

. Free Radical Copolymerization

➤ Radical copolymerization

Regular copolymer



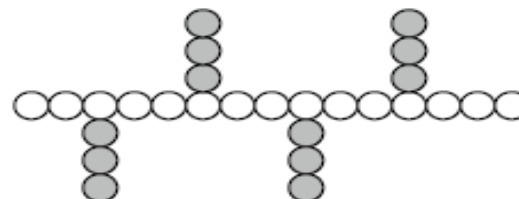
Random copolymer



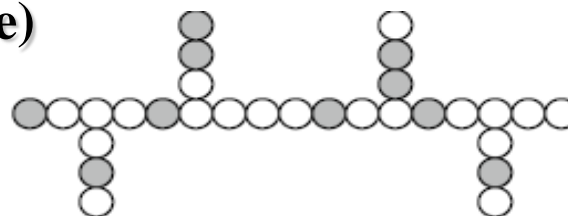
Block copolymer



Graft copolymer



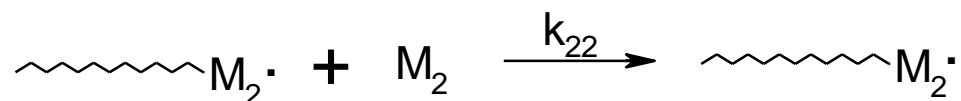
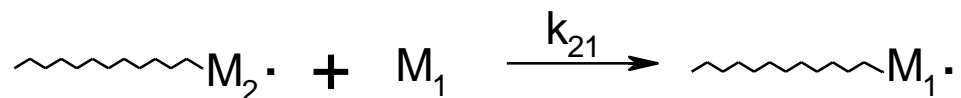
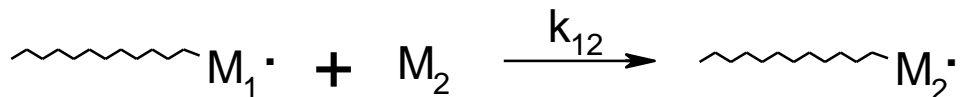
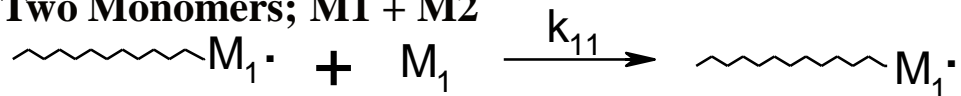
Actual copolymer (case)



Copolymer Equation

Only Binary Case

Two Monomers; M1 + M2



Steady State Assumption

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

and chain transfer & termination compared w/ propagation

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

$$\frac{[M_1\cdot]}{[M_2\cdot]} = \frac{k_{21}[M_1]}{k_{12}[M_2]} \quad \dots\dots\textcircled{1}$$



Copolymer Equation

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

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

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] k_{11}[M_1\cdot] + k_{21}[M_2\cdot][M_1]}{[M_2] k_{12}[M_1\cdot] + k_{22}[M_2\cdot][M_2]} \quad \dots\dots ②$$

Instantaneous ratio of monomers in copolymer

From ① and ②

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

where $r_2 = \frac{k_{22}}{k_{21}}$, $r_1 = \frac{k_{11}}{k_{12}}$ ← monomer reactivity ratio

← Copolymer Eq.



Meaning of r & Definition of f_1, F_1

Meaning of r

r_1 characterizes the reactivity of the 1 radical with respect to the two monomers, 1 and 2

$r_1 > 1$ then homopolymerization growth is preferred

$r_1 = 0$ then only reaction with 2 will occur

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

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \quad \dots\dots \textcircled{3} \quad F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad \dots\dots \textcircled{4}$$

From $\textcircled{3}, \textcircled{4}$

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad \dots\dots \textcircled{5}$$



Ideal Copolymerization

Ideal Copolymerization

$$\begin{aligned}\frac{d[M_1]}{d[M_2]} &= \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \\ &= r_1 \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_1[M_1] + [M_2]} \\ &= r_1 \frac{[M_1]}{[M_2]}\end{aligned}$$

$$\text{where } r_1 \cdot r_2 = 1 \quad \longrightarrow \quad r_2 = \frac{1}{r_1}$$

