



## Chapter 5. Copolymerization

5.1. Kinetics of copolymerization

5.2. Composition of copolymers

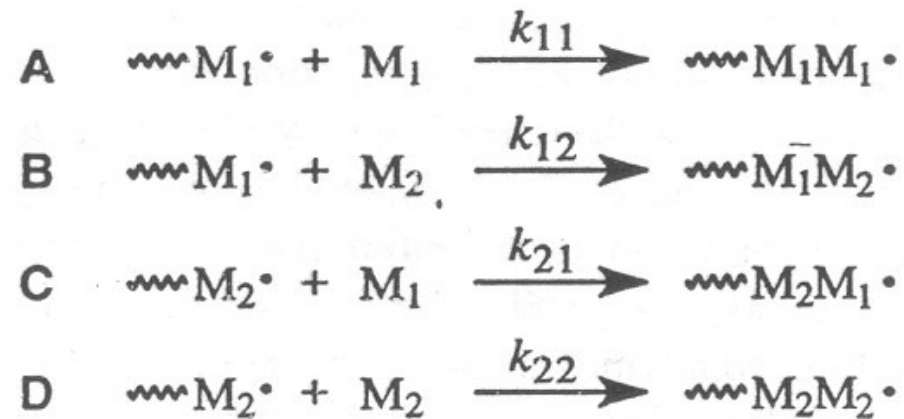
5.3. Mechanisms of copolymerization

5.4. Block and graft copolymers



## 5.1. Kinetics of copolymerization

Copolymerization involves 2 monomers so that the propagation involves 4 possibilities of steps.



The rate equations are:

$$\frac{-d[\text{M}_1]}{dt} = k_{11}[\sim\text{M}_1\cdot][\text{M}_1] + k_{21}[\sim\text{M}_2\cdot][\text{M}_1]$$

$$\frac{-d[\text{M}_2]}{dt} = k_{12}[\sim\text{M}_1\cdot][\text{M}_2] + k_{22}[\sim\text{M}_2\cdot][\text{M}_2].$$



The copolymer composition depends on the comonomer reactivity and concentration. This means that the monomer consumed during copolymerization depends on the polymer structure.

The **instantaneous copolymer equation** describes the relative change in the monomer composition.

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

### 5.1.2. Model I

The reactivity ratio:  $r_1 = \frac{k_{11}}{k_{12}}$        $r_2 = \frac{k_{22}}{k_{21}}$



Explanation:

$r_1$  is the reactivity ratio for monomer 1,

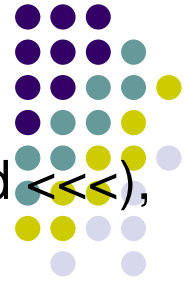
= the ratio of propagation rate-constants for the addition of  $M_1$  (homopol'n) and addition of  $M_2$  (copol'n) to a propagating radical-chain with monomer 1 at the radical end ( $\sim M_1\bullet$ ).

$r_2$  is the reactivity ratio for monomer 2,

= the ratio of propagation rate-constants for the addition of  $M_2$  (homopol'n) and addition of  $M_1$  (copol'n) to a propagating radical-chain with monomer 2 at the radical end ( $\sim M_2\bullet$ ).

Some cases:

- Both reactivity ratios are equal ( $k_{11} = k_{12}$  and  $k_{22} = k_{21}$ ), there is no preferential monomer incorporation into the propagating chain or the copolymer is **random**. (example: styrene and 4-chlorostyrene).
- Both reactivity ratios are zero ( $k_{11} = k_{22} = 0$ ), **alternating** copolymers (example: styrene and maleic anhydride).



Some cases:

- Both reactivity ratios are small but not exactly zero ( $k_{11} = k_{22} \neq 0$  and  $\ll \ll$ ), the copolymer are highly alternating with some random placement. (example: styrene and acrylonitrile).

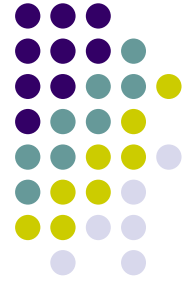
- Both reactivity are very much larger than unity ( $k_{ii} \gg \gg k_{jj}$ ), the copolymers are homopolymers only or block copolymers only.

The limitation of the **instantaneous copolymer equation** is that the radical-chain concentrations is usually not known or easily measured.

