Novel Generalized Rate Equation for Free Radical Copolymerization

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ABSTRACT: A generalized copolymerization rate equation is proposed. The North equation of copolymerization is a special case that can be derived from the generalized equation. According to the mass balance and charge-transfer complex (CTC) equilibrium equation, the free monomer concentration is differentiated from the feed monomer concentration. The effects on the copolymerization rate (the equilibrium constant, total monomer concentration, homopropagation constants, and reactivity ratios) are quantitatively calculated and discussed. The generalized equation may be applied to not only the systems with the participation of CTC, such as styrene/*N*-phenylmaleimide (PMI), but also those without the participation of CTC, such as methyl methacrylate/PMI. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2635–2639, 1999

Key words: generalized rate equation; copolymerization

INTRODUCTION

Copolymer composition and copolymerization rate are the characteristic parameters for free radical copolymerization. The first equation of copolymer composition against a monomer feed fraction was derived by Mayo and Lewis¹ in 1944. The equation may be used successfully in general cases, but a deviation exists from the experimental data that is caused by the affect of the penultimate² or even antipenultimate group.³ Thereafter, Walling⁴ and Atherton and North⁵ proposed copolymerization rate equations on the assumption of chemistry- or diffusion-controlled termination.

Alternative copolymerization is a special case in which both reactivity ratios of the monomer pair approach zero.⁶⁻⁸ In 1946 Bartlett and Nozaki⁹ pre-

pared alternative copolymers of styrene (St) and maleic anhydride and proposed a simple idea of a charge-transfer complex (CTC) formation resulting from the interaction of electropositive and electronegative monomers in the copolymerization. In 1971 Seiner and Litt¹⁰ first presented a mathematical expression in terms of the participation of a monomer-monomer complex in propagation for an alternative copolymerization system, but it could only be used in certain limited conditions because of its complexity. In 1976 Yoshimura et al.¹¹ presented a model and gave a kinetic treatment for 1:1alternating radical copolymerization systems. But it always led to a deviation from the 1:1 alternation at low and high monomer feed ratios. Thus, homopropagation and cross-propagation should be introduced into the kinetic model. A new kinetic model and treatment method was proposed and used in our previous article to quantitatively estimate the participation of the CTC and the free monomers in the copolymerization.¹²

This article derives a generalized equation of the copolymerization rate with or without the par-

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Figure 1 Copolymer composition curve for MMA/PMI system in $CHCl_3$ at 50°C with AIBN as the initiator.

ticipation of CTC. The effects of the equilibrium constant, total monomer concentration, reactivity ratios, and homopropagation constants on the overall copolymerization rate, CTC and free monomers reaction rates, and contribution of CTC to the copolymerization rate are discussed. The copolymerization systems of St/N-phenylmaleimide (PMI) and methyl methacrylate (MMA)/PMI are used to test and verify the reliability of the generalized equation of the copolymerization rate; the CTC and free monomer reaction rates are also estimated. The St/PMI system tends to form an alternative copolymer,¹² but the MMA/PMI system gives a random copolymer as shown in the copolymerization composition diagram (Fig. 1).

EXPERIMENTAL

The St and MMA were distilled under reduced pressure after removal of the inhibitor and stored in a refrigerator before use. The preparation, purification, and analysis of PMI and the composition determination of St/PMI and MMA/PMI copolymers by nitrogen analysis was the same as described in the literature.¹²

RESULTS AND DISCUSSION

Free Monomer Concentration

In the CTC formation system, [CTC] $\neq 0$, the free monomer concentration will be not equal to that of the feed monomer: $[M_1] \neq [M_1]_0$ and $[M_2] \neq [M_2]_0$,

where $[M_1]$ and $[M_2]$ represent the free monomer concentrations of M_1 and M_2 , respectively, and $[M_1]_0$ and $[M_2]_0$ are their feed monomer concentrations, respectively.

According to the mass balance and CTC equilibrium equation, we have

$$[M_1] + K[M_1][M_2] = [M_1]_0 \tag{1}$$

$$[M_2] + K[M_1][M_2] = [M_2]_0$$
(2)

The presence of CTC causes the difference between $[M_1]$ and $[M_1]_0$. The difference is shown in Figure 2 during the variation of the equilibrium constant K. $[M_1] = [M_1]_0$ only at K = 0. The larger the K value is, the greater the difference will be. This difference could not be neglected when the Kvalue was large enough. Hill and coworkers¹³ collected the K value of the usual copolymerization system from 0.01 to 3.2.

