Polymer Chemistry

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6. Copolymerization

I. INTRODUCTION

Copolymerization reactions may involve two or more monomers.

Compositions of copolymers may vary from only a small percentage of one component to comparable proportions of both monomers.

For example, the copolymers of olefins and dienes produced better elastomers than either polyolefins or polydienes alone.

II. THE COPOLYMER EQUATION

Some observations are relevant to the consideration of copolymerization kinetics are:

- The number of reactions involved in copolymerization of two or more monomers increases geometrically with the number of monomers. Consequently, the propagation step in the copolymerization of two monomers involves four reactions.

- The number of radicals to be considered equals the number of monomers. The terminal monomer unit in a growing chain determines almost exclusively the reaction characteristics; the nature of the preceding monomers has no significant influence on the reaction path.

- There are two radicals in the copolymerization of two monomers. Consequently, three termination steps need to be considered.

- The composition and structure of the resulting copolymer are determined by the relative rates of the different chain propagation reactions.

By designating the two monomers as M_1 and M_2 and their corresponding chain radicals as $M_1\cdot$ and $M_2\cdot$, the four propagation reactions and the associated rate equations in the copolymerization of two monomers may be written as follows:

Reaction	Rate equation
$M_1\cdot + M_1 \rightarrow M_1\cdot$	$k_{11}\left[M_1\cdot\right]\left[M_1\right]$
$M_1\cdot + M_2 \rightarrow M_2\cdot$	$k_{12}\left[M_1\cdot\right]\left[M_2\right]$
$M_2\cdot + M_1 \rightarrow M_1\cdot$	$k_{21}\left[M_2\cdot\right]\left[M_1\right]$
$M_2\cdot + M_2 \rightarrow M_2\cdot$	$k_{22}\left[M_2\cdot\right]\left[M_2\right]$

Here the first subscript in the rate constant refers to the reacting radical, while the second subscript designates the monomer.

At steady state, the concentrations of $M_1\cdot$ and $M_2\cdot$ remain constant. This implies that the rates of generation and consumption of these radicals are equal.

Therefore, the rate of conversion of $M_1\cdot$ to $M_2\cdot$ equals that of conversion of $M_2\cdot$ to $M_1\cdot$

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

The rates of disappearance of monomers M_1 and M_2 are given by

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

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

By dividing the above equation :

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

where r_1 and r_2 are monomer reactivity ratios defined by

$$r_1 = k_{11}/k_{12}$$

$$r_2 = k_{22}/k_{21}$$

F_1 and F_2 represent the mole fractions of monomers M_1 and M_2 in the increment of polymer formed at any instant during the polymerization process, then

$$F_1 = 1 - F_2 = d[M_1]/d([M_1]+[M_2])$$

Similarly, representing the mole functions of unreacted M_1 and M_2 in the monomer feed by f_1 and f_2, then

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

Substitution of the two above equations yields:

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

III. TYPES OF COPOLYMERIZATION

By definition, r_1 and r_2 represent the relative preference of a given radical that is adding its own monomer to the other monomer.

The quantity r_1r_2 represents the ratio of the product of the rate constants for the reaction of a radical with its own kind of monomer to the product of the rate constants for the cross-reactions.

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

Copolymerization may therefore be classified into three categories depending on whether the quantity r_1r_2 is **unity**, **less than unity**, or **greater than unity**.

A. IDEAL COPOLYMERIZATION ($r_1 r_2 = 1$)

$$r_1 r_2 = 1, \quad \text{then}$$

$$r_1 = 1/r_2 \quad \text{or} \quad k_{11}/k_{12} = k_{21}/k_{22}$$

In this case the copolymer equation reduces to

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]}{[M_2]} \qquad F_1 = \frac{r_1 f_1}{f_1(r_1 - 1) + 1} = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

It is evident that for ideal copolymerization, each radical displays the same preference for adding one monomer over the other.

Also, the end group on the growing chain does not influence the rate of addition.

For the ideal copolymer, the probability of the occurrence of an M_1 unit immediately following an M_2 unit is the same as locating an M_1 unit after another M_1 unit.

Therefore, the sequence of monomer units in an ideal copolymer is necessarily **random**.

The relative amounts of the monomer units in the chain are determined by the **reactivities** of the monomer and the **feed composition**.

The $r_1r_2 = 1$ can be satisfied under two conditions:

Case 1: $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$. In this case, one of the monomers is more reactive than the other toward the propagating species. Consequently, the copolymer will contain a **greater proportion** of the **more reactive monomer** in the random sequence of monomer units.

Case 2: $r_1 = r_2 = 1$. Under these conditions, the growing radicals cannot distinguish between the two monomers. The **composition of the copolymer** is the **same as** that of **the feed** and, the monomers are **arranged randomly** along the chain.

