Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 8 -

Overall and Local Composition
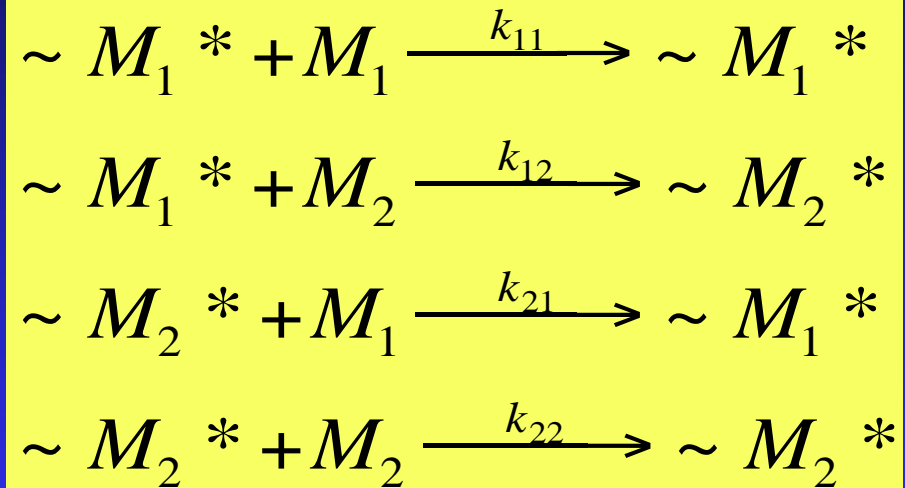
In Copolymers

February 2, 2001

Objectives

■ To determine the **overall composition** of a copolymer at early stages of the reaction based upon the identities of the constituent monomers, their concentrations in the feed, and some measure of the relative reactivities of the active centers.

■ To determine the "**local**" **composition**, as measured by the tendency to form sequences of a particular monomer, to alternate in a regular fashion, or to be statistically random.

Outline

- Instantaneous copolymer composition
  - Propagation equations for terminal control
  - Radical and monomer reactivity
  - Ideal copolymerization
  - Alternating copolymerization
  - Monomer reactivity ratios
  - Q-e scheme of Alfrey and Price
- Relationship between conditional probability and reactivity ratios

Propagation Equations for Terminal Control

Under conditions where only the terminal group is important in determining the rate of addition of a new monomer unit, the **propagation reactions** are:

$$\sim M_1{}^* + M_1 \xrightarrow{\quad k_{11} \quad} \sim M_1{}^*$$

$$\sim M_1{}^* + M_2 \xrightarrow{\quad k_{12} \quad} \sim M_2{}^*$$

$$\sim M_2{}^* + M_1 \xrightarrow{\quad k_{21} \quad} \sim M_1{}^*$$

$$\sim M_2{}^* + M_2 \xrightarrow{\quad k_{22} \quad} \sim M_2{}^*$$

Rates of monomer consumption:

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

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

Order of Radical and Monomer Reactivities

TABLE 6-4 Rate Constants (k_{12}) for Radical–Monomer Reactions[a]

| Monomer (M_2) | Polymer Radical | | | | | | | Q | e |
	Butadiene	Styrene	Methyl Methyacrylate	Acrylonitrile	Methyl Acrylate	Vinyl Acetate	Vinyl Chloride		
Butadiene	100	280	2,060	98,000	41,800		319,000	1.70	−0.50
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	0.78	0.40
Acrylonitrile	330	413	422	1,960	2,510	46,000	225,000	0.48	1.23
Methyl acrylate	130	215	268	1,310	2,090	23,000	187,000	0.45	0.64
Vinyl chloride	11	9.7	52	720	520	10,100	11,000	0.056	0.16
Vinyl acetate		3.4	26	230	230	2,300	6,490	0.026	−0.88

[a]k_{12} values calculated from data in Tables 3-11 and 6-3.

G. Odian, <u>Principles of Polymerization</u>, 3rd. Ed., 1991, p 482.

• The k_{12} values in each vertical column give the reference polymer radical reactivity toward the monomer (M_2). This establishes the **monomer reactivity sequence** (↓ top to bottom).

• The k_{12} values in each horizontal row give the polymer radical reactivity toward a reference monomer. This establishes the **radical reactivity sequence** (↑ left to right).

