Free-Radical Chain-Growth Polymerization II

16:160:509 – Polymer Chemistry

Lecture 7 to 8

RUTGERS
School of Arts and Sciences
DEPARTMENT OF CHEMISTRY
AND CHEMICAL BIOLOGY

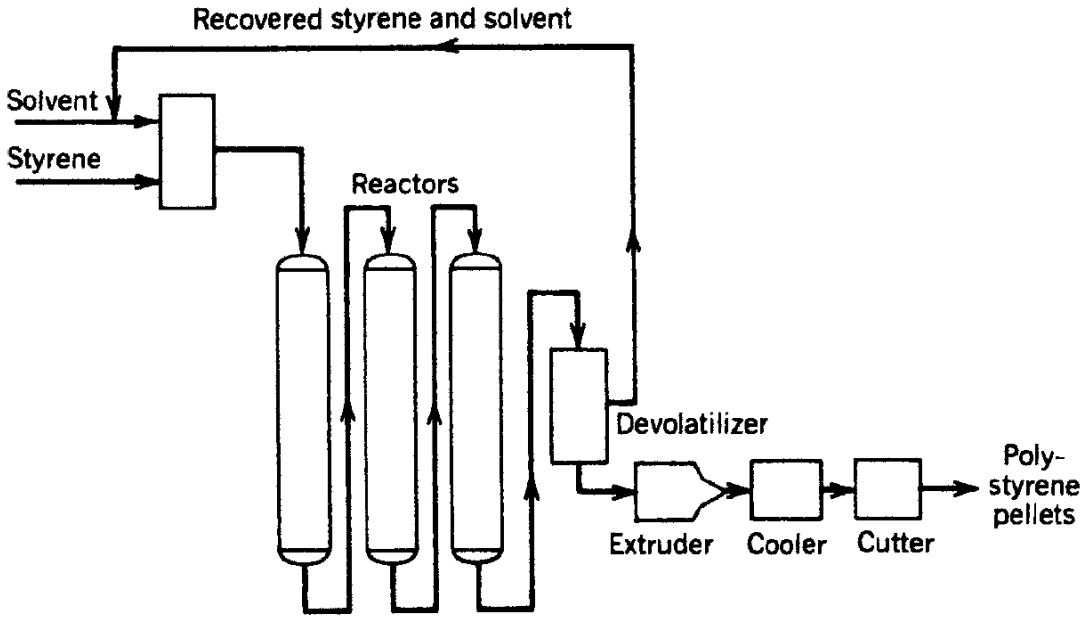
Process Conditions

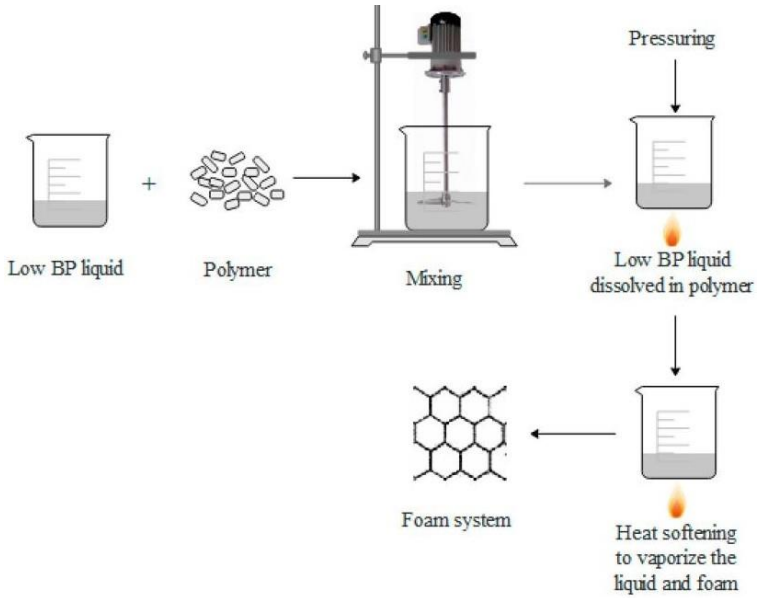
- **Bulk polymerization** is occasionally used in the industrial process of free-radical polymerization. Some potential disadvantages include:
  1. Free-radical polymerization is highly exothermic. Heat transfer is a problem in bulk.
  2. High molecular weight polymers are produced from the beginning, so the viscosity quickly increases from the onset of the reaction. This makes efficient stirring a problem and leads to autoacceleration.

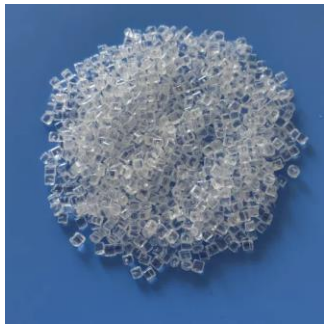
- **Solution polymerization** may also be used for free-radical polymerization. Some potential disadvantages include:
  1. It may be difficult to find a solvent that can dissolve high molecular weight polymers.
  2. Chain transfer to solvents may complicate the reaction.
  3. The reduced [M] in solution polymerization leads to decreases in the rate and degree of polymerization.

$$R_p = k_p[M]\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2} \qquad \overline{v} = \frac{k_p[M]}{2(fk_tk_d[I])^{1/2}}$$

Process of Polystyrene Production





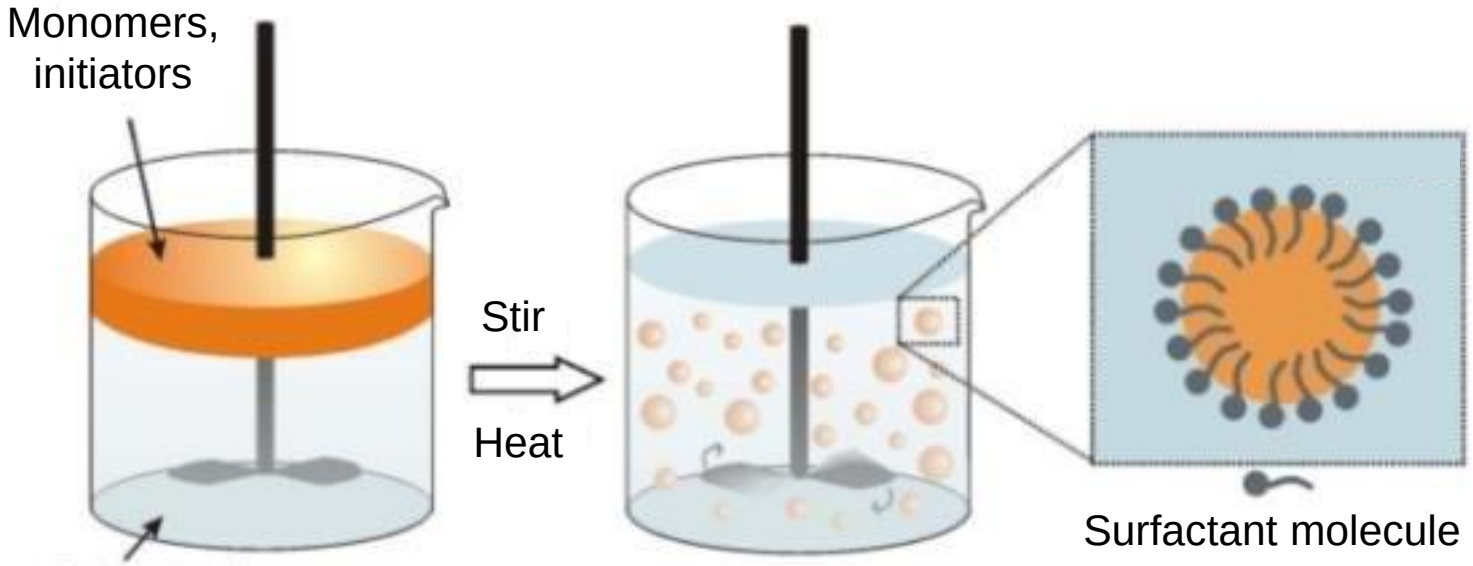


PS pellets

EPS beads

- In industry, the polymerization of styrene is done using solution polymerization, usually with ethylbenzene as the solvent in amounts of 2–30%.
- A secondary function of the solvent is the control of molecular weight by chain transfer, although more effective chain-transfer agents are also used.
- Final conversions of 60–90% are achieved in the last reactor.
- In expanded polystyrene (EPS) foam, pentane is often used as a blowing agent.

Suspension Polymerization



Surfactant-stabilized polymer particles
(50–500 μm in diameter)

Continuous phase with surfactant (< 0.1% wt)

- The continuous phase is often an aqueous phase.
- Initiators used in suspension polymerization have to be oil-soluble, so polymerization is initiated in the discontinuous droplet phase.
- Such process leads to low viscosity system and efficient heat transfer.
- Each monomer droplet in a suspension polymerization is considered to be a miniature bulk polymerization system, so the kinetics follow what we have derived to depict bulk polymerization.

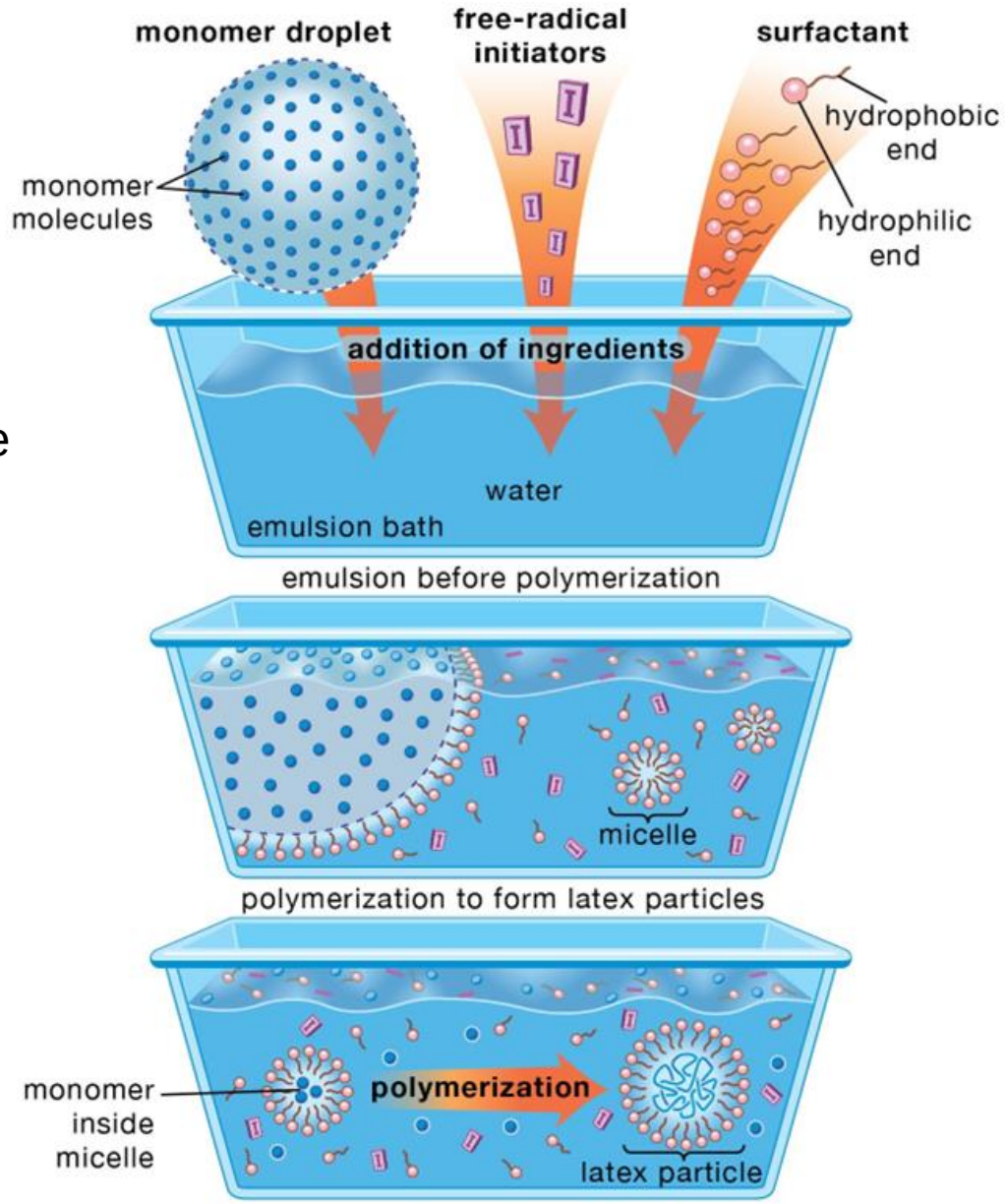
There is still no way to increase R_p and molecular weight at the same time.