The copolymer equation becomes:

$$F_1 = \frac{f_1 f.}{f_1 + f_2} = f_1$$

B. ALTERNATING COPOLYMERIZATION ($r_1 = r_2 = 0$)

When $r_1 = r_2 = 0$ (or $r_1r_2 = 0$), each radical reacts exclusively with the other monomer; that is neither radical can regenerate itself. Consequently, the monomer units are **arranged alternately** along the chain irrespective of the feed composition.

In this case the copolymer reduces to:

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

Polymerization continues until one of the monomers is used up and then stops.

Perfect alternation occurs when both r_1 and r_2 are **zero**. As the quantity r_1r_2 approaches zero, there is an increasing tendency toward alternation.

C. BLOCK COPOLYMERIZATION ($r_1 > 1$, $r_2 > 1$)

If r_1 and r_2 are both greater than unity, then each radical would **prefer** adding **its own monomer**.

The addition of the same type of monomer would continue successively until there is a chance addition of the other type of monomer and the sequence of this monomer is added repeatedly. Thus the resulting polymer is a **block copolymer**.

In the extreme case of this type of polymerization ($r_1 = r_2 = \infty$), both monomers undergo simultaneous and independent homopolymerization; however, there are no known cases of this type of polymerization.

Even though cases exist where r_1r_2 approaches 1 ($r_1r_2 = 1$), there are no established cases where $r_1r_2 > 1$. Indeed, the product r_1r_2 is almost always less than unity.