$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2} \qquad \frac{k_{11}}{k_{12}} \cdot \frac{k_{22}}{k_{21}} = 1 \qquad \frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$$

Most ionic copolymerizations are characterized by the ideal type of behavior

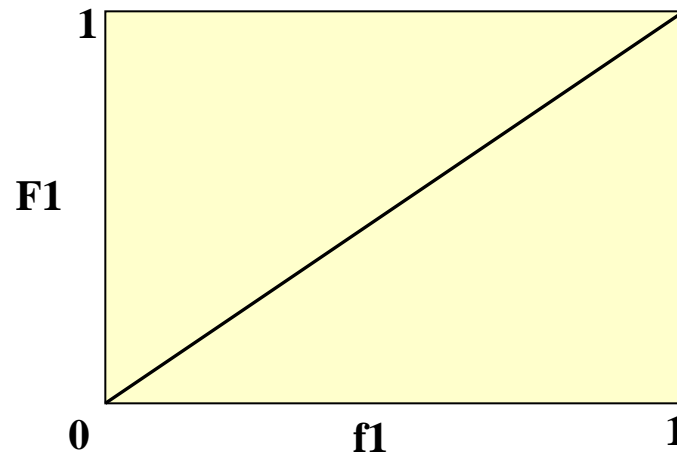
**When $r_1 = 1 = r_2$, the two monomers show equal reactivity toward both propagating species
 \longrightarrow random copolymer**



Ideal Copolymerization

$r_1 > 1$ $r_2 < 1$ or $r_1 < 1$ $r_2 > 1$ One of the monomer is more reactive than

The other toward both propagating species. The copolymer will contain a larger proportion of the more reactive monomer in random placement



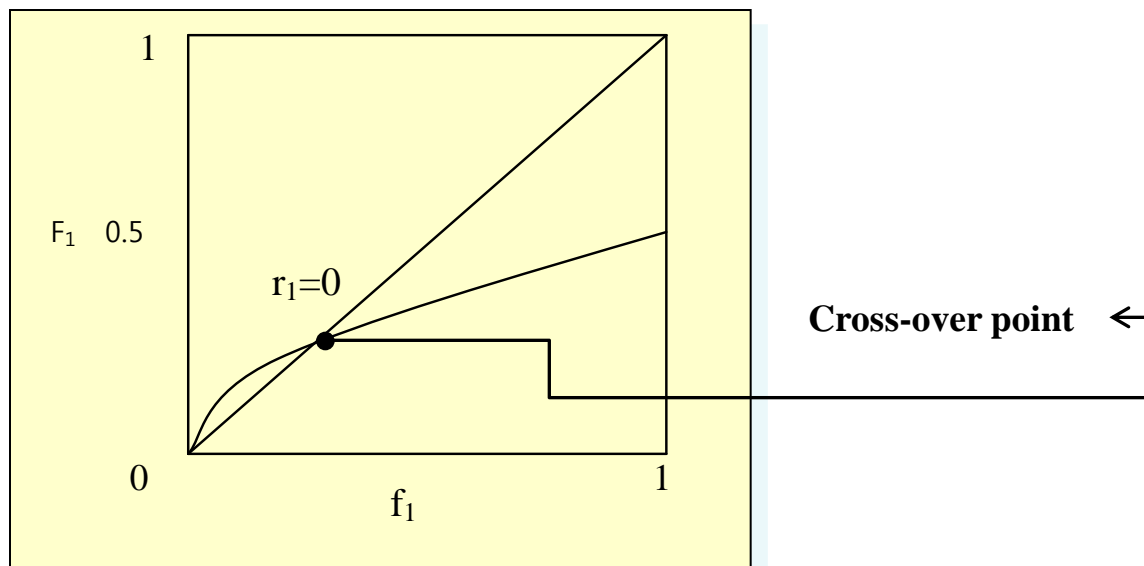
Alternating Copolymerization

Alternating Copolymerization

$$r_1 = r_2 = 0$$

or

$$r_1 r_2 = 0$$



As r_1, r_2 approach to zero, alternating tendency can be observed

If $r_1 = r_2 = 0 \rightarrow$ perfect alternation!

$$\frac{d[M_1]}{d[M_2]} = 1 \quad F_1 = 0.5 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

If $r_1 < 1, r_2 < 1$ F_1 / f_1 plots cross the line representing $F_1 = f_1$

If $r_1 = r_2 = \infty$, then, become a homopolymer



Alternating Copolymerization

Mean of Cross-over Point

$$F_1 = f_1$$

At these crossover points the copolymer and feed compositions are the same and copolymerization occurs without a change in the feed composition

Such copolymerizations are termed **Azeotropic copolymerizations**.