Instantaneous Copolymer Composition

The **instantaneous composition** of a copolymer formed by reaction of M_1 and M_2 may be given by the ratio of rates of entry of the two monomers into the copolymer:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1*][M_1] + k_{21}[M_2*][M_1]}{k_{12}[M_1*][M_2] + k_{22}[M_2*][M_2]}$$

Assume a **steady-state concentration of reactive centers**. The reactive center concentration will be unchanged when a new monomer is added that is identical to the chain end. The only way that the concentration could change is by **cross-over**, i.e., changing the identity of the terminal group. To eliminate this, make the following requirement:

$$k_{21}[M_2*][M_1] = k_{12}[M_1*][M_2]$$

Instantaneous Copolymer Composition

$$\frac{d[M_1]}{d[M_2]} = \frac{\dfrac{k_{11}k_{21}[M_2*][M_1]^2}{k_{12}[M_2]} + k_{21}[M_2*][M_2]}{k_{22}[M_2*][M_2] + k_{21}[M_2*][M_1]}$$

Define **monomer reactivity ratios.**

$$r_1 \equiv \frac{k_{11}}{k_{12}} \qquad r_2 \equiv \frac{k_{22}}{k_{21}}$$

The **instantaneous copolymer composition equation** is:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\big(r_1[M_1] + [M_2]\big)}{[M_2]\big([M_1] + r_2[M_2]\big)}$$

Molar Composition in Feed and Copolymer

Molar composition in feed:
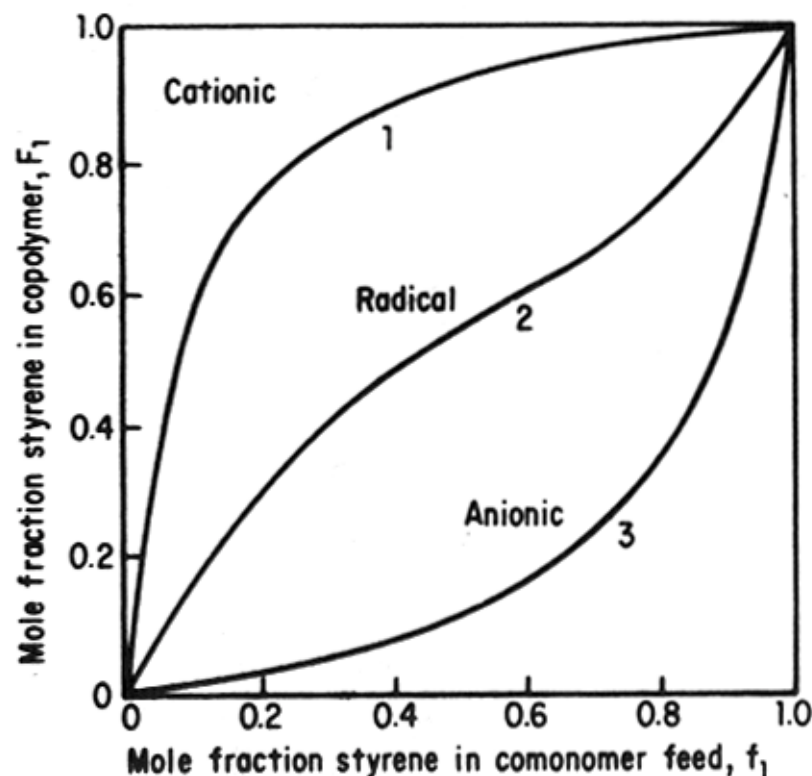
$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]}$$

Molar composition in copolymer:

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

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

Instantaneous Copolymer Composition for Different Modes of Initiation

Fig. 6-1 Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1 for styrene–methyl methacrylate in cationic (plot 1), radical (plot 2), and anionic (plot 3) copolymerizations initiated by $SnCl_4$, benzoyl peroxide, and Na/liquid NH_3, respectively. After Pepper [1954] (by permission of The Chemical Society, Burlington House, London) from data in Landler [1950] (by permission of Gauthier-Villars, Paris).

G. Odian, Principles of Polymerization, 3rd. Ed., 1991, p 459.

Ideal Copolymerization

Reactivity ratios:

$$r_1 r_2 = 1$$

$$\frac{k_{22}}{k_{21}} = \frac{k_{12}}{k_{11}}$$

M_1^* and M_2^* show the same tendency to add M_1 or M_2.

Instantaneous copolymer composition equation:

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

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

Both anionic and cationic copolymerizations exhibit ideal behavior.

# Ideal Copolymerization: Various Combinations of Reactivity Ratios

$r_1 = r_2 = 1$

- M_1 and M_2 show equal reactivities toward M_1^* and M_2^*.

- Copolymer composition is the same as the comonomer feed with random incorporation of M_1 and M_2 along the chain. This is Bernoullian behavior.