$$R_p = k_p[M]\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2} \qquad \overline{\nu} = \frac{k_p[M]}{2(fk_tk_d[I])^{1/2}}$$

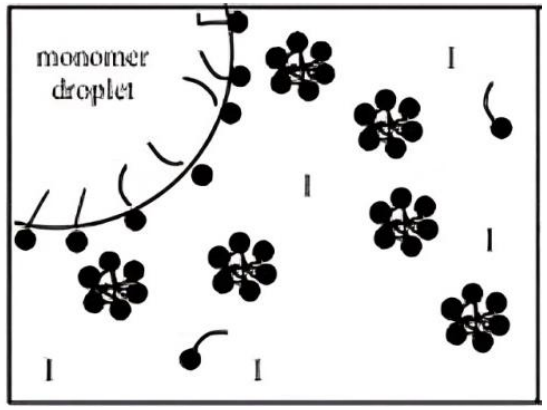
Emulsion Polymerization

- Emulsion polymerization might look similar to suspension polymerization at first glance, but there are a few important differences:
  1. The initiators used are **water-soluble** instead of oil-soluble.
  2. A much higher amount of surfactants is used (1–5% wt).
  3. The formed polymer particles (often referred to as latex) are much smaller (0.1–1 μm).

- The use of water-soluble initiators leads to polymerization initiated in the continuous water phase. This alone makes the kinetics of emulsion polymerization quite different from bulk polymerization.
- Most importantly, with emulsion polymerization, we have a convenient way to increase R_p and molecular weight at the same time.

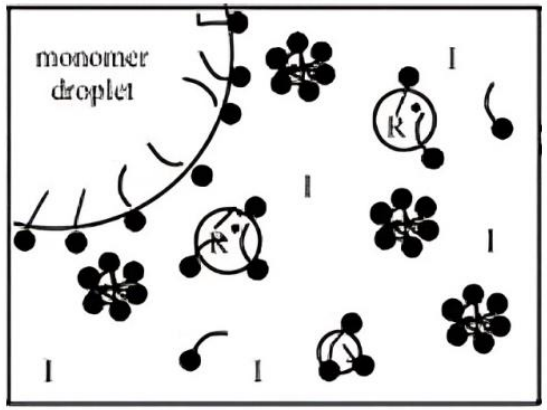


A Close Look at Emulsion Polymerization



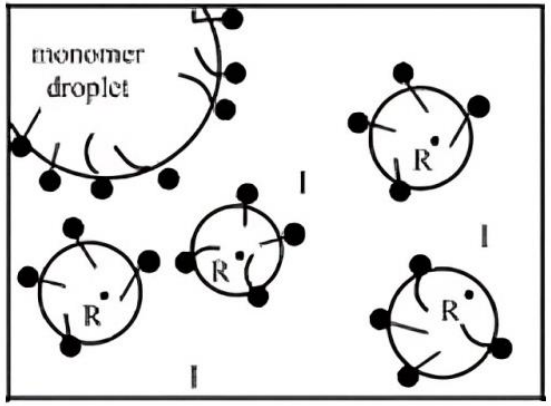
Before polymerization:

- Monomer droplets stabilized by surfactants
- Water-soluble initiators
- Empty micelles formed from surfactants



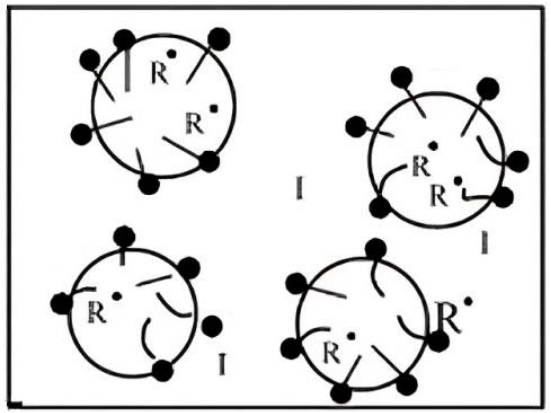
Interval I:

- Monomers diffuse into empty micelles.
- Polymer chains are initiated in the aqueous phase and quickly diffuse into micelles to form polymer particles.
- More polymer particles are generated as micelles are consumed.



Interval II:

- No more surfactant is available to generate new polymer particles.
- Monomers diffuse into the now constant number of polymer particles to maintain [M] within particles.
- Monomer droplets serve as a monomer reservoir and slowly decrease in size.



Interval III:

- All monomers exist in polymer particles (monomer droplets exhausted).
- [M] in particles continually decreases as conversion increases.
- Polymer particle size is approximately constant.

Why do free radicals go to micelles/particles instead of monomer droplets?

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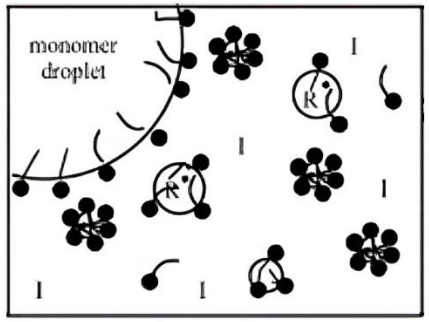
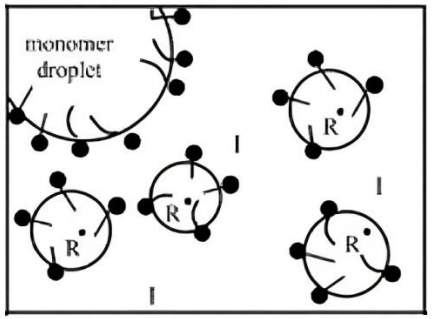
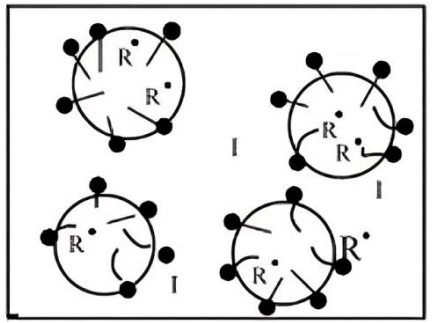
A Close Look at Emulsion Polymerization



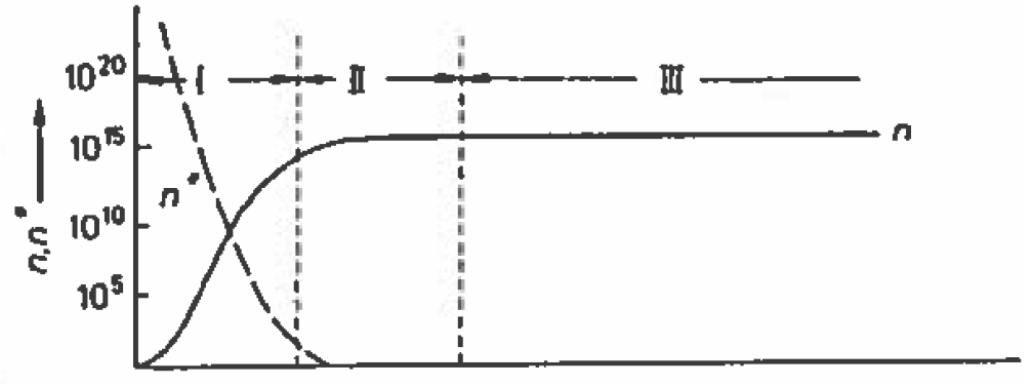
Interval I



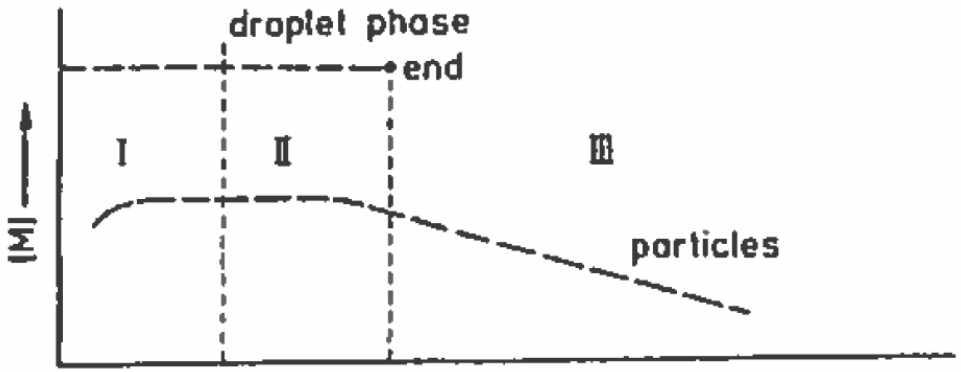
Interval II



Interval III

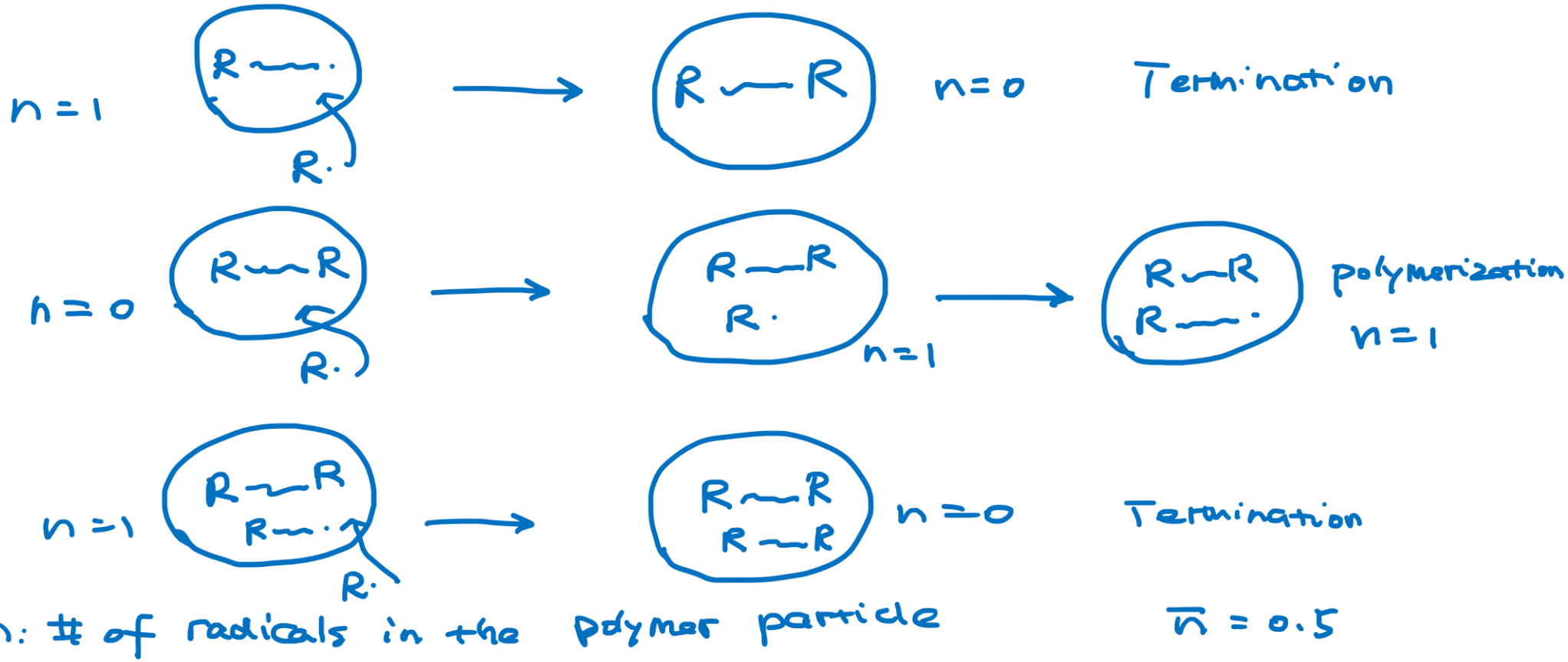


Number of empty micelles (*n**)
and polymer particles (*n*)



Monomer concentration within polymer
particles and monomer droplets

Smith–Ewart Case 2 Conditions



- No more than one radical may exist in one polymer particle; the entry of a second radical leads to immediate chain termination.
- Radicals can diffuse into the polymer particles but cannot diffuse out.
- On average, each particle contains one propagating chain radical for half the time of its existence and none for the remaining half (Smith–Ewart Case 2 conditions).