If $[M_1] = [M_1]_0$ and $[M_2] = [M_2]_0$, $[M_2]/[M_1]$ should be a constant at the same feed fraction and should not change with the total monomer concentration. According to eqs. (1) and (2), $[M_2]/[M_1]$ will not keep a constant at the same feed fraction with the participation of CTC and will change with the total monomer concentration as shown in Figure 3. The deviation becomes more considerable at the lower total monomer concentration.

Generalized Equation of Copolymerization Rate

The copolymerization rate equation with the participation of CTC was expressed in the literature¹² as the following: for monomolecular termination



Figure 2 Effect of the equilibrium constant on the concentration of free monomers $([M]_T = 1.0 \text{ mol/L})$.



Figure 3 Effect of the total monomer concentration on the concentration ratio of free monomers.

$$\begin{split} R_{p} &= (R_{i}/k_{td})\{(k_{11}k_{21}[M_{1}]^{2} + 2k_{12}k_{21}[M_{1}][M_{2}] \\ &+ k_{12}k_{22}[M_{2}]^{2}) + K(k_{1C}k_{21}[M_{1}]^{2}[M_{2}] \\ &+ k_{2C}k_{12}[M_{1}][M_{2}]^{2})\}/(k_{12}[M_{2}] + k_{21}[M_{1}]) \end{split} \tag{3}$$

for bimolecular termination

$$\begin{split} R_p &= (R_i / 2k_{tc})^{1/2} \{ (k_{11} k_{21} [M_1]^2 + 2k_{12} k_{21} [M_1] [M_2] \\ &+ k_{12} k_{22} [M_2]^2) + K (k_{1C} k_{21} [M_1]^2 [M_2] \\ &+ k_{2C} k_{12} [M_1] [M_2]^2) \} / (k_{12} [M_2] + k_{21} [M_1]) \end{split}$$

where k_{td} and k_{tc} represent the monomolecular and bimolecular termination constants, respectively. Let $R_{it} = R_i/k_{td}$ for the monomolecular termination or $R_{it} = (R_i/2k_{tc})^{1/2}$ for the bimolecular termination; $r_{12} = k_{11}/k_{12}$, $r_{21} = k_{22}/k_{21}$, $r_{1C} = k_{11}/k_{1C}$, and $r_{2C} = k_{22}/k_{2C}$. Equations (3) and (4) then change to

$$\begin{split} R_{p} &= R_{il} \bigg\{ \frac{r_{12}[M_{1}]^{2} + 2[M_{1}][M_{2}] + r_{21}[M_{2}]^{2}}{r_{12}[M_{1}]/k_{11} + r_{21}[M_{2}]/k_{22}} \\ &+ K \frac{r_{12}[M_{1}]^{2}[M_{2}]/r_{1C} + r_{21}[M_{2}]^{2}[M_{1}]/r_{2C}}{r_{12}[M_{1}]/k_{11} + r_{21}[M_{2}]/k_{22}} \bigg\} \\ &= R_{il} \{A([M_{1}], [M_{2}])/C([M_{1}], [M_{2}]) \\ &+ KB([M_{1}], [M_{2}])/C([M_{1}], [M_{2}])\} \end{split}$$
(5)

In eq. (5)

$$\begin{split} A([M_1], \, [M_2]) &= r_{12}[M_1]^2 \\ &+ \, 2[M_1][M_2] + r_{21}[M_2]^2 \quad (6) \end{split}$$

$$B([M_1], [M_2]) = r_{12}[M_1]^2[M_2]/r_{1C} + r_{21}[M_1][M_2]^2/r_{2C}$$
(7)

$$C([M_1], [M_2]) = r_{12}[M_1]/k_{11} + r_{21}[M_2]/k_{22} \quad (8)$$

The contribution of CTC to the copolymerization can be written as

$$R_p(CTC)/R_p = KB([M_1], [M_2])/\{A([M_1], [M_2]) + KB([M_1], [M_2])\}$$
(9)