Assume that a steady-state radical-concentration for either ( $\wedge \vee \wedge \vee$   $M_1 \bullet$ ) and ( $\wedge \vee \wedge \vee$   $M_2 \bullet$ ) is reached during propagation.

Mayo and Lewis used the definitions of reactivity ratios and the i.c.equation becomes:

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



For a given monomer concentration, the Mayo-Lewis i.c equation can be used to calculate the copolymer composition.

It is defined that:

$f_1$   $\equiv$  the mole fraction of monomer 1 in the monomer mixture and  $f_1 + f_2 = 1$ ,  
 $F_1$   $\equiv$  the mole fraction of monomer 1 in the copolymer and  $F_1 + F_2 = 1$ .

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

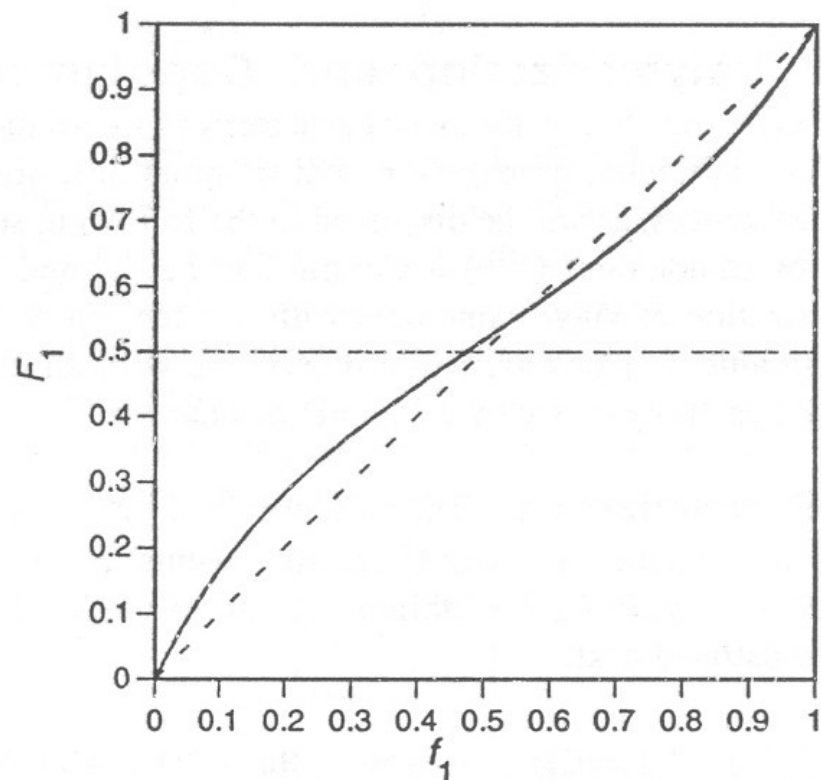
$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

Some conditions:

If  $r_1 = r_2 = 1$  then  $F_1 = f_1$ , ideal of statistical copolymerization (---),

If  $r_1 = r_2 = 0$  then  $F_1 = 0.5$ , alternating polymer (---),

If  $r_1$  and  $r_2$  are random, partially alternating (——).



**Figure 2.4.** Plot of mole fraction of monomer 1 in copolymer,  $F_1$ , versus mole fraction of monomer 1 in the feed,  $f_1$ , for (---) ideal ( $r_1 = r_2 = 1$ ), (—) alternating ( $r_1 = r_2 = 0$ ), and (—) partially alternating copolymerization (copolymerization of styrene and methyl methacrylate, where  $r_1 = 0.585$  and  $r_2 = 0.478$ ).



Example:

Partially alternating copolymers of styrene and methyl methacrylate,

$r_1 = 0.585$  and  $r_2 = 0.478$ .

In fact, neither ideal (random) or perfectly alternating happens.

Most of reactive monomers will be preferentially consumed.

The monomer feed composition varies with time.

- $t \gg \tau$ , high monomer conversion  $\longrightarrow$  heterogeneous mixture of individual copolymers having different composition  $\longrightarrow$  low mechanical strength.
- $t \ll \tau$ , low monomer conversion  $\longrightarrow$  high cost copolymer recovery.





