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(4) Poland, D.; Scheraga, H. A. "Theory of Helix-Coil Transitions in Biopolymers"; Academic Press: New York, 1970 and references cited therein.
(5) Privalov, P. L.; Tiktopulo, E. I. *Biopolymers* **1970**, *9*, 127.
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(7) Lifson, S. *J. Chem. Phys.* **1964**, *40*, 3705.
(8) Goldstein, B.; DeLisi, C. *J. Chem. Phys.* **1969**, *51*, 431. *Ibid.* **1970**, *52*, 476. These papers discuss a model similar to ours but assume $\gamma = 1$. With this value of γ, the subsequent formulas for θ and C are greatly simplified. However, we found that these θ and C give a very poor fit to the data.
(9) Perfect-matching loops were discussed previously by: Schwarz, M.; Poland, D. *Biopolymers* **1974**, *13*, 1873. In the limit of an infinitely long chain, the contribution of perfect-matching loops, eq 10, is only a very small part of the total entropy (eq 9, 11, and 12 with $\gamma \sim 0.85$–0.95).
(10) Reference 4, p 223.

Studies on the Radical Chain Copolymerization of Methyl Methacrylate and Styrene at Their Azeotropic Composition

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Received August 27, 1980

ABSTRACT: In this work the radical chain copolymerization of methyl methacrylate and styrene at their azeotropic composition is studied. The propagation and termination reactions for this copolymerization are described by the apparent rate expressions. The apparent rate constants of propagation and termination, k_{pa} and k_{ta}, determined at low extent of reaction are 334.0 L mol^{-1} s^{-1} and 10.45×10^7 L mol^{-1} s^{-1}, respectively, and the Φ value obtained is 15. The latter coincides with that obtained when a chemically-controlled termination model is assumed. The relative importance of combination in the termination is evaluated as 68.2%. When the monomer conversion reaches 11 mol %, the monomer conversion vs. reaction time curve predicted with the k_{pa} and k_{ta} values mentioned above starts to deviate from the experimental data. The deviation is attributed to a gel effect. Thus, the Hamielec equation is used in correlating k_{ta}. We find that $k_{ta} = [10.45 \times 10^7/(1 - X)^2] \exp(0.412X - 12.50X^2)$ and $k_{pa} = 334.0$ L mol^{-1} s^{-1} can satisfactorily describe the reaction course of the conversion vs. reaction time for this copolymerization.

Introduction

In free radical polymerization the termination reaction has been proposed to occur by following three steps:[1] (1) the two macromolecules diffuse together so that it becomes possible for the two radical chain ends to move into proximity; (2) segmental rearrangement occurs so as to bring the free-radical sites into a position in which chemical change can occur; (3) chemical change takes place by either a combination or a disproportionation process. If the first two steps are controlling steps, the reaction will be diffusion controlled. If, on the other hand, the third step is the controlling step, the reaction becomes chemically controlled. North et al.[2-4] claim that for most cases the termination reaction is diffusion controlled even in the most mobile solvents available. They present a single value of the rate constant k_{t12} to describe the termination reaction between like radicals and between unlike radicals. Walling,[5] Bevington et al.,[6] and Fukui et al.[7] adopt the chemically-controlled model to study the copolymerization of methyl methacrylate with styrene and introduce a factor Φ $(k_{t12}/2(k_{t1}k_{t2})^{1/2})$ to explain the cross-termination reaction of this copolymerization. Eastmond[8] recalculated the data of Bevington et al.,[6] assuming a single value of k_{t12}, and found that, even when termination is diffusion controlled, a single value of k_{t12} cannot provide an adequate description of the termination process and that some preference for the cross-termination reaction still exists. Russo and Munari[9] adopt the approach that it is only the flexibility of the chain end which is important physically, rather than the overall chain composition and flexibility. They propose the existence of termination reactions to take account of both chemical and physical effects of the penultimate unit. It is then assumed that the rate constants for the cross termination are given by the geometric means of appropriation of homotermination reactions. Finally, they are able to describe the copolymerization of styrene with methyl methacrylate.