Condition of Azeotropic copolymerization

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \quad \text{and} \quad \frac{[M_1]}{[M_2]} = \frac{(r_2 - 1)}{(r_1 - 1)}$$

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



Alternating Copolymerization

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

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

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

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

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

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

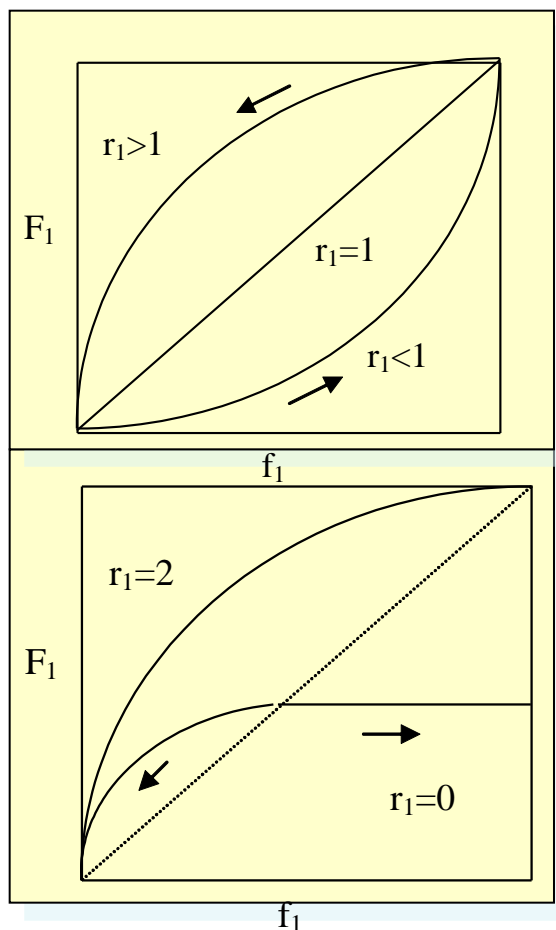


Alternating Copolymerization

$$r_1 \gg r_2 \quad (r_1 \gg 1 \text{ and } r_1 \ll 1)$$

Both types of propagating species preferentially add monomer M_1 . there is a tendency toward consecutive Homopolymerization of the two monomers.

And then monomer M_2 will subsequently homopolymerize.



In the result $r_1 r_2 = 1$ ideal or random

fix $r_2 = 0.5$

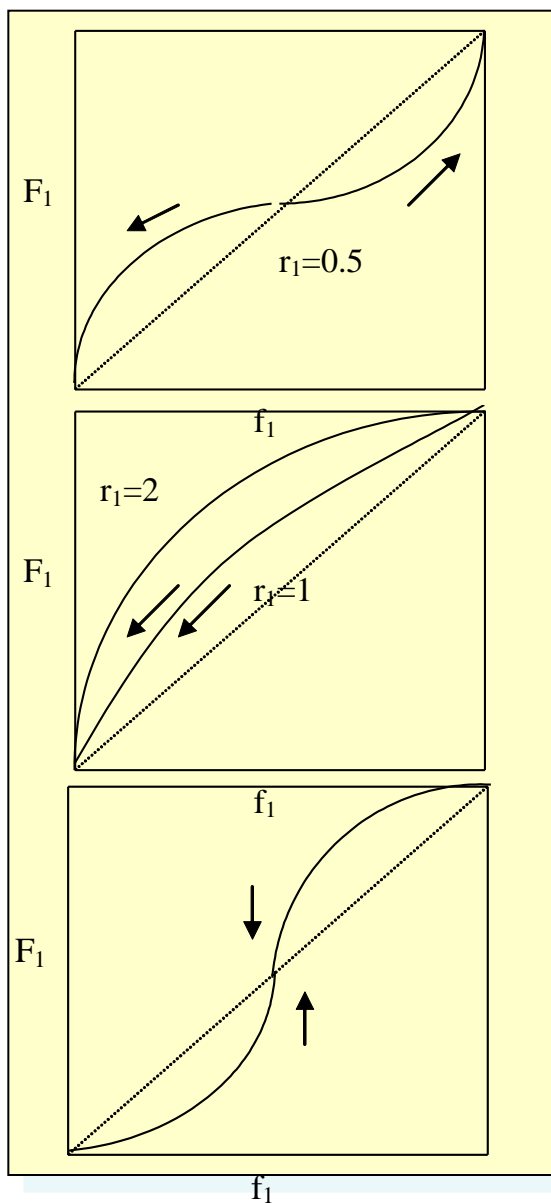
$$r_1 = 0 = \frac{k_{11}}{k_{12}} \quad \text{Addition monomer A and A}^*$$