Simple Kinetics of Emulsion Polymerization

Based on this simplified picture, we can derive the simple kinetics of emulsion polymerization, assuming at a given moment that the monomer concentration within polymer particles is [M], and the total number of polymer particles in the system is N_p.

Each propagating chain adds monomers at a rate $r_p = k_p[M]$

Total # of radicals in the system $N_p \times \bar{n} = \frac{1}{2} N_p$

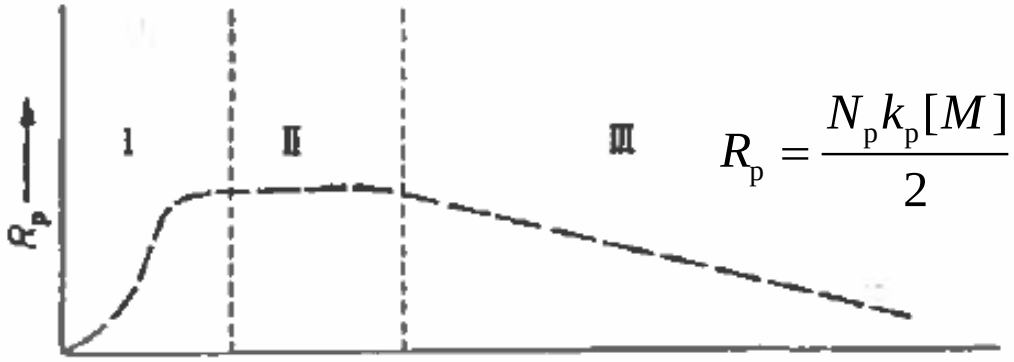
$$R_p = \frac{N_p k_p [M]}{2}$$

The rate at which radicals enter each polymer particle is $r_i = \frac{R_i}{N_p}$

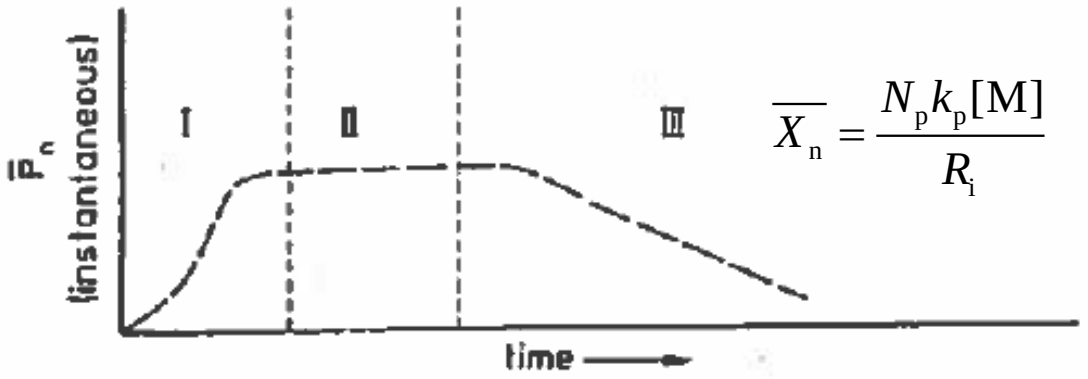
Consider each chain:

$$\overline{X_n} \approx \bar{\nu} = \frac{r_p}{r_i} = \frac{k_p[M]}{\frac{R_i}{N_p}} = \frac{N_p k_p [M]}{R_i}$$

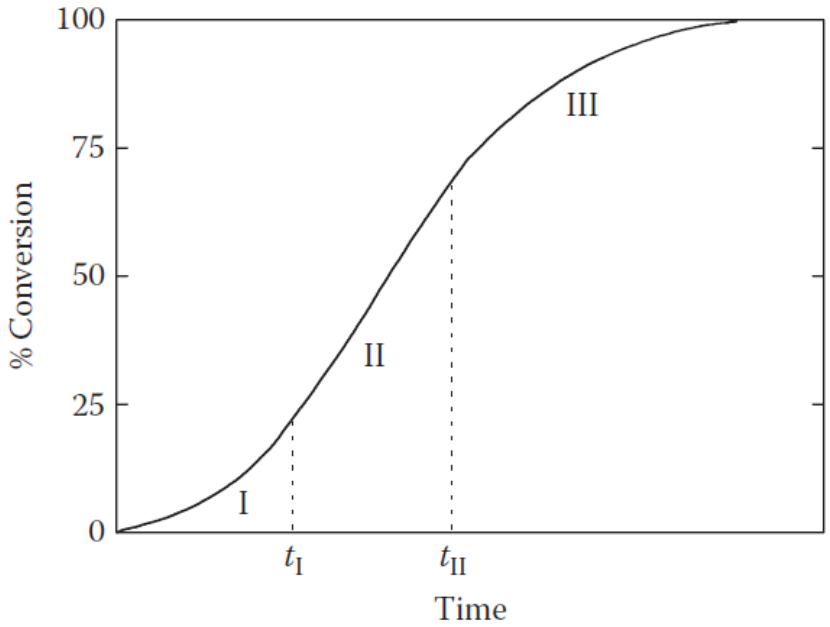
Simple Kinetics of Emulsion Polymerization



$$R_p = \frac{N_p k_p [M]}{2}$$



$$\overline{X_n} = \frac{N_p k_p [M]}{R_i}$$



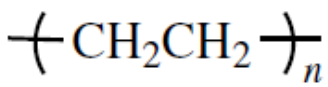
- In emulsion polymerization, there is a simple way to increase R_p and molecular weight simultaneously: by increasing N_p.

$$N_p \propto S^{3/5}$$

- S is the total concentration of surfactant in the system (micelles, solution, monomer droplets). Hence, by simply increasing the concentration of surfactant, we can increase R_p and molecular weight simultaneously in emulsion polymerization. Refer to Page 362 in Odian for details of the above expression.

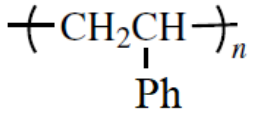
Common Commodity Polymers Made from Free-Radical Polymerization

Polyethylene (LDPE)



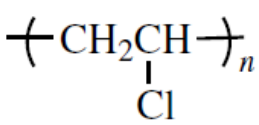
Bulk polymerization

Polystyrene (PS)



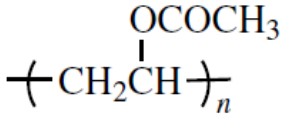
Solution polymerization

Poly(vinyl chloride) (PVC)



Suspension polymerization

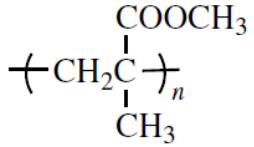
Poly(vinyl acetate) (PVAc)



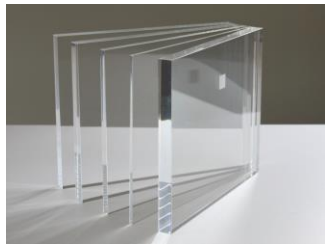
Emulsion polymerization

Common Commodity Polymers Made from Free-Radical Polymerization

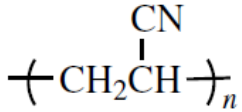
Poly(methyl methacrylate) (PMMA)



Solution/suspension/emulsion polymerization

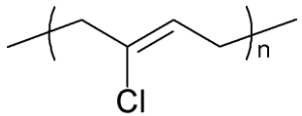


Polyacrylonitrile



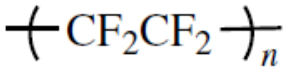
Solution/suspension polymerization

Polychloroprene (Neoprene)



Emulsion polymerization

Polytetrafluoroethylene (PTFE)



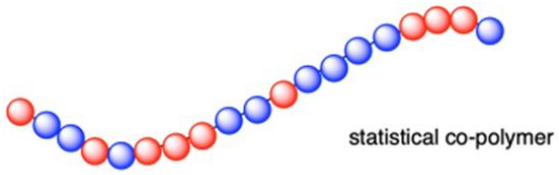
Suspension/emulsion polymerization

An Introduction to Copolymers

- Copolymerization of at least two kinds of monomers offers a facile means to tune material properties.
- As the properties of copolymers are controlled by the nature and proportions of the repeat units, along with their sequence distribution along the chain, it is important to understand the composition and repeat unit sequence distribution for polymers resulting from a copolymerization process.

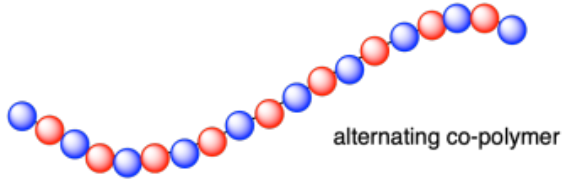
Statistical Copolymers

–AAABABAABBABBB–



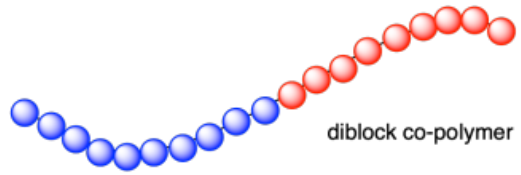
Alternating Copolymers

–ABABABABABAB–



Block Copolymers

–AAAAAAAAAAAABBBBBBBBBBBB–



- **Statistical copolymer**: The probability of finding a monomer at any point in the chain is equal to the mole fraction of that monomer.
- **Alternating copolymer**: Two kinds of monomers add consecutively to create a polymer chain with a strict -ABABAB- sequence.
- **Block copolymer**: A polymer with a linear arrangement of blocks.

It should be noted that these three categories are not exclusive—as we will see soon: 1) the formation of block copolymers is extremely rare in free-radical copolymerization; 2) free-radical copolymerization often leads to copolymers that are *neither perfectly statistical nor perfectly alternating*.