In the absence of CTC formation between the two monomers, K = 0, eq. (5) can be reduced to

$$R_{p} = R_{il} \left\{ \frac{r_{1}[M_{1}]^{2} + 2[M_{1}][M_{2}] + r_{2}[M_{2}]^{2}}{r_{1}[M_{1}]/k_{11} + r_{2}[M_{2}]/k_{22}} \right\}$$
(10)

When the termination reaction is in the bimolecular, cross-terminated, and diffusion-controlled mode, the copolymerization rate equation can be expressed as

$$R_{p} = \left[\frac{R_{i}}{2k_{t12}}\right]^{1/2} \left\{\frac{r_{1}[M_{1}]^{2} + 2[M_{1}][M_{2}] + r_{2}[M_{2}]^{2}}{r_{1}[M_{1}]/k_{11} + r_{2}[M_{2}]/k_{22}}\right\} \quad (11)$$

Equation (11) is the same as that proposed by Atherton and North.⁵ Besides their equation, the equations of copolymerization rate with various initiation and termination modes can all be derived from eq. (5). Thus, eq. (5) may be regarded as a generalized rate equation with or without the participation of CTC in free radical copolymerization.

Effects of Equilibrium Constant and Total Monomer Concentration on Rates

The formation of CTC is an equilibrium process. The equilibrium constant will affect the concentrations of CTC and free monomers; thus, it further affects the copolymerization rate. From the calculation with an increasing K value the $R_p(\text{CTC})/R_p$ and $R_p(\text{CTC})/R_{it}$ increase and $R_p(f)/R_{it}$ \vec{R}_{it} decreases. In Figure 4 the curves of f_1 versus $R_{n}(f)/R_{it}$ indicate that there is a point at which the first derivative is zero and the second derivative is less than zero, no matter how large the equilibrium constant is. The location of this point changes with the total monomer concentration, reactivity ratios, and homopropagation constants. The equilibrium constant of complex formation is usually from 0.01 to 3.2.¹³ The rates and behavior of copolymerization systems for large K values



Figure 4 Effect of the equilibrium constant on the rate of free monomers ($[M]_T = 1.0 \text{ mol/L}, k_{11} = k_{22} = 100, r_{12} = r_{21} = 0.1, r_{1C} = r_{2C} = 0.01$).

can be predicted by the proposed generalized copolymerization rate equation. We proved that the maximum rate is located at the equimolar feed ratio ($f_1 = f_2 = 0.5$) where there is only CTC and no free monomer participation.¹² But if $k_{11} = k_{22}$, $r_{12} = r_{21}$, and $r_{1C} = r_{2C}$, the maximum rate will also be located at the equimolar feed ratio with the participation of both CTC and free monomer.

From the calculation the $R_p(\text{CTC})/R_p$, $R_p(\text{CTC})/R_{it}$, and $R_p(f)/R_{it}$ increase with the increasing of the total monomer concentration. The change of $R_p(\text{CTC})/R_{it}$ is larger than that of $R_p(f)/R_{it}$ because the $R_p(\text{CTC})/R_{it}$ is more dependent on the total monomer concentration.

Effects of Homopropagation Parameters and Reactivity Ratios on Rates

In eq. (9) the $R_p(\text{CTC})/R_p$ is independent of the homopropagation parameters when the reactivity ratios are kept constant. The R_p/R_{it} , $R_p(\text{CTC})/R_{it}$, and $R_p(f)/R_{it}$ increase with an increase of the homopropagation parameter. There is a maximum rate on the curves of f_1 versus R_p/R_{it} , $R_p(\text{CTC})/R_{it}$, and $R_p(f)/R_{it}$; the location (f_1) of these maximum rates shifts from 0 to 1 with the increase of the homopropagation parameter. But the maximum rate of $R_p(f)/R_{it}$ will disappear when the homopropagation parameter is large enough $(k_{11}$ = 2000) or less than a value of $k_{11} = 5$ (see Fig. 5).