In this work the copolymerization of methyl methacrylate and styrene (MMA–St) at their azeotropic composition is studied. It is known that the types of rate expressions and the values of rate constants depend on the mechanism chosen for the reaction. However, as described above, the kinetic treatment on the termination reaction is still somewhat controversial. In this study we do not start by giving a kinetic scheme of the reaction as most standard texts do but represent all rate equations of radical chain copolymerization by the apparent rate expressions, regardless of the true reaction mechanism. The equations for determining the rate constants of propagation and termination and the relative importance of combination and disproportionation in the overall termination reaction are established. Then, following the possible reaction mechanisms, we work out relationships between the apparent rate constants and all rate constants involved in the elementary reactions. Finally, we compare the theoretical and observed values of the apparent rate constants and discuss the mechanism of the termination reaction for this azeotropic copolymerization.

Theory

1. Aspects of Apparent Rate Coefficients of Propagation and Termination. With the application of the long-chain hypothesis, we introduce the apparent rate expression for the disappearance of the two types of monomers, A and B, for the free-radical copolymerization

$$R_p = -dM/dt = k_{pa}X_TM \qquad (1)$$

where k_{pa} denotes the apparent rate constant of propagation. M refers to the total concentrations of monomers A and B in the reaction mixture at reaction time t, and

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X_T represents the concentration of the two types of polymeric radicals in the reaction mixture at t.

The apparent rate equation for the formation of the total polymeric radicals at t may be represented by

$$R_{ap} = dX_T/dt = 2fk_dI - 2k_{ta}X_T^2 \qquad (2)$$

where k_{ta} represents the apparent rate constant of termination. k_d and f are the rate constant and the efficiency of initiation, respectively, and I denotes the initiator concentration. If the pseudo-steady-state condition is valid for X_T, we have, setting $dX_T/dt = 0$

$$X_T = (fk_dI/k_{ta})^{1/2} \qquad (3)$$

Substitution of eq 3 into eq 1 gives

$$R_p = (k_{pa}/k_{ta}^{1/2})(fk_dI)^{1/2}M \qquad (4)$$

The value of $k_{pa}/k_{ta}^{1/2}$ can be determined from this equation by plotting R_p vs. $(fk_dI)^{1/2}M$.

We consider that the stable copolymers are formed by both combination and disproportionation reactions. We let the apparent rate constants of the combination and disproportionation reactions be k_{tca} and k_{tda}; then the apparent rate expression for the formation of stable copolymers at time t is given as

$$R_{sp} = dD_0/dt = (k_{tca} + 2k_{tda})X_T^2 \qquad (5)$$

where D_0 denotes the concentration of stable copolymers formed at time t. The relative importance of combination in the termination reaction, defined as $\beta = k_{tca}/(k_{tca} + k_{tda})$, is introduced; after X_T is replaced by $(fk_dI/k_{ta})^{1/2}$, integration of eq 5 yields

$$D_0 = (2 - \beta)fI_0(1 - \alpha) \qquad (6)$$

where $\alpha = \exp(-k_dt)$.

We introduce the average molecular weight, M_{av}, of a structural unit of the resulting copolymers

$$M_{av} = F_1'm_A + F_2'm_B$$

then the number-average molecular weight, $\bar{M}_n$ of the resulting copolymers may be written as

$$\bar{M}_n = M_0XM_{av}/(X_T + D_0) \qquad (7)$$

where F_1' and F_2' denote the cumulative copolymer compositions of the monomer units A and B, respectively. m_A and m_B represent separately the molecular weights of the monomer units A and B. X is the monomer conversion and is defined as $X = (M_0 - M)/M_0$.