Kinetics of Copolymerization

Terminal control mechanism: only the nature of the radical chain end influences the rate constant for propagation.

$$-\mathrm{M_1}\bullet + \mathrm{M_1} \xrightarrow{k_{11}} -\mathrm{M_1M_1}\bullet \qquad R_{\mathrm{p},11} = k_{11}[\mathrm{M_1}\bullet][\mathrm{M_1}]$$

$$-\mathrm{M_1}\bullet + \mathrm{M_2} \xrightarrow{k_{12}} -\mathrm{M_1M_2}\bullet \qquad R_{\mathrm{p},12} = k_{12}[\mathrm{M_1}\bullet][\mathrm{M_2}]$$

$$-\mathrm{M_2}\bullet + \mathrm{M_1} \xrightarrow{k_{21}} -\mathrm{M_2M_1}\bullet \qquad R_{\mathrm{p},21} = k_{21}[\mathrm{M_2}\bullet][\mathrm{M_1}]$$

$$-\mathrm{M_2}\bullet + \mathrm{M_2} \xrightarrow{k_{22}} -\mathrm{M_2M_2}\bullet \qquad R_{\mathrm{p},22} = k_{22}[\mathrm{M_2}\bullet][\mathrm{M_2}]$$

Penultimate control mechanism: the effect of the next-to-last (i.e., penultimate) unit is considered.

$$-\mathrm{M_1M_1}\bullet + \mathrm{M_1} \xrightarrow{k_{111}} -\mathrm{M_1M_1M_1}\bullet$$

$$-\mathrm{M_2M_1}\bullet + \mathrm{M_1} \xrightarrow{k_{211}} -\mathrm{M_2M_1M_1}\bullet$$

$$R_{\mathrm{p},111} = k_{111}[\mathrm{M_1M_1}\bullet][\mathrm{M_1}]$$

$$R_{\mathrm{p},211} = k_{211}[\mathrm{M_2M_1}\bullet][\mathrm{M_1}]$$

Terminal Model and Monomer Reactivity Ratios

Let's restrict ourselves to the simpler case and derive kinetic equations for the *terminal control mechanism.*

$$-\mathrm{M_1}\bullet + \mathrm{M_1} \xrightarrow{k_{11}} -\mathrm{M_1M_1}\bullet \qquad R_{\mathrm{p},11} = k_{11}[\mathrm{M_1}\bullet][\mathrm{M_1}]$$

$$-\mathrm{M_1}\bullet + \mathrm{M_2} \xrightarrow{k_{12}} -\mathrm{M_1M_2}\bullet \qquad R_{\mathrm{p},12} = k_{12}[\mathrm{M_1}\bullet][\mathrm{M_2}]$$

$$-\mathrm{M_2}\bullet + \mathrm{M_1} \xrightarrow{k_{21}} -\mathrm{M_2M_1}\bullet \qquad R_{\mathrm{p},21} = k_{21}[\mathrm{M_2}\bullet][\mathrm{M_1}]$$

$$-\mathrm{M_2}\bullet + \mathrm{M_2} \xrightarrow{k_{22}} -\mathrm{M_2M_2}\bullet \qquad R_{\mathrm{p},22} = k_{22}[\mathrm{M_2}\bullet][\mathrm{M_2}]$$

$$-\frac{\mathrm{d}[\mathrm{M_1}]}{\mathrm{d}t} = k_{11}[\mathrm{M_1}\bullet][\mathrm{M_1}] + k_{21}[\mathrm{M_2}\bullet][\mathrm{M_1}]$$

$$-\frac{\mathrm{d}[\mathrm{M_2}]}{\mathrm{d}t} = k_{12}[\mathrm{M_1}\bullet][\mathrm{M_2}] + k_{22}[\mathrm{M_2}\bullet][\mathrm{M_2}]$$

The ratio of the two kinds of repeat units incorporated in the copolymer:

$$\frac{\mathrm{d}[\mathrm{M_1}]/\mathrm{d}t}{\mathrm{d}[\mathrm{M_2}]/\mathrm{d}t} = \frac{k_{11}[\mathrm{M_1}\bullet][\mathrm{M_1}] + k_{21}[\mathrm{M_2}\bullet][\mathrm{M_1}]}{k_{12}[\mathrm{M_1}\bullet][\mathrm{M_2}] + k_{22}[\mathrm{M_2}\bullet][\mathrm{M_2}]}$$

Steady-state assumption applies to $\mathrm{M_1}\bullet$ (you will reach the same result if you choose to work with $\mathrm{M_2}\bullet$):

$$R_{\mathrm{p},12} = R_{\mathrm{p},21} \qquad k_{12}[\mathrm{M_1}\bullet][\mathrm{M_2}] = k_{21}[\mathrm{M_2}\bullet][\mathrm{M_1}] \qquad \frac{[\mathrm{M_1}\bullet]}{[\mathrm{M_2}\bullet]} = \frac{k_{21}[\mathrm{M_1}]}{k_{12}[\mathrm{M_2}]}$$

Terminal Model and Monomer Reactivity Ratios

$$\frac{d[M_1]/dt}{d[M_2]/dt} = \frac{[M_1]}{[M_2]} \frac{(k_{11}/k_{12})[M_1]+[M_2]}{(k_{22}/k_{21})[M_2]+[M_1]}$$

Define monomer reactivity ratios: $r_1 = \frac{k_{11}}{k_{12}}$ $r_2 = \frac{k_{22}}{k_{21}}$

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

Define F_1/F_2 and f_1/f_2: $F_1 = 1 - F_2 = \frac{d[M_1]/dt}{d[M_1]/dt + d[M_2]/dt}$ $f_1 = 1 - f_2 = \frac{[M_1]}{[M_1]+[M_2]}$

$$\frac{F_1}{1-F_1} = \frac{1 + r_1 \cdot \frac{f_1}{f_2}}{1 + r_2 \cdot \frac{f_2}{f_1}} \Rightarrow \frac{F_1}{1-F_1} = \frac{f_1 f_2 + r_1 f_1^2}{f_1 f_2 + r_2 f_2^2} \Rightarrow$$

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

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

Some Extreme Cases of Copolymerization Behavior

Mayo–Lewis equation: $$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad r_1 = \frac{k_{11}}{k_{12}} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

This equation relates the composition of the copolymer formed to the instantaneous composition of the feedstock and to the reactivity ratios r_1 and r_2 that characterize the specific system.

Let's first consider three extreme cases:

- $r_1 = r_2 = 1$ (**random copolymerization**)

The two monomers show equal reactivities toward both propagating species. The copolymer composition is the same as the comonomer feed with a random placement of the two monomers along the copolymer chain.

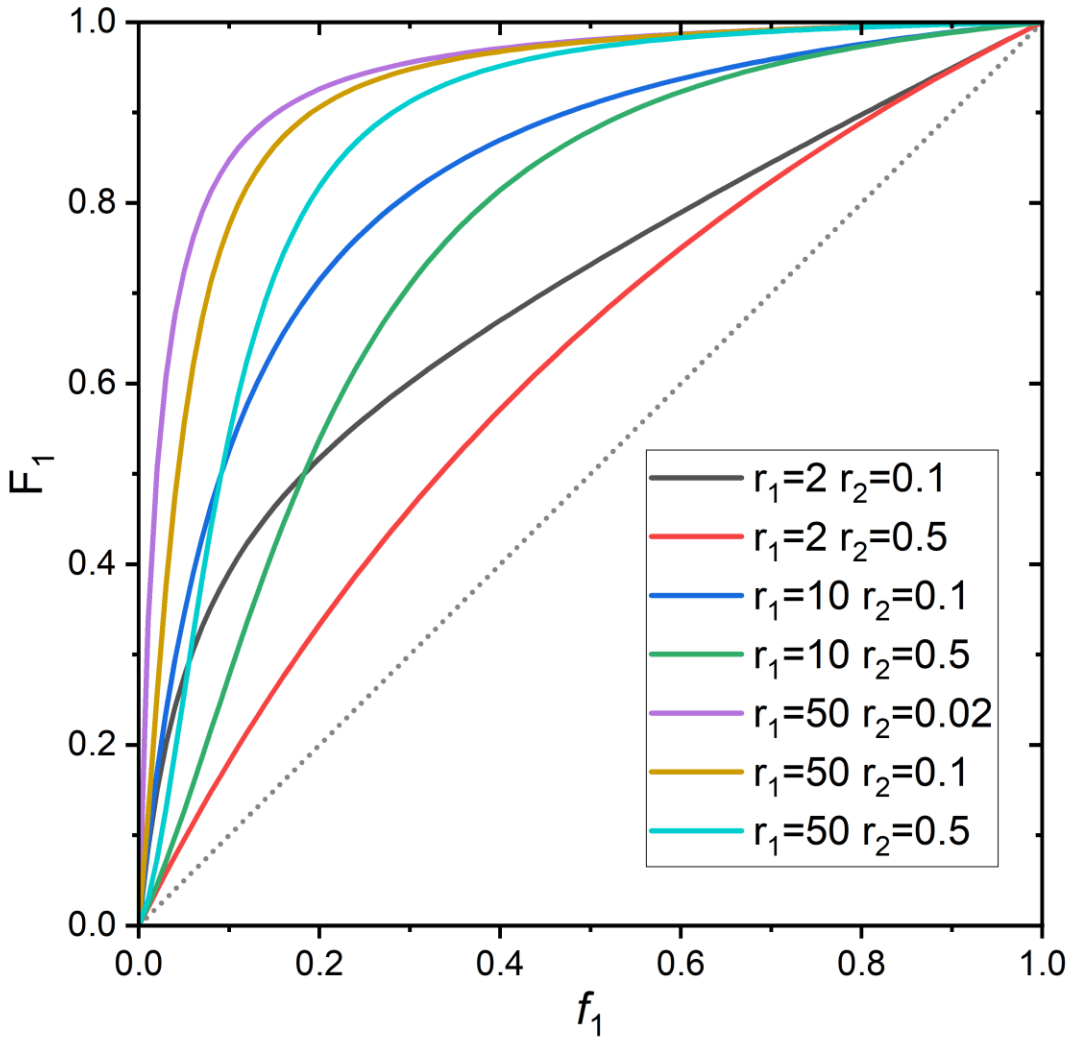
- $r_1 = r_2 = 0$ (**alternating copolymerization**)

The two monomers enter into the copolymer in equimolar amounts in a nonrandom, alternating arrangement along the copolymer chain, regardless of the feed ratio.

- $r_1 >> 1$ and $r_2 >> 1$ (**block copolymerization**)

There is a tendency to form a block copolymer in which there are blocks of both monomers in the chain. This type of behavior is rarely encountered in free-radical copolymerization.