**TABLE 2.6 EXAMPLES OF REACTIVITY RATIOS FOR FREE-RADICAL COPOLYMERIZATION**

Monomer 1	Monomer 2	$r_1$	$r_2$
Ethylene	Vinyl acetate	0.130	1.230
	Carbon monoxide	0.025	0.004
	Propylene	3.200	0.620
Styrene	Acrylonitrile	0.290	0.020
	Butadiene	0.820	1.380
	Divinylbenzene	0.260	1.180
	Maleic anhydride	0.097	0.001
	Methyl methacrylate	0.585	0.478
	4-Chlorostyrene	0.816	1.062
	Vinylidene chloride	1.700	0.110
Vinyl chloride	Vinylidene chloride	0.205	3.068

The value of a reactivity ratio is independent of the nature of the initiator and the solvent in a free-radical copol'n, but there is a weak temperature dependence.



### 5.1.2. Model II (Alfrey & Price)

The propagation rate-constant,  $k_{ij}$  is defined as:

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

where:  $P_i$  is a proportionality constant,

$Q_i$  is a measure of the monomer reactivity,

$e_1$  and  $e_2$  are the polarity of the radical  $M_1 \bullet$  and  $M_2 \bullet$  respectively.

The reactivity ratio:

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

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



**TABLE 2.7  $Q$ - $e$  VALUES FOR FREE-RADICAL COPOLYMERIZATION**

Monomer	$Q$	$e$
Acrylamide	0.23	0.54
Acrylonitrile	0.48	1.23
Butadiene	1.70	-0.50
Ethylene	0.016	0.05
Isobutylene	0.023	-1.20
Isoprene	1.99	-0.55
Maleic anhydride	0.86	3.69
Methacrylic acid	0.98	0.62
Methyl methacrylate	0.78	0.40
<i>N</i> -Vinyl pyrrolidone	0.088	-1.62
Styrene	1.00	-0.80
Vinyl acetate	0.026	-0.88
Vinyl chloride	0.056	0.16
Vinylidene chloride	0.31	0.34



### 5.1.3. Extensions of copolymerization kinetics

#### Multicomponent copolymerization

The copolymer equation for 3 or more monomers are quite complex. However, some simple approaches, such as steady-state condition and the prob of finding certain monomers, result in a good agreement with experiment.

#### Penultimate and remote-unit effects

The mer units before the last polymer may affect the reactivity of chain radical.

#### Depropagation during copolymerization

A monomer or both monomers has/have a tendency to depropagate during copolymerization. This deviation can be observed by the dependence of the copolymer composition on the absolute concentration of the monomers (and temperature), even though their concentration vary.

## Complex participation

The presence of complexes between comonomers can cause deviation from normal copolymerization kinetics. This behaviour can be observed from experimental data.



## 5.2. Composition of copolymers

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



This copolymer equation can predict the average composition of the polymer formed at any instant in the polymerization.

There 3 methods to determined the copolymer composition.

### 5.2.1. Statistical fluctuation of i. c. composition

Alternating copolymers give the minimum spread in composition.

$$N(n) = p^{n-1} (1-p) \quad p = \frac{r_1[M_1]}{r_1[M_1] + [M_2]} \quad (\text{Alfrey, 1952})$$

where N is the prob to find n similar monomer unit in an ideal copolymer,  
p is the prob of addition of that monomer

## 5.2.2. Integration of copolymer equation



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

For a system in which  $F_1 > f_1$ , when  $dM$  moles of monomer have polymerized, the polymer contains  $F_1 dM$  moles of monomer 1, and the feed contains  $(f_1 - df_1)(M - dM)$  moles of monomer 1.

For a material balance:

$$M f_1 - (M - dM)(f_1 - df_1) = F_1 dM \quad \longrightarrow \quad \frac{dM}{M} = \frac{df_1}{F_1 - f_1}$$

$$\varepsilon = \frac{1 - r_2}{(2 - r_1 + r_2)} \quad (\text{Meyer, 1965, 1967})$$



$$\log\left(\frac{M}{M_0}\right) = \frac{r_2}{1 - r_2} \log\left(\frac{f_1}{(f_1)_0}\right) + \frac{r_1}{1 - r_1} \log\left(\frac{f_2}{(f_2)_0}\right) + \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \log\left(\frac{(f_1)_0 - \varepsilon}{f_1 - \varepsilon}\right)$$

### 5.2.3. Variation of copolymer composition with conversion

**An ideal system:** styrene – vinylthiophene,  $r_1 = 0.35$  and  $r_2 = 3.10$ .  
The greater reactivity of the vinylthiophene causes it to be depleted until at the last only styrene remains, and pure PS is the final product.