Combination of eq 7, 3, and 6 results in

$$(M_0XM_{av}/\bar{M}_n)/(I_0\alpha)^{1/2} = (fk_d/k_{ta})^{1/2} + (2 - \beta)f(1 - \alpha)(I_0/\alpha)^{1/2} \qquad (8)$$

Using eq 8 and 4, one can find the absolute values of k_{pa}, k_{ta}, and β from plots of R_p vs. $(fk_dI)^{1/2}M$ and $(M_0M_{av}X/\bar{M}_n)/(I_0\alpha)^{1/2}$ vs. $f(1 - \alpha)(I_0/\alpha)^{1/2}$ if the number-average molecular weight and the monomer conversion are provided.

2. Relationship of k_{ta} and k_{pa} to the Reaction Mechanism. For k_{pa}. The kinetics of copolymerization elucidated by Alfrey,[10] Mayo,[11] Simha,[12] and Wall[13] are

$$\begin{gathered} P_i + A \xrightarrow{k_{11}} P_{i+1} \\ P_i + B \xrightarrow{k_{12}} Q_{i+1} \\ Q_i + A \xrightarrow{k_{21}} P_{i+1} \\ Q_i + B \xrightarrow{k_{22}} Q_{i+1} \end{gathered} \qquad (9)$$

The rates of disappearance of the A and B monomers are given by

$$-dA/dt = (k_{11}P_0 + k_{21}Q_0)A \qquad (10)$$

$$-dB/dt = (k_{12}P_0 + k_{22}Q_0)B \qquad (11)$$

Addition of eq 10 and 11 yields

$$R_p = (k_{11}P_0 + k_{21}Q_0)A + (k_{12}P_0 + k_{22}Q_0)B \qquad (12)$$

where k_{ij}'s are the rate constants of each elementary reaction in eq 9. P_0 denotes the species and the concentration of polymeric radicals of monomer unit A as their active terminal, and Q_0 the species and the concentration of polymeric radicals of monomer unit B as their active terminal. Equation 12 may further be rearranged to

$$R_p = \left\{\frac{k_{11}P_0A + k_{12}P_0B + k_{21}Q_0A + k_{22}Q_0B}{(A + B)(P_0 + Q_0)}\right\}(A + B) \times (P_0 + Q_0) = \frac{k_{11}P_0A + k_{12}P_0B + k_{21}Q_0A + k_{22}Q_0B}{MX_T}MX_T \qquad (13)$$

Comparison of eq 13 and 1 and introduction of $f_1 = A/(A + B) = 1 - f_2$ yield

$$k_{pa} = (k_{11}f_1 + k_{12}f_2)P_0/X_T + (k_{21}f_1 + k_{22}f_2)Q_0/X_T \qquad (14)$$

Dividing eq 10 by eq 11 gives

$$F_1/F_2 = \{(k_{11}P_0 + k_{21}Q_0)f_1\}/\{(k_{12}P_0 + k_{22}Q_0)f_2\}$$

or

$$P_0/Q_0 = (F_1f_2k_{22} - F_2f_1k_{21})/(F_2f_1k_{11} - F_1f_2k_{12}) \qquad (15)$$

Combination of eq 14 and 15 results in

$$k_{pa} = \frac{(k_{12}k_{21} - k_{11}k_{22})f_1f_2}{(k_{21} - k_{11})F_2f_1 + (k_{12} - k_{22})F_1f_2} \qquad (16)$$

If the copolymerization is carried out at its azeotropic composition, that is, if $F_1 = f_1$ and $F_2 = f_2$, k_{pa} reduces to

$$k_{pa}^{az} = \frac{k_{12}k_{21} - k_{11}k_{22}}{k_{21} + k_{12} - k_{11} - k_{22}} \qquad (17)$$

The values of the k_{ij} rate constants appearing on the right-hand sides of eq 16 and 17 may be obtained from the literature.[15,16] Thus, k_{pa} and k_{pa}^{az} can be theoretically calculated by using eq 16 and 17, respectively.