- Ex: ethylene (0.79) - vinyl acetate (1.4); $r_1r_2=1.1$

$r_1 > 1, r_2 < 1$

- M_1 is more reactive than M_2 toward both M_1^* and M_2^*.

- It is increasingly more difficult to prepare copolymers having significant amounts of both monomers as the difference in reactivities of the two monomers increases.

- Ex: methacrylic acid (24) - vinyl chloride (0.064); $r_1r_2=1.5$

Instantaneous Copolymer Composition for Ideal Copolymerization
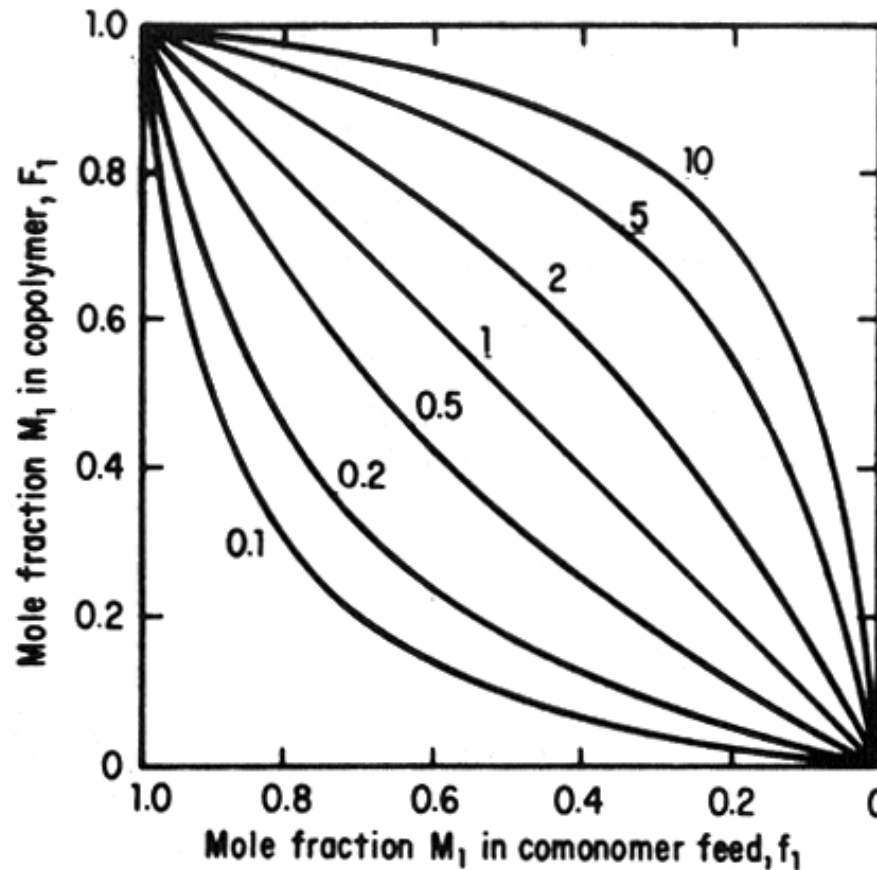
Fig. 6-2 Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1 for the indicated values of r_1 where $r_1 r_2 = 1$. After Walling [1957] (by permission of Wiley, New York) from plot in Mayo and Walling [1950] (by permission of American Chemical Society, Washington, D.C.).

G. Odian, Principles of Polymerization, 3rd. Ed., 1991, p 461.

Alternating Copolymerization

Reactivity ratios:

$$r_1 = r_2 = 0$$

Neither monomer will react with itself but will react with the other monomer.

Instantaneous copolymer composition equation:

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

Polymerization involves incorporation of equal amounts of both monomers.

Dependence of copolymer composition on feed:

$$F_1 = 0.5$$

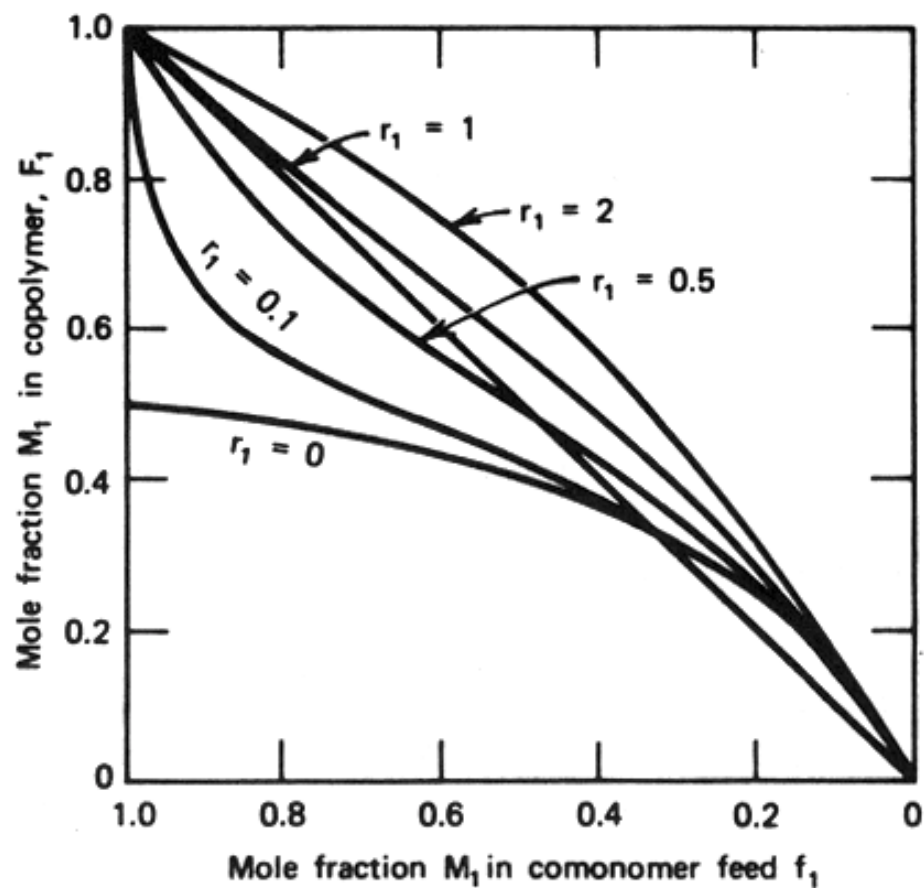The copolymer composition is fixed and independent of the feed.

Examples:

maleic anhydride (0.005) - styrene (0.05); $r_1r_2 = 2.5E\text{-}4$
maleic anhydride (0) - vinyl acetate (0.019); $r_1r_2 = 1.7E\text{-}4$
maleic anhydride (0) - vinyl chloride (0.098); $r_1r_2 = 2.4E\text{-}3$

Instantaneous Copolymer Composition for Systems with a Tendency Toward Alternation

Fig. 6-3 Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1 for the indicated values of r_1 with r_2 being constant at 0.5. After Walling [1957] (by permission of Wiley, New York) from plot in Mayo and Walling [1950] (by permission of American Chemical Society, Washington, D.C.).

G. Odian, <u>Principles of Polymerization</u>, 3rd Ed., 1991, p 462.

Block Copolymerization

Reactivity ratios:

$$r_1 > 1$$

$$r_2 > 1$$

In principle, monomers will tend to react with ones of the same type until a statistical fluctuation occurs and the sequence switches to the other type.

Examples:

This behavior has been observed infrequently and only for copolymerizations initiated by coordination catalysts. The established route for obtaining block copolymers is sequential anionic polymerization.

Monomer Reactivity Ratios

Consider the copolymerization of acrylonitrile (M_1) with each of the following monomers (M_2):

r_1	$1/r_1$	M_2	r_2	$r_1 r_2$	
0.86	1.16	Acrylamide	0.81	0.697	⬅ ~ ideal
0.046	21.7	1,3-Butadiene	0.36	0.0166	⬅ ~ alt.
0.69	1.45	Ethyl vinyl ether	0.060	0.0414	
0.98	1.02	Isobutylene	0.020	0.0196	
1.5	0.667	Methyl acrylate	0.84	1.26	⬅ ~ ideal
0.14	7.14	Methyl methacrylate	1.3	0.182	
0.020	50	Styrene	0.29	0.0058	⬅ ~ alt.
5.5	0.182	Vinyl acetate	0.060	0.33	
3.6	0.278	Vinyl chloride	0.044	0.158	
0.92	1.09	Vinylidene chloride	0.32	0.294	
0.020	50	2-Vinyl pyridine	0.43	0.0086	⬅ ~ alt.
0.11	9.09	4-Vinyl pyridine	0.41	0.0451	

$$\frac{1}{r_1} = \frac{k_{12}}{k_{11}}$$

A large value of $1/r_1$ indicates that M_1 reacts more rapidly with M_2 than with itself.

Q-e Scheme of Alfrey and Price

This empirical scheme allows estimation of reactivity ratios.