Types of Copolymerization Behavior



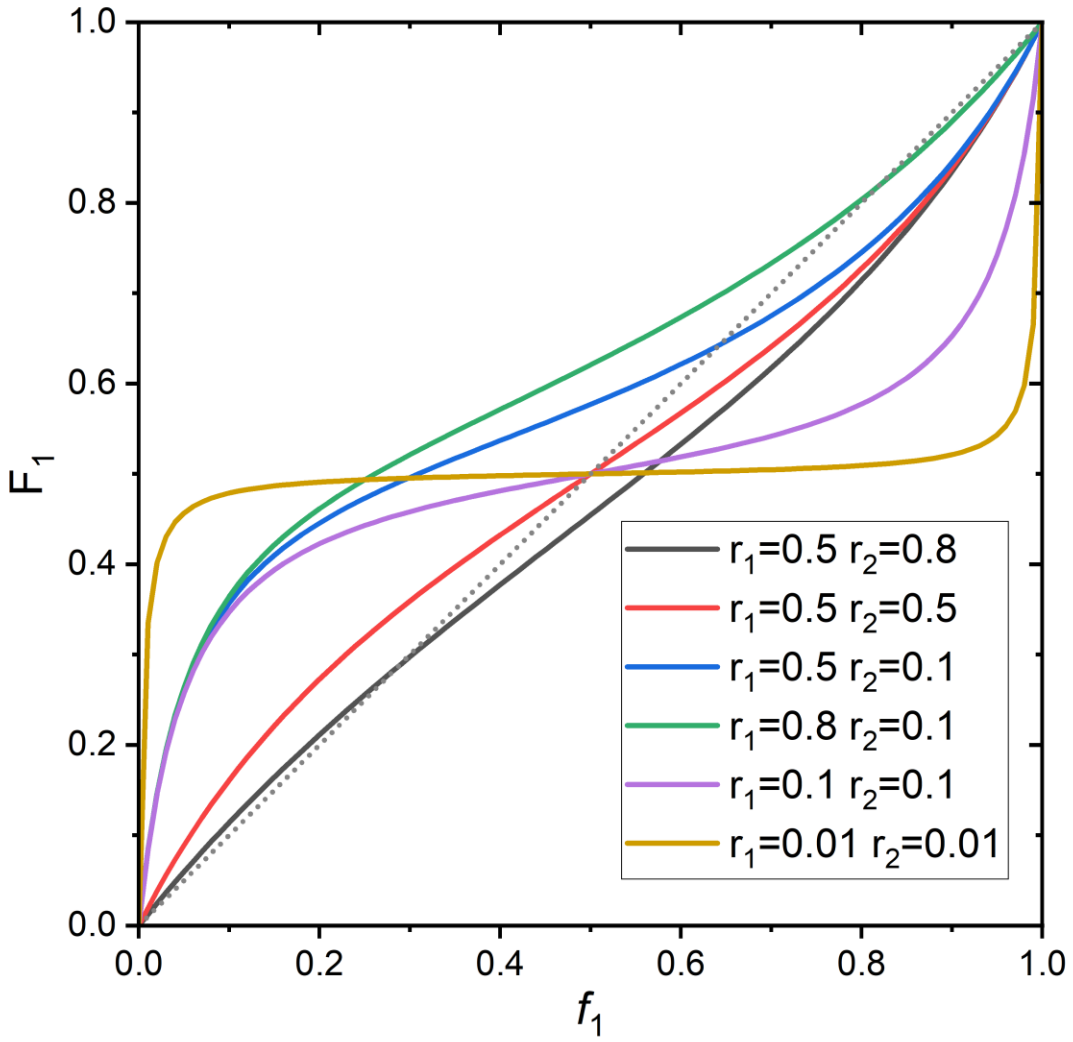
Type 1: $r_1 > 1$, $r_2 < 1$

- Both types of propagating radicals prefer to add M_1 over M_2, so the copolymer will contain a larger proportion of the more reactive monomer M_1.
- It becomes progressively more difficult to produce copolymers containing appreciable amounts of both monomers as the difference in r_1 and r_2 increases. When $r_1 \gg 1$ with $r_2 \ll 1$, there is a tendency towards consecutive homopolymerization of the two monomers.
- When $r_1 r_2 = 1$, we call such copolymerization ideal. In *ideal copolymerization*, the relative rates at which the two monomers are incorporated into the copolymer chains are the same for both types of radical species. Hence, the monomers add at random in the proportion governed by the specific values of the *r*'s.

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

- Random structures are promoted by $r_1 r_2 \rightarrow 1$.

Types of Copolymerization Behavior



Type 2: $r_1 < 1$, $r_2 < 1$

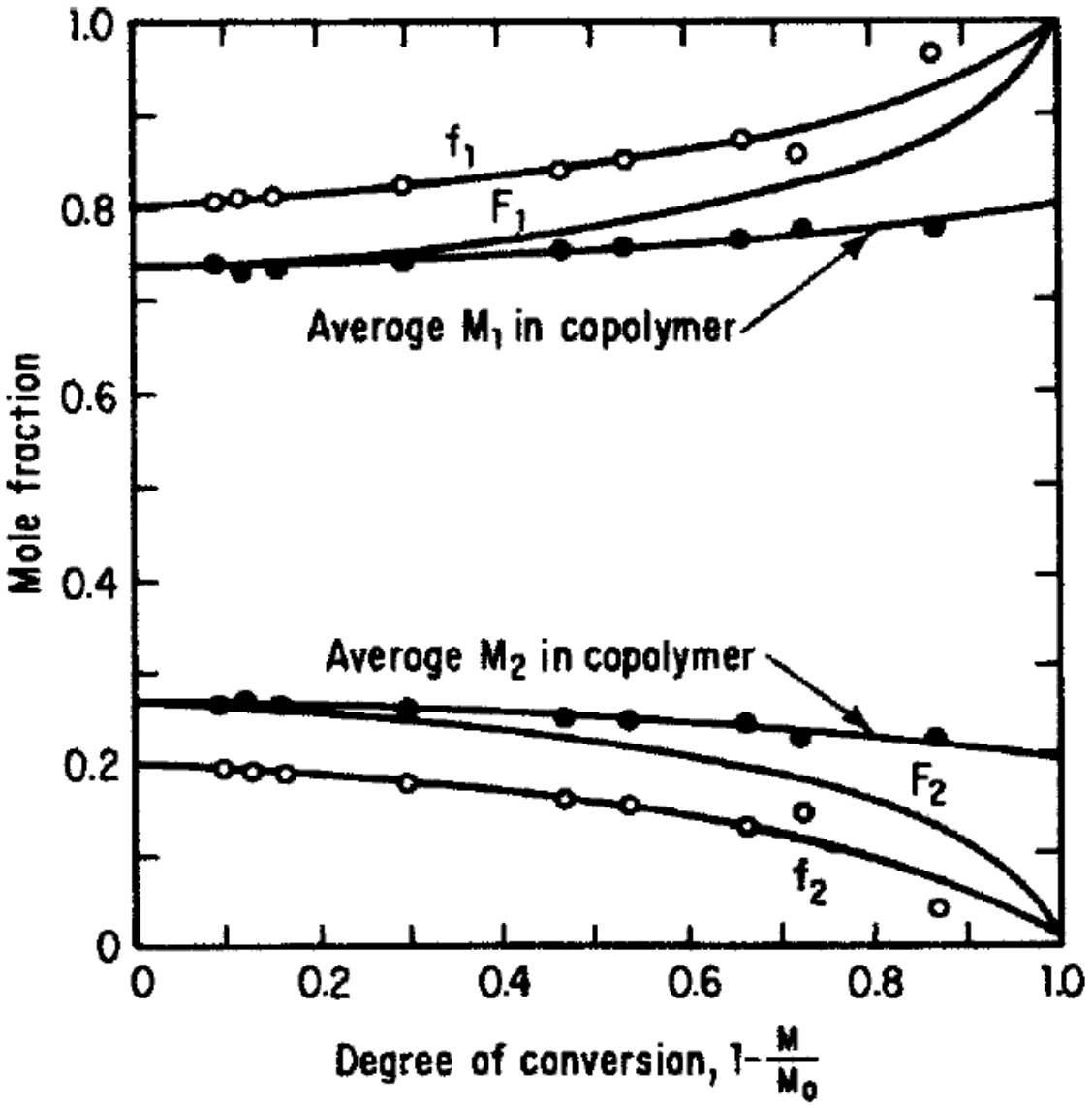
- The copolymer starts out richer in M_1 than the feed mixture and then crosses the 45° line, and it is richer in M_2 beyond this crossover point. The value of f_1 at this crossover point can be calculated as

$$f_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)}$$

- At the crossover point the copolymer and feed compositions are the same and copolymerization occurs without a change in the feed composition. Such copolymerizations are termed *azeotropic copolymerizations*.
- As $r_1 r_2 \rightarrow 0$, there is an increasing tendency towards alternation in the additions of monomer molecules to the propagating chains.

***Note*: It is rare (if not impossible) to encounter a free-radical copolymerization with $r_1 > 1$ and $r_2 > 1$**

Variation of Copolymer Composition with Conversion



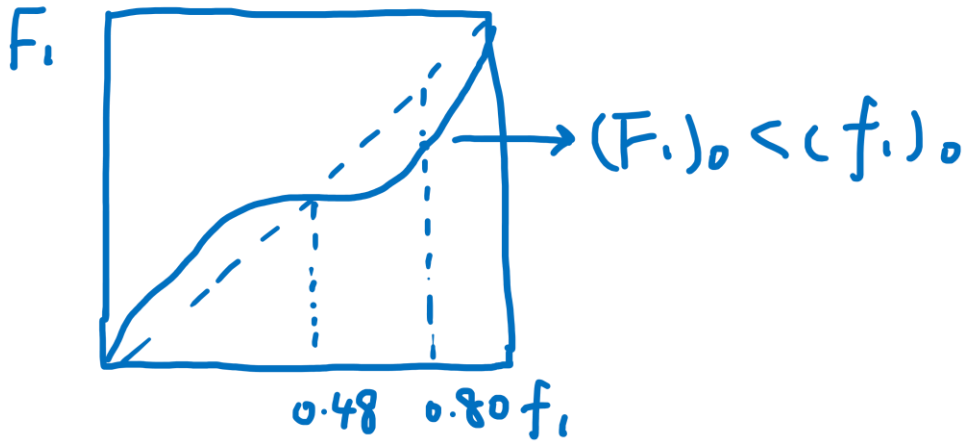
$r_1 = 0.53$, $r_2 = 0.56$

$(f_1)_0 = 0.80$, $(f_2)_0 = 0.20$

This fits the Type 2 scenario. To determine the initial feedstock location, we can calculate the crossover point as

$$f_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)}$$

$$(f_1)_c = \frac{1 - 0.56}{2 - 0.53 - 0.56} = 0.48 < 0.80$$



Microstructure of Copolymers

Random structure $M_1M_2M_2M_2M_1M_1M_2M_1M_1M_2M_1M_2M_1M_2M_1M_2M_2M_1M_1M_2$

An r_1 value of 2 does not imply that 100% of all M_1 units will be found as part of $M_1M_1M_1M_2$ sequences. A very large fraction of, but not all, M_1 units will be found in such a sequence; a small fraction of M_1 units will be randomly distributed.

Let's first consider the following question: What is the probability (p_{11}) that an M_1 unit is followed by an M_1 unit in the polymer?

$$p_{11} = \frac{k_{11}[M_1\bullet][M_1]}{k_{11}[M_1\bullet][M_1]+k_{12}[M_1\bullet][M_2]} = \frac{r_1[M_1]}{r_1[M_1]+[M_2]}$$

Similarly, we have

$$p_{12} = \frac{[M_2]}{r_1[M_1]+[M_2]}$$

Consider what is followed by an M_2 unit, we will similarly have

$$p_{22} = \frac{k_{22}[M_2\bullet][M_2]}{k_{22}[M_2\bullet][M_2]+k_{21}[M_2\bullet][M_1]} = \frac{r_2[M_2]}{r_2[M_2]+[M_1]}$$

$$p_{21} = \frac{[M_1]}{r_2[M_2]+[M_1]}$$

Sequence Length Distributions

For a copolymer of M_1 and M_2, let us consider the probability of finding a sequence of repeat units in the copolymer, which is exactly v units of M_1 in length (represented as $M_2(M_1)_vM_2$). Note that as the sample size becomes large (there are enormous amount of polymer chains in a polymerization), the various lengths of the M_1 sequences will follow a statistical distribution (sequence length distributions).

Let's define ϕ_v as the fraction of sequences of length v. We have

$$\phi_v = p_{11}^{v-1} p_{12} = \left(\frac{r_1 [M_1]}{r_1 [M_1] + [M_2]} \right)^{v-1} \left(\frac{[M_2]}{r_1 [M_1] + [M_2]} \right)$$

For a M_1-M_2 copolymer with sufficient length N

$$\sum_{v=1}^{N} \phi_v = \sum_{v=1}^{N} p_{11}^{v-1} p_{12} = p_{12} \sum_{v=1}^{N} p_{11}^{v-1} = p_{12} \cdot \frac{1}{1-p_{11}} \quad (N \to \infty)$$

Since $p_{12} + p_{11} = 1$, $\sum_{v=1}^{N} \phi_v = 1$. So this is indeed a normalized distribution

We focus our discussion on M_1, but the same analysis equally applies to M_2.