Can not prepare copolymer

It's alternating up to 0.5, and above 0.5 there's no formation of copolymer



Alternating Copolymerization



$$r_2 = 0.5$$

azeotropic comp

alternating

$$r_2 = 0.5$$

$r_1 = 1$ no azeotrope

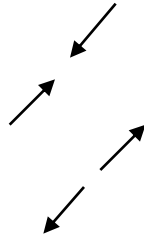
$r_1, r_2 > 1$ Case

tend to be a block copolymerization



Alternating Copolymerization

Drift:



$r_1, r_2 > 1$ **block azeotrope**

$r_1, r_2 < 1$ **alternating**

$r_1 > 1$, $r_2 > 1$ **finally** $r_1 r_2 > 1 \rightarrow$ **Block COPOLYMERIZATION**



Experimental Determination of r_1 & r_2

Experimental Determination of r_1 & r_2

1. Mayo and Lewis

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

$$[M_1]/[M_2]$$

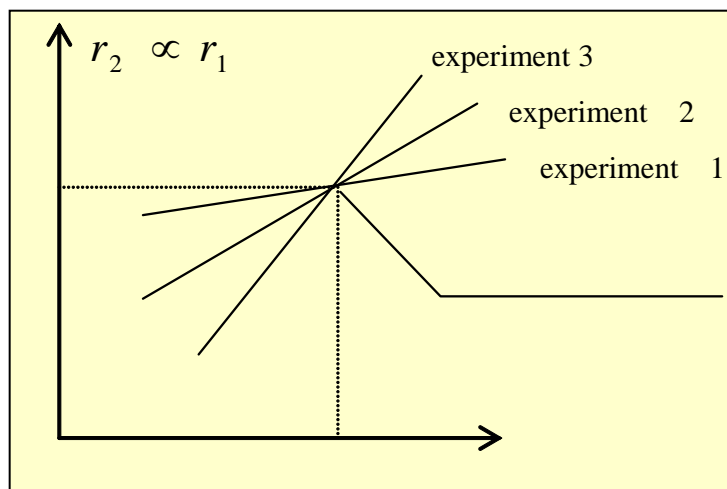
⋮

copolymer comp.

$$d[M_1]/d[M_2]$$

⋮

then vary r_1 value (put) and iterate



This Δ is more for
smaller, r_1 , r_2 value
calculate with accuracy



Experimental Determination of r_1 & r_2

2. Finemann and Ross

Recall

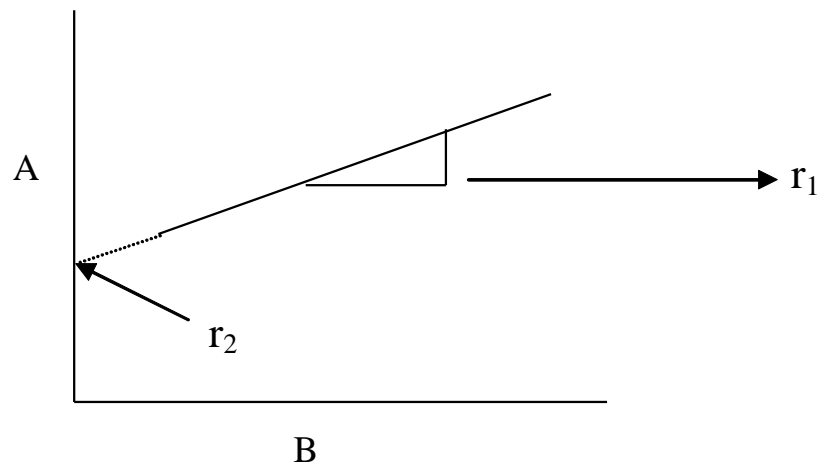
$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