**An alternating system:** styrene – diethyl fumarate,  $r_1 = 0.30$  and  $r_2 = 0.07$ .  
A strong tendency to alternate and an azeotropic composition at 57 mol% styrene.





## Homogeneity in copolymer

- a. Styrene – diethyl fumarate copolymer containing 40% styrene, stopped at 75% conversion, contains only 44 – 52% styrene
- b. Feed the desired polymer and add more reactive monomer.



## 5.3. Mechanisms of copolymerization

### 5.3.1. Free-radical copolymerization

The behaviour of monomers in copolymerization is determined by 2 factors: the general monomer reactivity and the alternating tendency. These depend on the nature of the attacking radical.

The reactivity of monomers and radicals is determined by the nature of the substituents on the double bond of the monomer.

There are 3 ways that these substituents influence the reactivity. They may :

- activate the double bond, making the monomer more reactive,
- stabilize the resulting radical by resonance,
- provide steric hindrance at the reaction site.



## Reactivity of monomers

The relative reactivities of monomers to a reference radical can be derived from the monomer reactivity ratio. The inverse of this ratio is the rate of reaction of the reference radical with another monomer (See Table 5.2., Billmeyer, p. 114).

## Resonance stabilization

Resonance stabilization of monomers and radicals can be considered in terms of their potential energy.

## Reactivity of radicals

The reactivity of radicals to a reference monomer can be derived by combining the absolute propagation rate constant ( $k_{11}$ ) and reactivity ratio to obtain the rate constants for radical 1 adding monomer 2 ( $k_{12}$ ) (See Table 5.3., Billmeyer, p. 117).



## Steric effects

The effect of steric hindrance in reducing reactivity may be demonstrated by comparing the reactivities of monomers to reference radicals.

## Charge-transfer complexes

A charge-transfer complex can be formed from 2 monomers with different polarities (e.g. an electron donor and an electron acceptor).

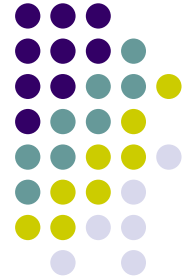
This complex may act as a single species in polymerization, leading to 1:1 alternating polymers. The formation of such complexes is detected by spectroscopy evidence.

Example of electron acceptors: methyl methacrylate, methyl acrylate.

Example of electron donors: vinyl chloride, vinyl acetate, propylene.

## Polarity and alternation

By giving the product of  $r_1 r_2$ , it is possible to calculate 2 monomers with a tendency to alternate.



## The Alfrey-Price treatment

See slide no. 10.

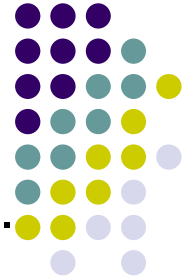
The product of  $r_1 r_2$  possibly calculate 2 monomers with a tendency to alternate.

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

## 5.4. Block and graft copolymers

Polymers with long sequences of 2 monomers can have 2 arrangements of chains: the block copolymers and the graft copolymers.

The aims of obtaining these types of polymer is having copolymer free from homopolymers to enhance physical properties.



### 5.4.1. Block copolymers

The 2 monomers follow one another along the main polymer chain.



The usual method:

Using a polymer with end groups that can be made to react under different conditions with different ways.

- Labile end groups

Labile end groups can be activated the thermal or uv scission of the weak bond.

- Disfunctional initiators

Two initiator groups can be decomposed independently

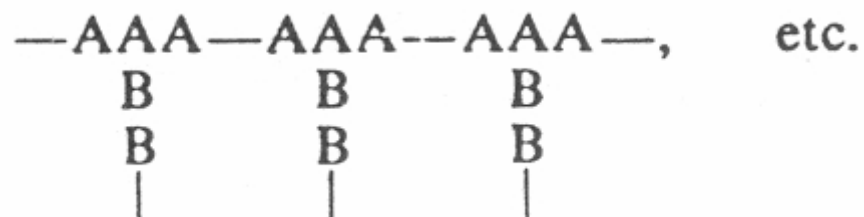
- Living polymers

Unterminated anionic polymerization produces “living” polymers.



## 5.4.2. Graft copolymers

One monomer are “grafted” onto a “backbone” the 2<sup>nd</sup> monomer.



Graft copolymer is a result from the formation of an active site at a point on a polymer molecule and exposure to a 2<sup>nd</sup> monomer.

Most graft copolymer are formed by radical polymerization after uv or ionizing radiation, or redox initiation.