Sequence Length Distributions

Let's consider the average value of a sequence length of M_1

$$\bar{\nu} = \frac{\sum_{\nu=1}^{\infty} \nu \phi_\nu}{\sum_{\nu=1}^{\infty} \phi_\nu} = \frac{\sum_{\nu=1}^{\infty} \nu p_{11}^{\nu-1} p_{12}}{\sum_{\nu=1}^{\infty} p_{11}^{\nu-1} p_{12}}$$

This is the exact same math we calculated in step-growth polymerization, so we have

$$\bar{\nu} = \frac{1}{1 - p_{11}} = \frac{1}{p_{12}}$$

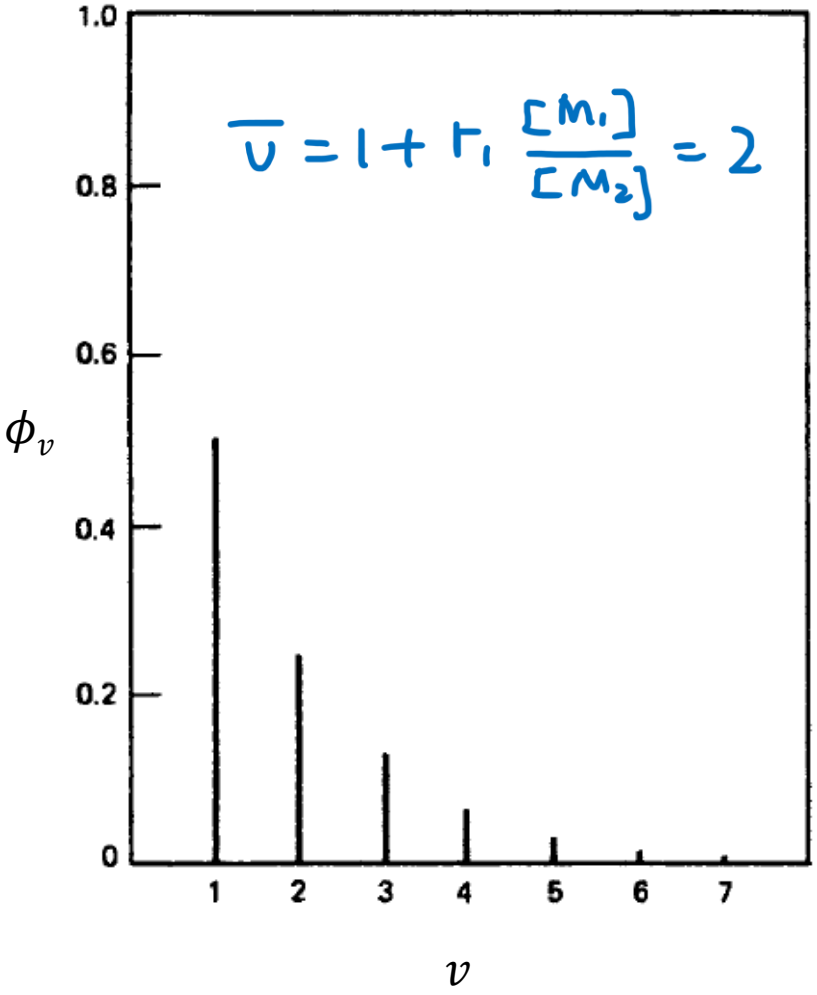
Since $p_{12} = \frac{[M_2]}{r_1[M_1] + [M_2]}$ we have $\bar{\nu} = 1 + r_1 \frac{[M_1]}{[M_2]}$

We can similarly derive the average value of a sequence length of M_2

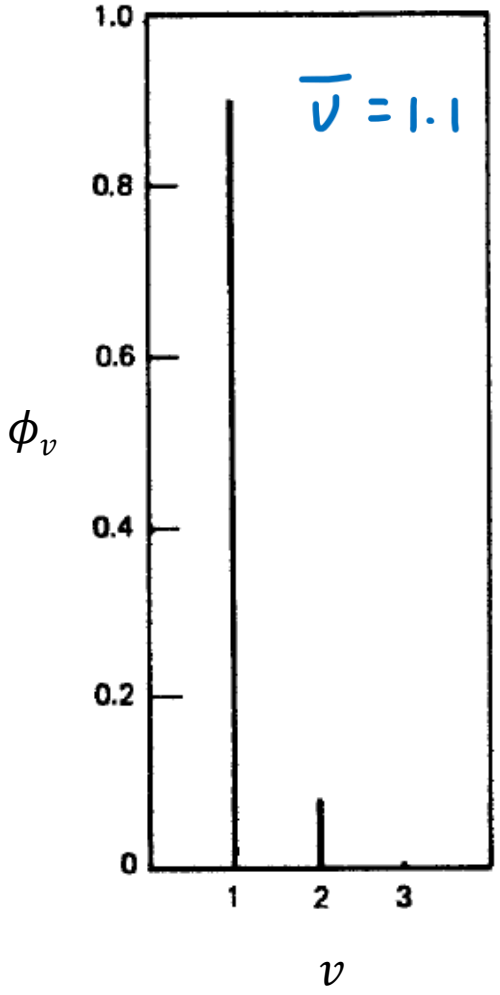
$$\bar{\mu} = 1 + r_2 \frac{[M_2]}{[M_1]}$$

Sequence Length Distributions

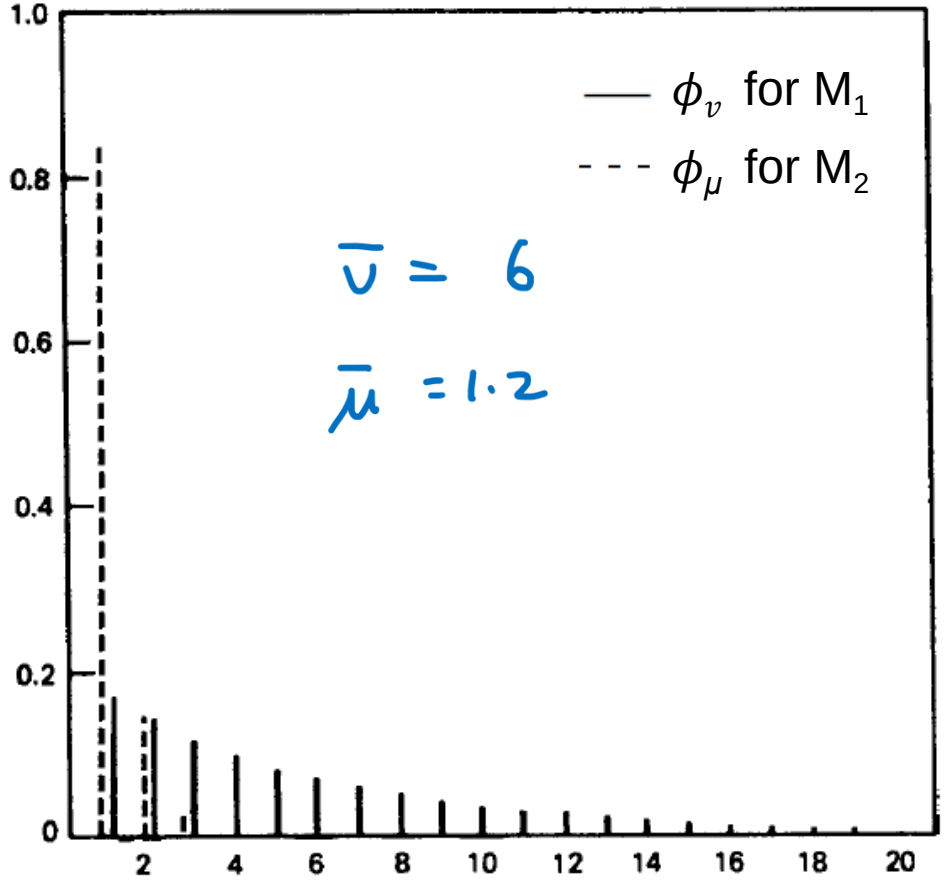
$r_1 = r_2 = 1$ and $f_1 = f_2 = 0.5$



$r_1 = r_2 = 0.1$ and $f_1 = f_2 = 0.5$

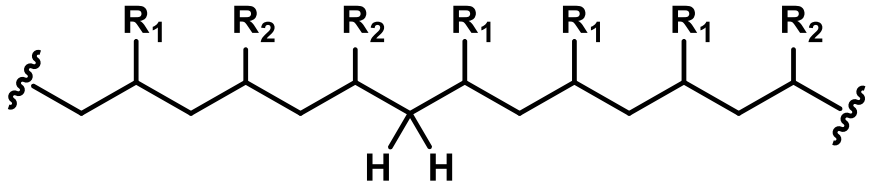


$r_1 = 5$, $r_2 = 0.2$ and $f_1 = f_2 = 0.5$



Experimental Determination of Sequence Distribution

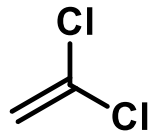
…$M_1M_2M_2M_1M_1M_1M_2$…

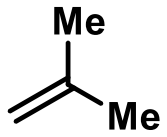


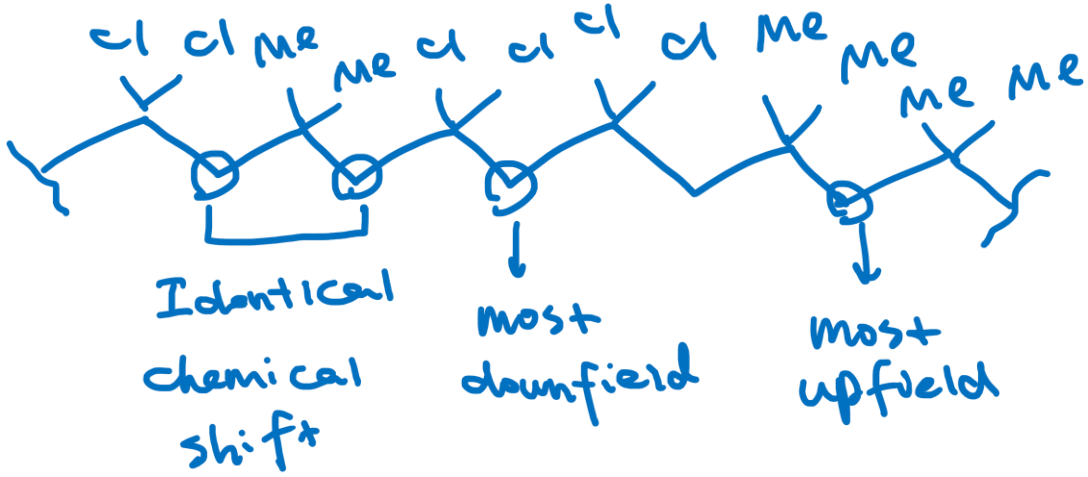
Dyads: sequences of two units (of any definite composition). M_1M_1, M_2M_2, M_1M_2 (or M_2M_1)

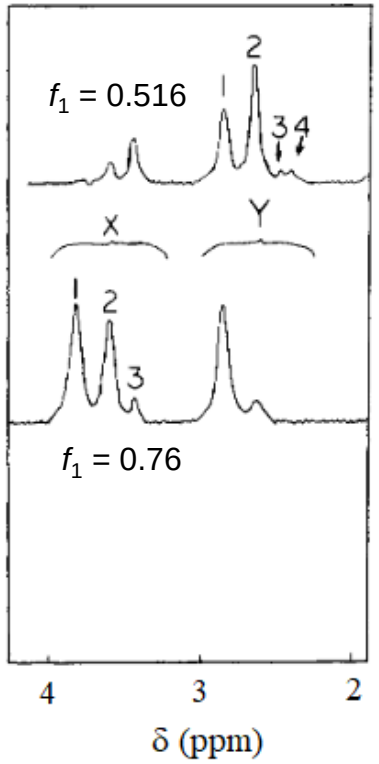
The chemical shift of methylene protons might potentially be used to distinguish different dyads, or even tetrads.