$$\underbrace{\frac{f_1(1-2F_1)}{F_1(1-f_1)}}_A = r_2 + \underbrace{\frac{f_1^2(F_1-1)}{F_1(1-f_1)^2}}_B \cdot r_1$$

A
const.

B
const.

at low conversion



Slope : r_1
Intersection : r_2



Relationship Between ξ and F_1, f_1

Relationship Between ξ and F_1, f_1

Material Balance for M_1

$$-d([M]f_1) = -d[M]F_1 \quad \text{where } [M] = \text{total \# of moles of monomers}$$

↑

decrease of M_1 monomer

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

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

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

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

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



Effect of Reaction Condition

Reaction medium

Depend on Solubility, PH, Viscosity, and Polarity

Temperature

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{A_{11}}{A_{12}} \exp \left[\frac{(E_{12} - E_{11})}{RT} \right]$$

But the effect of temperature on r is not large

Pressure

$$\frac{d \ln r_1}{dP} = \frac{-(df_1 \Delta V_{11} - \Delta V_{12})}{RT}$$

But the effect of pressure on r is not large

Reactivity

Next page



Effect of Reaction Condition

Structure and Reactivity

- I. Resonance Stabilization
- II. Polar Effects
- III. Steric Effects

I. Resonance Stabilization

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 ₂ H ₃ , -C ₆ H ₅	50-100	3-4	25

* Walling's "Free Radicals in Solution"



Structure and Reactivity

Define

r_A, r_B : monomer reactivity ratios

R_A, R_B : active center reactivity ratios

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

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

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

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



Structure and Reactivity

TABLE I. Propagation Rate Constants, Monomer Reactivity Ratios, and Active Center Reactivity Ratios for Radical Chain-Growth Polymerizations¹

Mon A ²	Mon B ²	$K_{AA} \times 10^{-3}$	$K_{BB} \times 10^{-3}$	r_A	r_B	R_A	R_B
AN	MA	1.96	2.09	1.26	0.67	6.28×10^{-1}	1.34×10^0
AN	MMA	1.96	0.515	0.15	1.20	4.57×10^0	3.94×10^{-2}
AN	STY	1.96	0.165	0.04	0.40	4.8×10^0	3.4×10^{-3}
AN	VA	1.96	2.30	5.4	0.050	4.3×10^{-2}	6.3×10^0
MA	MMA	2.09	0.515	0.25	3.22	1.31×10^1	6.16×10^{-2}
MA	STY	2.09	0.165	0.20	0.75	9.5×10^0	1.6×10^{-2}
MA	VA	2.09	2.30	9.	0.1	$9. \times 10^{-2}$	$1. \times 10^1$
MMA	STY	0.515	0.165	0.46	0.52	1.6×10^0	1.5×10^{-1}
MMA	VA	0.515	2.30	20	0.015	3.4×10^{-3}	8.9×10^1
STY	VA	0.515	2.30	55	0.01	$7. \times 10^{-4}$	$8. \times 10^2$

1All values are based on data collected at 60°C

2AN=acrylonitrile; MA=methylacrylate; MMA=methylmetacrylate;

STY=styrene; VA=vinyl acetate



Structure and Reactivity

Active Center Reactivity Ratios vs. Monomer Reactivity Ratios

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

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

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

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

The effect in relative reactivity of the active center is more stronger than that of monomer.

The monomer reactivity gets affect in opposite way comparing to the active center reactivity.



Structure and Reactivity

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



Structure and Reactivity

@ Substituent Effects

Φ , $\text{CH}_2=\text{CH}- > -\text{C}\equiv\text{N}$, $-\text{COR} > -\text{COOH}$, $-\text{COOR} > -\text{Cl} > -\text{O}-\text{COR}$, $-\text{R} > -\text{OR}$, $-\text{H}$

monomers increase relative reactivity by resonance stabilization.