When $r_{1C} = r_{2C}$ and $k_{11} = k_{22}$, $R_p(\text{CTC})/R_{it}$ does not vary with the free monomer reactivity ratio but R_p/R_{it} and $R_p(f)/R_{it}$ decrease with increasing r_{12} . The location (f_1) of the maximum rate shifts from 0 to 1 for $R_p(f)/R_{it}$ and from 0.5 to 1 for R_p/R_{it} . When $r_{12} = r_{21}$ and $k_{11} = k_{22}$, $R_p(f)/R_{it}$ does not change with the CTC reactivity ratio but R_p/R_{it} and $R_p(\text{CTC})/R_{it}$ decrease with the increasing of r_{1C} . The location (f_1) of the maximum rate shifts from 0 to 1 for $R_p(\text{CTC})/R_{it}$ and R_p/R_{it} .

Application of Generalized Copolymerization Rate Equation

St/PMI System with Participation of CTC

The equilibrium constant of St/PMI complex formation in chloroform at 50°C is 0.2726.¹⁴ We have $r_{12} = 0.03370, r_{21} = 0.01157, r_{1C} = 0.002972$, and $r_{2C} = 0.003379.^{12}$

In order to quantitatively estimate the copolymerization rate of CTC and free monomers, the generalized rate equation was used on the assumption that initiation and termination parameters are independent of the feed fraction. The model and experimental results for a bimolecular termination are given in Figure 6. The maximum rate of CTC copolymerization is located at the approximate to 0.35 (experimental data) and 0.36 (model data) molar fraction of St, approximate to 0.25 (experimental data) and 0.24 (model data) for those of $R_p(f)$, and approximate to 0.30 (experimental data) and 0.31 (model data) for R_p .

Using the generalized copolymerization rate equation, if $k_{11} < k_{22}$, the location order of the maximum rate is: $0 < f_{1|\max\{R_p(f)\}} < f_{1|\max\{R_p\}} < f_{1|\max\{R_p(CTC)\}} < 0.5$, and if $k_{11} > k_{22}$, the order is: $0.5 < f_{1|\max\{R_p(CTC)\}} < f_{1|\max\{R_p\}} < f_{1|\max\{R_p(f)\}} < 1.0$. In St/PMI copolymerization, $k_{11} < k_{22}$, ¹² so $0 < f_{1|\max\{R_p(f)\}} < f_{1|\max\{R_p(f)\}} < f_{1|\max\{R_p(TCC)\}} < 0.5$. Accord-



Figure 5 Effect of the homopropagation constant on the rate of free monomers $([M]_T = 1.0 \text{ mol/L}, K = 0.5, k_{22} = 100, r_{12} = r_{21} = 0.1, r_{1C} = r_{2C} = 0.01).$

ing to the effect of the total monomer concentration on rates, the location of maximum rate changes with total monomer concentration. The results show that $f_{1|\max\{R_p\}} \approx 0.35$ in the bulk copolymerization¹⁴ and $f_{1|\max\{R_p\}} \approx 0.30$ in the solution copolymerization.¹²

MMA/PMI system without Participation of CTC

Without the participation of CTC, K = 0, the generalized copolymerization rate equation was used on the assumption of the independence of the initiation and termination parameters on the feed fraction. The model and experimental results are given in Figure 7.

CONCLUSIONS

A generalized copolymerization rate equation with or without participation of the CTC in free radical copolymerization was proposed in this article. It may be applied to estimating the copolymerization rate for CTC and free monomers of the St/PMI system with CTC participation, and it may also be suitable for MMA/PMI system with no participation of CTC in the copolymerization. Besides the North equation of copolymerization with cross and diffusion-controlled bimolecular termination, other rate equations with various initiation and termination modes could be derived from the generalized equation. The free monomer concentration was differentiated from the feed monomer concentration, but they are usually re-



Figure 6 Rates comparison between the model calculation value and the experimental data in the St/PMI system at 50°C in chloroform ($[M]_T = 1.0 \text{ mol/L}$, [AIBN] = 0.01 mol/L).



Figure 7 Rates comparison between the model calculation value and the experimental data in the MMA/ PMI system at 50°C in chloroform $([M]_T = 1.0 \text{ mol/L}, [AIBN] = 0.01 \text{ mol/L}).$

garded as equal in all previous articles. The effects of the equilibrium constant, total monomer concentration, homopropagation, and reactivity ratios on the rates were quantitatively calculated and discussed. The results calculated from the generalized equation were in good agreement with the experimental data.

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