Vinylidene chloride-isobutylene copolymers

(A) 

(B) 





Diad	Region	Tetrad structure
AA	X_1	AAAA
	X_2	AAAB (and BAAA)
	X_3	BAAB

Diad	Region	Tetrad structure
AB (or BA)	Y_1	AABA (and ABAA)
	Y_2	BABA (and ABAB)
	Y_3	AABB (and BBAA)
	Y_4	BABB (and BBAB)

Kinsinger, J. B.; Fischer, T.; Wilson III, C. W., *J. Polym. Sci., Part B: Polym. Lett.* **1967,** *5*, 285-294.

Experimental Determination of Sequence Distribution

Assuming *terminal control*, evaluate r_1 from each of the first three sets of data, and r_2 from each of the last three.

	Mole fraction of dyads		
f_1	11	12	22
0.584	0.68	0.29	–
0.505	0.61	0.36	–
0.471	0.59	0.38	–
0.130	–	0.67	0.08
0.121	–	0.66	0.10
0.083	–	0.64	0.17

Notice that a 12 dyad can come about from 1 adding to 2 as well as from 2 adding to 1, and the chances of these two events are equal (i.e., steady-state assumption).

$$p_{11} = \frac{N_{11}}{N_{11} + \frac{N_{12}}{2}} \qquad p_{11} = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

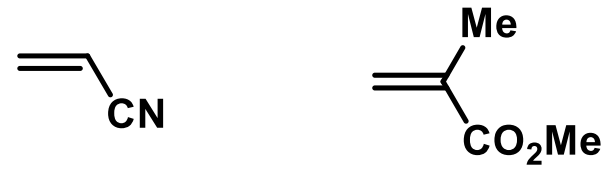
$$\frac{f_2}{r_1 f_1} = \frac{N_{12}}{2N_{11}} \qquad r_1 = \frac{f_2}{f_1} \cdot \frac{2N_{11}}{N_{12}}$$

Similarly, we have $r_2 = \frac{f_1}{f_2} \cdot \frac{2N_{22}}{N_{12}}$

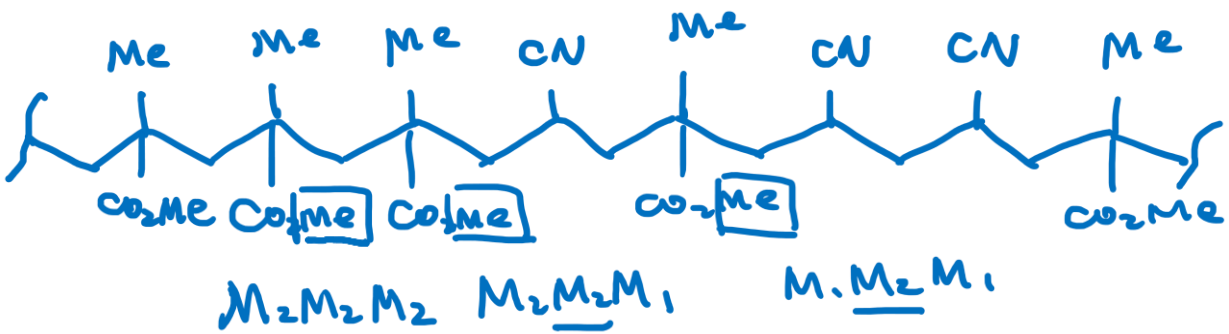
f_1	r_1	f_1	r_2
0.584	3.33	0.130	0.036
0.505	3.32	0.121	0.042
0.471	3.48	0.083	0.048
Average	3.38	Average	0.042

Experimental Determination of Sequence Distribution

acrylonitrile–methyl methacrylate copolymers



(M_1) (M_2)

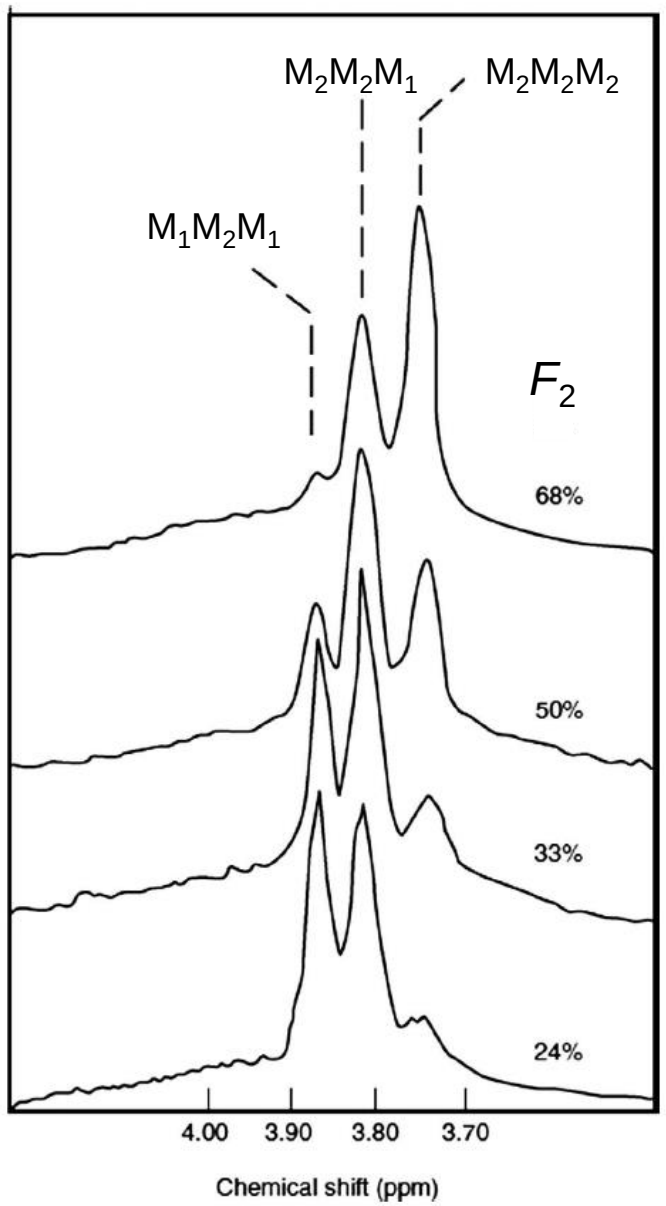


Triads: sequences of three units (of any definite composition).

$M_1M_1M_1$, $M_1M_1M_2$ (or $M_2M_1M_1$), $M_2M_1M_2$

$M_1M_2M_1$, $M_1M_2M_2$ (or $M_2M_2M_1$), $M_2M_2M_2$

In each of these cases the central repeat unit is in a different environment, and a characteristic proton in that repeat unit is in a different location, depending on the effect of that environment.



Experimental Determination of Sequence Distribution

Polymerization temp, °C	Feed ratio, $[M_1^\circ]/[M_2^\circ]$	Triad fraction		
		I (121)	I (122)	I (222)
40	1.26	0.236	0.506	0.258
60	1.26	0.241	0.501	0.258
80	1.02	0.214	0.497	0.289
100	1.26	0.260	0.503	0.243

r_{22}	r_{12}
1.28	1.34
1.30	1.31
1.19	1.18
1.22	1.22

Use these triad fractions to determine whether the polymerization follows terminal or penultimate control mechanism

$$r_{22} = \frac{k_{222}}{k_{221}} \qquad r_{12} = \frac{k_{122}}{k_{121}}$$

we can derive

$$r_{22} = \frac{f_1}{f_2} \cdot \frac{2\,I_{(222)}}{I_{(122)}} \qquad r_{12} = \frac{f_1}{f_2} \cdot \frac{I_{(122)}}{2\,I_{(121)}}$$

r_{22} is close to r_{12}, which indicates that the next-to-last unit does not have a significant role in dictating the radical reactivity. Therefore, the polymerization follows the thermal control mechanism.

Resonance Stabilization

Values of the Cross-Propagation Constants k_{12} (L mol^{-1} s^{-1}) for Four Monomer–Radical Combinations

	Radical			
Monomer	**Styrene**	**Acrylonitrile**	**Methyl acrylate**	**Vinyl acetate**
Styrene	145	49,000	14,000	230,000
Acrylonitrile	435	1,960	2,510	46,000
Methyl acrylate	203	1,310	2,090	23,000
Vinyl acetate	2.9	230	230	2,300

- Radical activity: styrene < acrylonitrile < methyl acrylate < vinyl acetate
- Monomer reactivity: styrene > acrylonitrile > methyl acrylate > vinyl acetate

- The reactivity of a monomer is strongly dependent upon the ability of its substituent group(s) to stabilize (i.e., resonance stabilization) the corresponding polymeric radical: the greater is the stability of the polymeric radical, the more readily it is formed by reaction of the monomer.
- Resonance stabilization produces a bigger effect in the radical than in the monomer.

Resonance and Reactivity

1. **Unstabilized monomer** converts **stabilized radical** to **unstabilized radical** $R_{rs}\bullet + M \rightarrow P\bullet$

   An overall loss of resonance stabilization and it is a radical which suffers the loss.

2. **Stabilized monomer** converts **stabilized radical** to another **stabilized radical** $R_{rs}\bullet + M_{rs} \rightarrow P_{rs}\bullet$

   An overall loss of resonance stabilization but it is monomer stabilization which is lost.

3. **Unstabilized monomer** converts **unstabilized radical** to another **unstabilized radical** $R\bullet + M \rightarrow P\bullet$

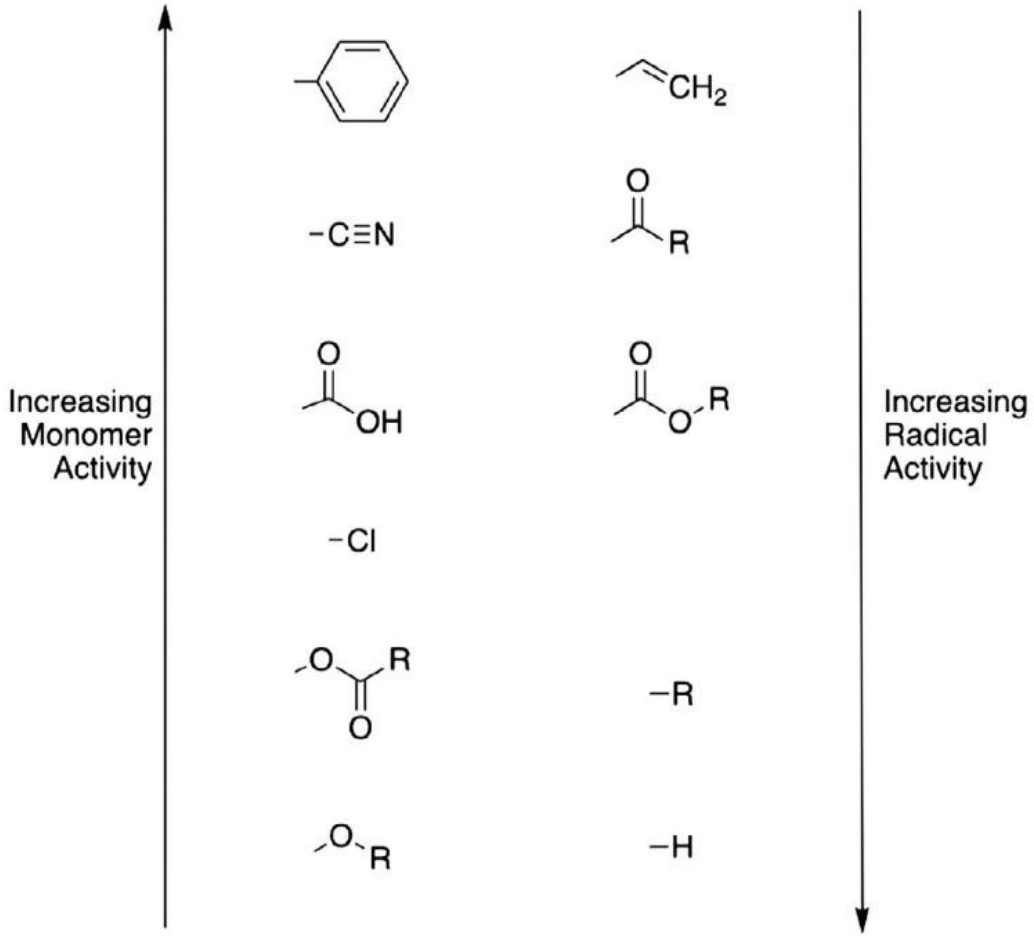
   Suffers none of the reduction in resonance stabilization.