The resonance stability of the monomer increases the reactivity of the monomer.

The resonance stability of the radical is weakened reactivity of the radical.

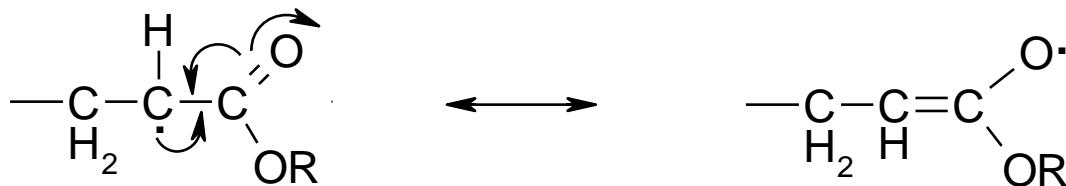
Table 6-4 Rate Constant(k_{12}) for Radical-Monomer Reactions

Monomer(M_1)	Polymer Radical							Q_1	e_1
	Buta- diene	Sty- rene	Methyl Metacrylate	Acrylo- nirile	Methyl Acrylate	Vinyl Acetate	Vinyl Chloride		
Butadiene	100	280	2,060	98,000	41,800	230,000	319,000	2.39	-1.05
Styrene	70	165	1,130	49,000	10,045	154,000	550,000	1.00	-0.80
Methyl methacrylate	130	314	515	13,100	4,180	46,000	110,000 225,000	0.74 0.60	0.40 1.20
Acrylonitrile	330	413	422	1,960	2,510	23,000	187,000	0.42	0.60
Methyl acrylate							11,000	0.044	0.20
Vinyl chloride	130	215	268	1,310	2,090	0,100	6,490	0.026	-0.22
Vinyl acetate	11	9.7	52	720	520	2,300			
		3.4	26	230	530				