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2)$$

P_1 = measure of resonance stabilization of M_1 radical
Q_2 = measure of resonance stabilization of M_2 monomer
e_1 = measure of polar properties of M_1 radical
e_2 = measure of polar properties of M_2 monomer

$$r_1 = \frac{Q_1}{Q_2} \exp\{-e_1(e_1 - e_2)\} \qquad r_2 = \frac{Q_2}{Q_1} \exp\{-e_2(e_2 - e_1)\}$$

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

For large differences in polarity, (e_1-e_2) is large and $r_1 r_2$ is small.

For monomers with identical polarity, $r_1 = \dfrac{Q_1}{Q_2}$ and $r_2 = \dfrac{Q_2}{Q_1}$

Q and e Values for Monomers

monomer	e	Q	monomer	e	Q
t-butylvinylether	-1.58	0.15	vinyl chloride	0.20	0.044
α-methyl styrene	-1.27	0.98	vinylidene chloride	0.36	0.22
isoprene	-1.22	3.33	methyl methacrylate	0.40	0.74
ethylvinylether	-1.17	0.032	methyl acrylate	0.60	0.42
Nvinylpyrrolidone	-1.14	0.14	methacrylic acid	0.65	2.34
allyl acetate	-1.13	0.028	methyl vinyl ketone	0.68	0.69
1,3-butadiene	-1.05	2.39	methacrylonitrile	0.81	1.12
isobutylene	-0.96	0.033	acrylonitrile	1.20	0.60
styrene	-0.80	1.00	diethyl fumarate	1.25	0.61
propylene	-0.78	0.002	vinyl fluoride	1.28	0.012
2-vinyl pyridine	-0.50	1.30	acrylamide	1.30	1.18
4-vinyl pyridine	-0.28	1.00	fumaronitrile	1.96	0.80
vinyl acetate	-0.22	0.026	maleic anhydride	2.25	0.23
ethylene	-0.20	0.015			

Relationship Between Conditional Probability and Reactivity Ratios

$$P\{A/A\} = \frac{\text{Rate of reaction producing AA*}}{\text{Sum of all reactions using A*}}$$

$$P\{A/A\} = \frac{k_{AA}[A^*][A]}{k_{AA}[A^*][A] + k_{AB}[A^*][B]}$$

$$r_A = \frac{k_{AA}}{k_{AB}} \qquad r_B = \frac{k_{BB}}{k_{BA}} \qquad x = \frac{[A]}{[B]} \quad \text{feed ratio}$$

$$P\{A/A\} = \frac{\dfrac{k_{AA}[A]}{k_{AB}[B]}}{\dfrac{k_{AA}[A]}{k_{AB}[B]} + 1} = \frac{r_A x}{1 + r_A x}$$

Relationship Between Conditional Probability and Reactivity Ratios

$$P\{A/A\} = \frac{r_A x}{1 + r_A x}$$

$$P\{B/A\} = 1 - P\{A/A\} = \frac{1}{r_A x + 1}$$

$$P\{B/B\} = \frac{r_B}{r_B + x}$$

$$P\{A/B\} = 1 - P\{B/B\} = \frac{x}{r_B + x}$$

$$P_2\{AB\} = P_2\{BA\}$$

$$P_1\{A\}P\{B/A\} = P_1\{B\}P\{A/B\}$$

$$y = \frac{P_1\{A\}}{P_1\{B\}} = \frac{P\{A/B\}}{P\{B/A\}} = \frac{1 + r_A x}{1 + \dfrac{r_B}{x}}$$

Measure of the Deviation from Random Statistics

$$\chi = P\{A/B\} + P\{B/A\}$$

$$\chi = \frac{r_A x + 2 + \dfrac{r_B}{x}}{r_A x + 1 + r_A r_B + \dfrac{r_B}{x}}$$

Number Fraction of Sequences

$$N_A(n) = \left(\frac{r_A x}{1 + r_A x}\right)^{n-1}\left(1 - \frac{r_A x}{1 + r_A x}\right)$$

$$N_B(n) = \left(\frac{\dfrac{r_B}{x}}{1 + \dfrac{r_B}{x}}\right)^{n-1}\left(1 - \dfrac{\dfrac{r_B}{x}}{1 + \dfrac{r_B}{x}}\right)$$

Number Average Length

$$\overline{l_A} = \frac{1}{P\{B/A\}} = 1 + r_A x$$

$$\overline{l_A} = \frac{1}{P\{A/B\}} = 1 + \frac{r_B}{x}$$