4. **Stabilized monomer** converts **unstabilized radical** to **stabilized radical** $R\bullet + M_{rs} \rightarrow P_{rs}\bullet$

Converts the less effective resonance stabilization of a monomer to a more effective form of radical stabilization.

Radical	Styrene		Styrene		Vinyl acetate		Vinyl acetate
	+	<	+	<	+	<	+
Monomer	Vinyl acetate		Styrene		Vinyl acetate		Styrene
	Case 1		Case 2		Case 3		Case 4

Relation of Resonance to Chemical Structure



Monomer	$k_p \times 10^{-3}$
Vinyl acetate	2.30
Methyl acrylate	2.09
Acrylonitrile	1.96
Methyl methacrylate	0.515
Styrene	0.165
Ethylene	0.242
1,3-Butadiene	0.100

A comparison of the self-propagation rate constants shows that while the resonance effects of monomer and radical reactivity compensate each other, it produce a bigger effect in the radical than in the monomer (e.g., the k_p of vinyl acetate is 16 times larger than that of styrene).

Resonance Stabilization Energy

- For the copolymerization of M_1 and M_2, calculations based on resonance stabilization predict the following (see derivation on Page 193 in Lodge). where ε represents the resonance stabilization energy for the corresponding species.

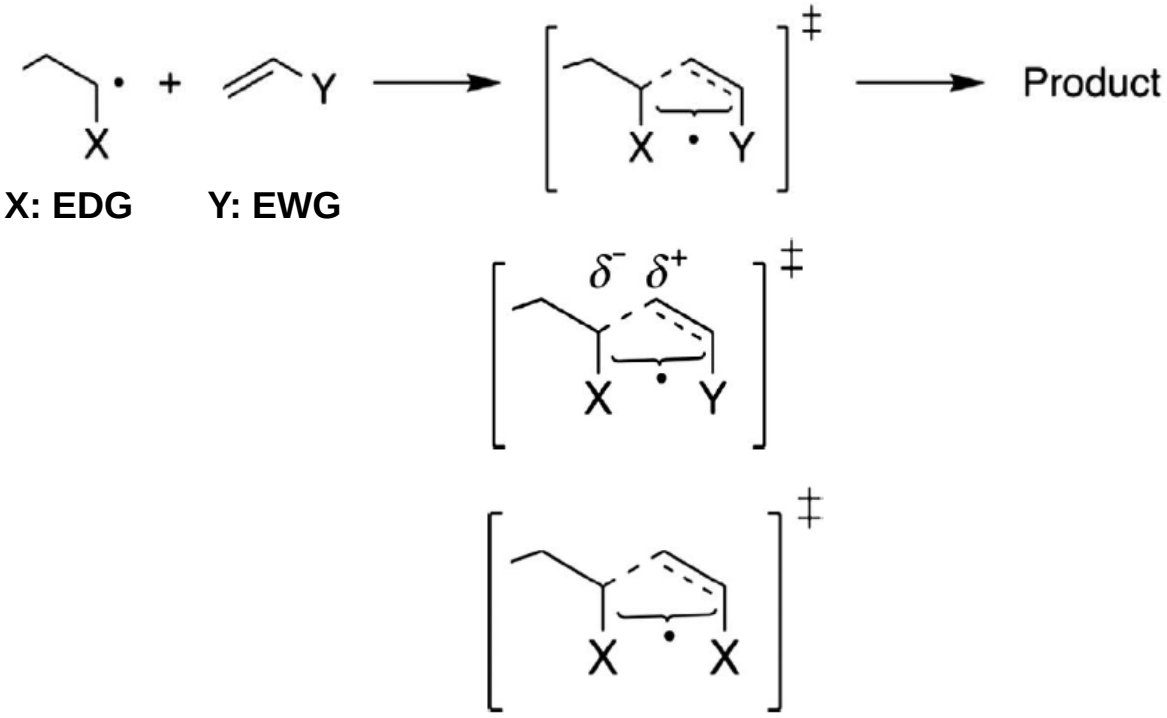
$$r_1 \propto \exp\left(\frac{\varepsilon_{P_1\bullet} - \varepsilon_{M_1}}{RT}\right) \exp\left(\frac{-\left(\varepsilon_{P_2\bullet} - \varepsilon_{M_2}\right)}{RT}\right)$$

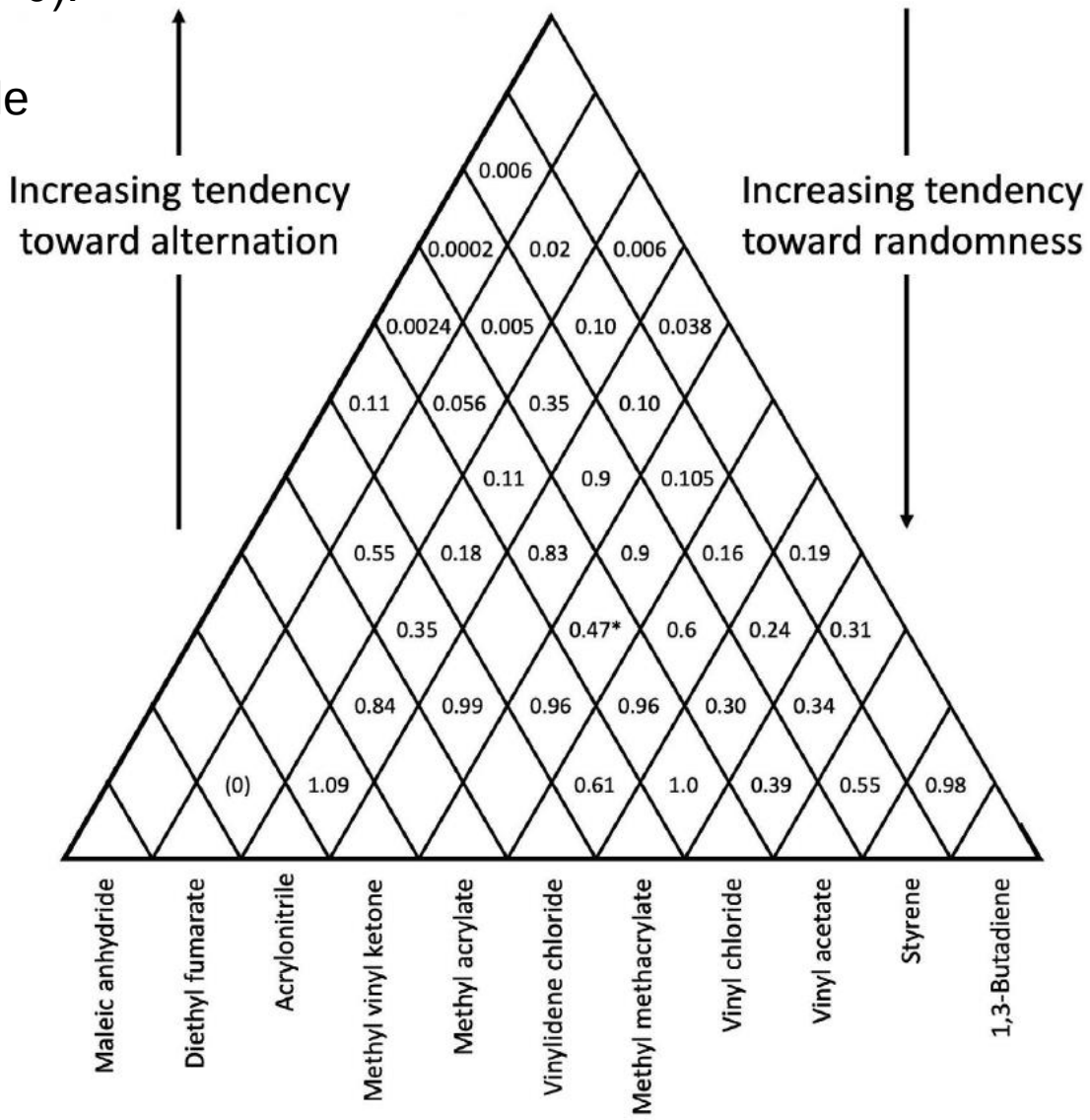
$$r_2 \propto \exp\left(\frac{\varepsilon_{P_2\bullet} - \varepsilon_{M_2}}{RT}\right) \exp\left(\frac{-\left(\varepsilon_{P_1\bullet} - \varepsilon_{M_1}\right)}{RT}\right)$$

- This leads to $r_1 r_2$ =1. In other words, arguments based on resonance effects alone suggest that all copolymerization will be ideal. That is, the two monomers have the same relative tendency to add to both radicals, predicting only a random microstructure.
- However, in reality, we often see copolymerization that deviates from ideal copolymerization ($0 < r_1 r_2 < 1$). Clearly, there are other factors that come into play.

Polar Effects

- Polar effects might lead to alternating copolymerization ($r_1 r_2 \rightarrow 0$):
  1. Electron-donating tendency: acetoxy < phenyl < vinyl
  2. Electron-withdrawing tendency: chloro < carbonyl < nitrile





- Polar effects and resonance are both operative, and, if these still fall short of explaining all observations, there is another old standby to fall back on: steric effects

Let's Put Things Together

TABLE 9.1
Some Typical Values of Reactivity Ratios for Free-Radical Copolymerization at 60 °C

Monomer A	Monomer B	r_A	r_B	$r_A r_B$
Styrene	Butadiene	0.78	1.39	1.08
Styrene	Methyl methacrylate	0.52	0.46	0.24
Styrene	Methyl acrylate	0.75	0.18	0.14
Styrene	Acrylonitrile	0.40	0.04	0.02
Styrene	Maleic anhydride	0.02	0	0
Styrene	Vinyl chloride	17	0.02	0.34
Vinyl acetate	Vinyl chloride	0.23	1.68	0.39
Vinyl acetate	Acrylonitrile	0.06	4.05	0.24
Vinyl acetate	Styrene	0.01	55	0.55
Methyl methacrylate	Methyl acrylate	1.69	0.34	0.57
Methyl methacrylate	*n*-Butyl acrylate	1.8	0.37	0.67
Methyl methacrylate	Acrylonitrile	1.20	0.15	0.18
Methyl methacrylate	Vinyl acetate	20	0.015	0.30
trans-Stilbene	Maleic anhydride	0.03	0.03	0.001

Commercial Use of Copolymers

Styrene–butadiene rubber (SBR)

Styrene–acrylonitrile copolymer (SAN)

Acrylonitrile–butadiene–styrene copolymer (ABS)

Ethylene–vinyl acetate copolymer (EVA)

Acrylonitrile–butadiene copolymer (nitrile rubber)

Polyvinyl chloride-acetate copolymer (PVCA)