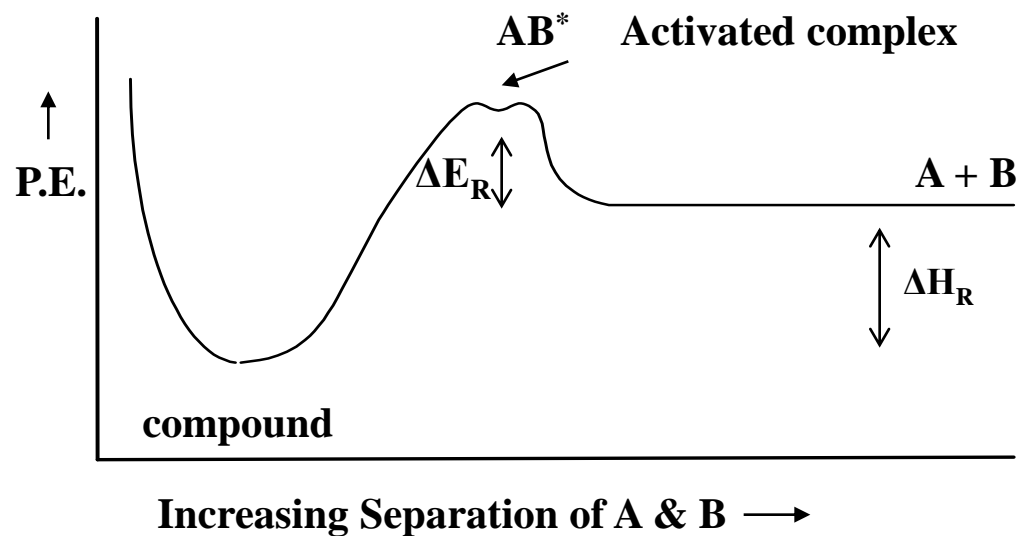


Structure and Reactivity

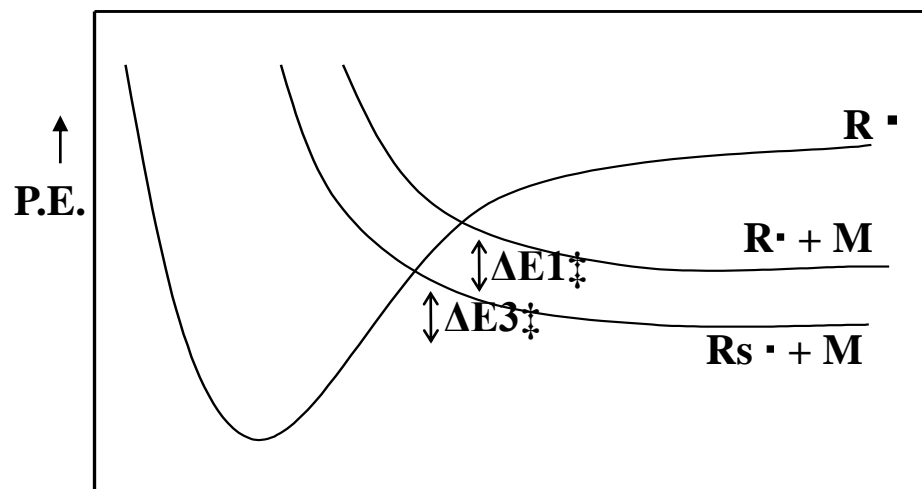
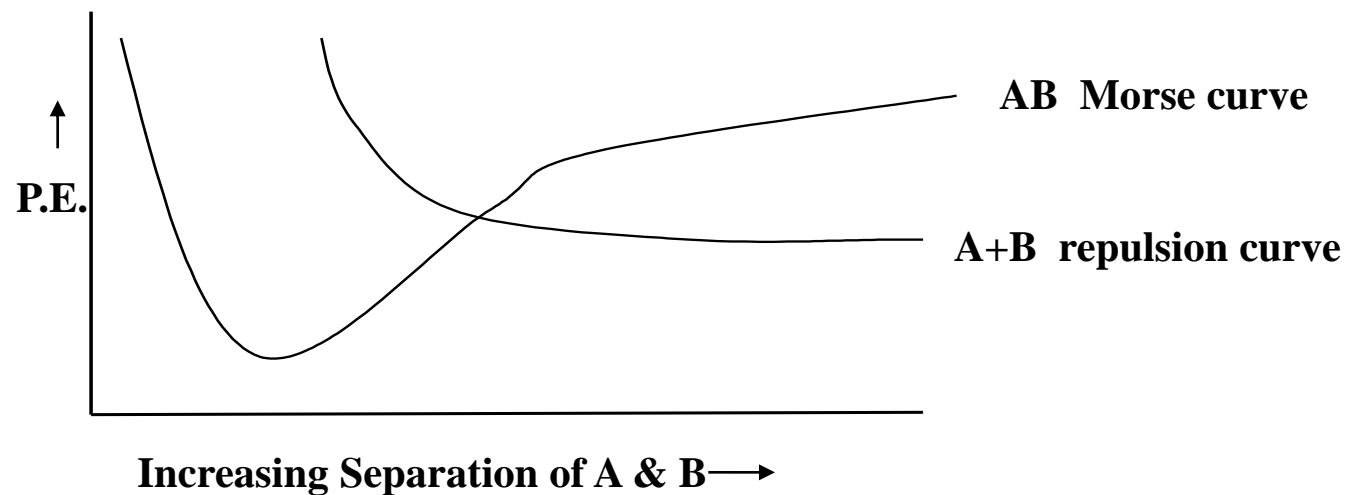
Resonance stabilization of Active Center



Transition State Theory



Structure and Reactivity



$$\Delta E1^\ddagger > \Delta E3^\ddagger$$

then Rxn III is less stable than Rxn I
 $\Delta HR3^\ddagger < \Delta HR1^\ddagger$

Reaction I → $R \cdot$

Reaction III → $R \cdot$



Structure and Reactivity

Resonance stability of Active Center becomes primary
Resonance stability of Monomer becomes secondary

