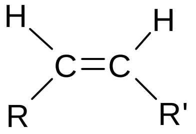
Exercise)

Copolymer 의 randomness 가 Q-e scheme 으로 어떻게 표시될 수 있나를 보아라

왜 Q-e scheme 은 alternation 이나 randomness 를 predict 하지만 block 을 예측할 수 없나? (algebraic standpoint)

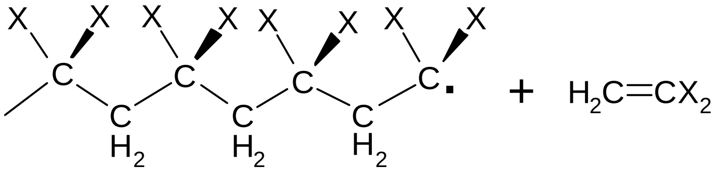
12.8.3 Steric Effect

1. 1,2-disubstituted ethylene do not homopolymerize readily



polar effect 말고 이것을 어떻게 설명?

2. 1,1-disubstituted ethylene

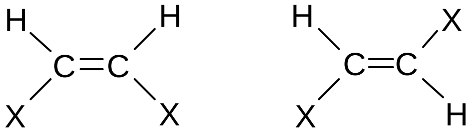


planar conformation

tetrahedral conformation

more reactive

3. Cis-trans Effect



열역학적으로 trans **가** cis **보다 더 안정**(Heat of Hydrogenation)

cis **가 더** reactive?   No!

Planarity! Easier for trans than cis

Steric Effect!

(**분자괘도**)

<u>Steric Effect</u>

Table 6-5 Rate Constants(k_{12}) for Radical-Monomer Reactions[a]

Monomer	Polymer Radical		
	Vinyl Acetate	Styrene	Acrylonitrile
Vinyl chloride	10,000	9.7	725
Vinylidene chloride	23,000	89	2,150
Cis-1,2-Dichloroethylene	365	0.79	
Trans-1,2-Dichloroethylene	2,320	4.5	
Trichloroethylene	3,480	10.3	29
Tetrachloroethylene	338	0.83	4.2

[a] k_{12} values calculated from data in Table 3-11 and 6-2 and [66]

Highly reactive ↑

1,1-disubs.

Mono subs.

Tri subs.

Trans 1,2

Cis 1,2