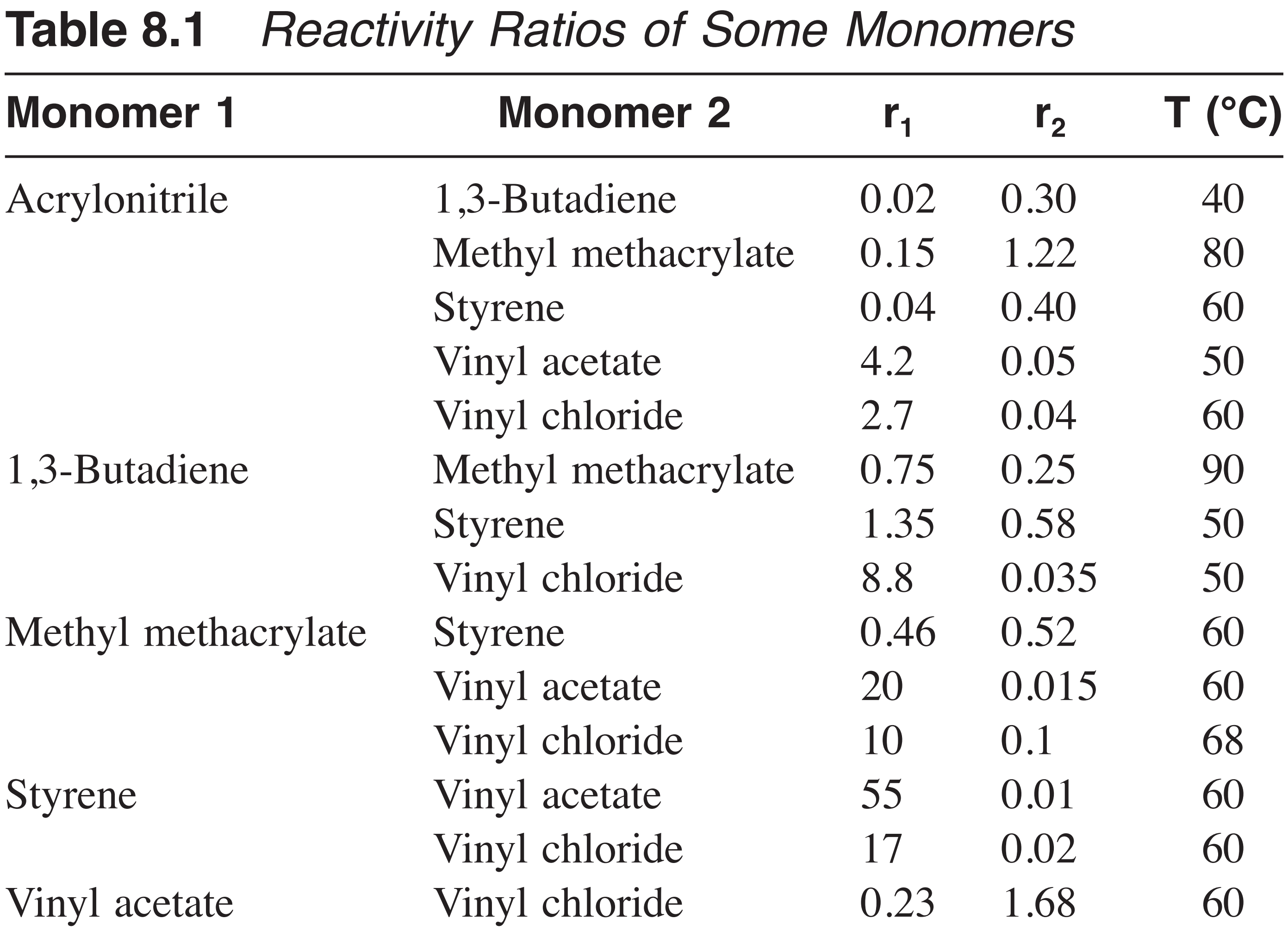

Table 8.1 *Reactivity Ratios of Some Monomers*

Monomer 1	Monomer 2	r_1	r_2	T (°C)
Acrylonitrile	1,3-Butadiene	0.02	0.30	40
	Methyl methacrylate	0.15	1.22	80
	Styrene	0.04	0.40	60
	Vinyl acetate	4.2	0.05	50
	Vinyl chloride	2.7	0.04	60
1,3-Butadiene	Methyl methacrylate	0.75	0.25	90
	Styrene	1.35	0.58	50
	Vinyl chloride	8.8	0.035	50
Methyl methacrylate	Styrene	0.46	0.52	60
	Vinyl acetate	20	0.015	60
	Vinyl chloride	10	0.1	68
Styrene	Vinyl acetate	55	0.01	60
	Vinyl chloride	17	0.02	60
Vinyl acetate	Vinyl chloride	0.23	1.68	60

IV. POLYMER COMPOSITION VARIATION WITH FEED CONVERSION

Since the reactivity ratios r_1 and r_2 are different, there are differences in the rate of growth reactions. Consequently, the composition of the feed, f_1, and that of the polymer, F_1, is neither equal nor constant throughout the polymerization. Therefore, the polymer produced consists of a summation of increments of polymer differing in composition.

For copolymerization of styrene (1) and vinyl acetate (2), the reactivity ratios are $r_1 = 55$ and $r_2 = 0.015$. This means that either radical has a much greater preference to add styrene than vinyl acetate. The first polymer formed consists mainly of styrene. This also means a faster depletion of styrene in the feed.

As polymerization proceeds, styrene is essentially used up and the last polymer formed consists mostly of vinyl acetate. Thus, the copolymers generally have a **heterogeneous composition**.

Azeotropic copolymerization; polymerization proceeds without a change in the composition of either the feed or the copolymer.

V. CHEMISTRY OF COPOLYMERIZATION

Monomer **reactivity** ratios are **independent** of the **initiation** and **termination** steps of copolymerization reaction.

In addition, they are virtually **independent** of the **reaction medium**, and their **dependence** on **temperature** is **minimal**.

The **reactivities** of **monomers and radicals** are themselves dependent on the **nature** of the **substituents** on the monomer double bond:

- Enhancement of monomer reactivity through activation of the double bond
- Conferment of resonance stabilization on the resulting radical
- Provision of steric hindrance at the reaction site

A. MONOMER REACTIVITY

The effect of substituents in enhancing monomer reactivity is in the order:

$$-C_6H_5 > -CH{=}CH_2 > -COCH_3 > -CN > -COOR > -Cl > -CH_2Y > -OCOCH_3 > -OR$$

The monomer reactivities corresponds to the order of increased resonance stabilization of the resulting radical by the particular substituent.

Substituents with unsaturation leading to a monomer with conjugated bonds are most effective in conferring resonance stabilization on radicals.

Substituents such as chlorine (have only nonbonding electrons for interaction with the radical) show only weak stabilization.

In the case of styrene, the resonance stabilization energy is about 20 kcal/mol compared with 1 to 4 kcal/mol for the unconjugated systems.

The substituents that stabilize the product radical also stabilize the monomer.

B. RADICAL REACTIVITY

The order of enhancement of radical reactivity due to substituents is the reverse of that for the monomers.

The enhancement of monomer reactivity by a substituent is due to its stabilization and the consequent decrease of the reactivity of the corresponding radical.

The styrene radical is about 1000 times less reactive than the vinyl acetate radical to a given monomer, but the styrene monomer is only about 50 times more reactive than the vinyl acetate to a given radical.

C. STERIC EFFECTS

Monomer–radical reaction rates are also influenced by steric hindrance.

The addition of a second substituent to the 1- or α-position increases monomer reactivity. However, when the same substituent is in the 2- or β-position (i.e., 1,2-disubstitution), the reactivity of the monomer decreases 2- to 20-fold. This has been attributed to the resulting steric hindrance between the substituent and the attacking radical.