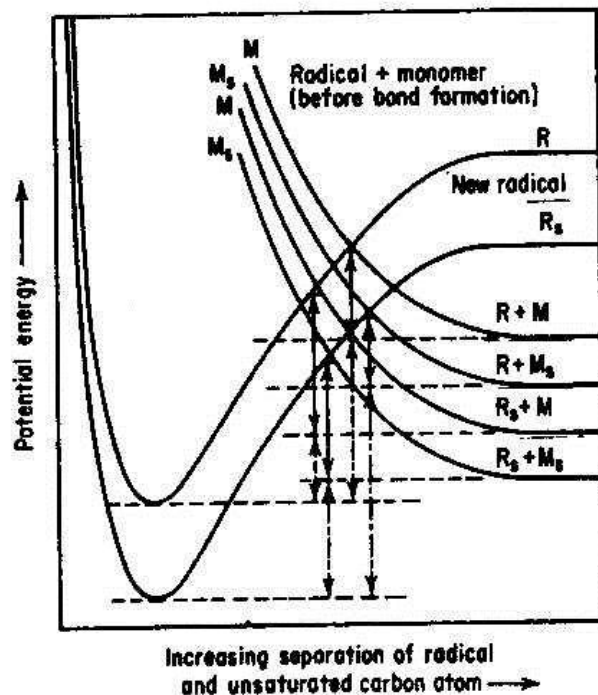


Fig. 6-12 Reaction coordination diagram for the reaction of a polymer radical with a monomer. The dependence of the potential energy of the system (radical + monomer) on the separation between the radical and the unsaturated carbon atom of the monomer is shown. The subscript s indicates the presence 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).

Structure and Reactivity

	$-\Delta H$	ΔE^\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

$$|-\Delta H| \quad ① > ② > ③ > ④$$

$$\Delta E^\ddagger \quad ④ > ③ > ② > ①$$

Structure and Reactivity

II. Polar Effects

TABLE 6-6 Values of r_1, r_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)	Maleic anhydride (3.69)
	0.78		0.55							
		0.31	0.34	0.39	1.0	0.61	0.99	1.1		
		0.19	0.24	0.30	0.96	0.18	0.34			
		<0.1	0.16	0.6	0.83		0.56			
0.0004	0.006	0.016	0.21	0.11	0.18	0.34				
~0		0.021	0.0049	0.056		0.56				
~0.002		0.006	0.00017	0.0024	0.13					

^a r_1, r_2 values are calculated from data in Table 6-2 Greeley [1989a].

^b values are shown in parentheses after each monomer.

Tend to cause alternation in a copolymerization

i.e.

$$r_A \cdot r_B < 1 \quad \text{for polar effects}$$

e : tendency to give monomer a polar effects

Alfrey-Price Q,e scheme (Polarity Values)



Structure and Reactivity

@ Q-e scheme of Alfred Price

r_A , r_B forecast randomness of copolymerization

As know r, prediction is possible to polar, resonance effect

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

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

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



Structure and Reactivity

So that, this equation forecasts r_i

Base materials use styrene : $Q = 1$
(arbitrary)

$$e = -0.8$$

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

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

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

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

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

\therefore alternating tendency is correct



Structure and Reactivity

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

$$R_i = \frac{P_i Q_i \exp(-e_i e_i)}{P_j Q_i \exp(-e_j e_i)} = \frac{k_{ii}}{k_{ji}}$$

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

	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



Structure and Reactivity

The criticism against Q-e scheme

Reference state arbitrarily set.

Alternating effect was observed due to fixed charges not due to the induced dipole

Exercise)

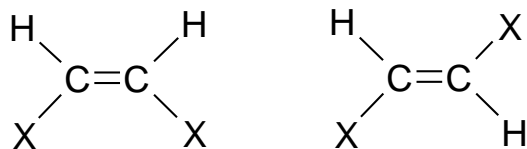
How to indicate Randomness of Copolymer with Q-e scheme ?

We can forecast alternation or randomness through Q-e scheme, however, why can not forecast Blockcopolymerization? (algebraic standpoint)



Structure and Reactivity

3) Cis-trans Effect



The trans is stabilized the cis than thermodynamics(Heat of Hydrogenation)

**Planarity! Easier for trans than cis
Steric Effect!**



Structure and Reactivity

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 were calculated from data in Table 3-11 and 6-2 and [66]

High reactive
 ↑
 1,1-disubs.
 Mono subs.
 Tri subs.
 Trans 1,2
 Cis 1,2