For k_{ta}. The diffusion-controlled[2-4] and chemically-controlled[5-7] processes have been taken into account for the termination reaction. In the latter case, the kinetic scheme of Walling[4] and Bevington et al.[5] is given as

$$\begin{gathered} P_i + P_j \xrightarrow{k_{t1}} D_{i+j} + D_i + D_j \\ k_{t1} = k_{tc1} + k_{td1} \\ P_i + Q_j \xrightarrow{k_{t12}} D_{i+j} + D_i + D_j \\ k_{t12} = k_{tc12} + k_{td12} \\ Q_i + Q_j \xrightarrow{k_{t2}} D_{i+j} + D_i + D_j \\ k_{t2} = k_{tc2} + k_{td2} \end{gathered} \qquad (18)$$

where k_{tci} and k_{tc12} refer to the rate constants of combination between like radicals and between unlike radicals, respectively, and k_{tdi} and k_{td12} denote separately the rate constants of disproportionation between like radicals and between unlike radicals. They introduce the Φ factor,

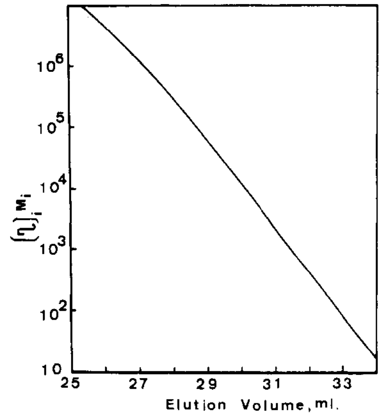

Figure 1. Universal calibration curve of $([\eta]M_n)_i$ vs. the elution volume.

defined by $k_{t12} = 2\Phi(k_{t1}k_{t2})^{1/2}$, to take account of the cross-termination reaction.

The rate of formation for total polymeric radicals is represented by

$$dX_T/dt = 2fk_dI - 2(k_{t1}P_0^2 + k_{t12}P_0Q_0 + k_{t2}Q_0^2) \quad (19)$$

Comparison of eq 19 and 2 gives

$$k_{ta} = (k_{t1}P_0^2 + k_{t12}P_0Q_0 + k_{t2}Q_0^2)/(P_0 + Q_0)^2 \quad (20)$$

Upon substitution of eq 15 into eq 20, we have

$$k_{ta} = \{k_{t1}(F_2f_1k_{11} - F_1f_2k_{12})^2 + k_{t12}(F_2f_1k_{11} - F_1f_2k_{12}) \times (F_1f_2k_{22} - F_2f_1k_{21}) + k_{t2}(F_1f_2k_{22} - F_2f_1k_{21})^2\}/(F_2f_1k_{11} + F_1f_2k_{22} - F_1f_2k_{12} - F_2f_1k_{21})^2 \quad (21)$$

At the azeotropic composition, eq 21 becomes

$$k_{ta}^{az} = \{k_{t1}(k_{11} - k_{12})^2 + k_{t12}(k_{11} - k_{12}) \times (k_{22} - k_{21}) + k_{t2}(k_{22} - k_{21})^2\}/(k_{11} + k_{22} - k_{12} - k_{21})^2 \quad (22)$$

Equation 22 indicates that in the case of the chemically-controlled termination process, k_{ta}^{az} at the azeotropic composition is independent of copolymer composition. The values of k_{t12} and β can be estimated if the experimental value of k_{pa}^{az} and the values of all k_{ij}'s and k_{ti}'s are available.

If, on the other hand, the termination reaction is a diffusion-controlled process, we treat the apparent rate constants k_{ta} and k_{ta}^{az} as k_{t12} of North's model.[2,3] This means we use k_{ta} and k_{ta}^{az} to account for three termination reactions.

Experimental Section

Materials. Commercially available methyl methacrylate (MMA) and styrene (St) were purified by conventional methods, refluxed, and distilled over calcium hydroxide under vacuum just before use.

Azobis(isobutyronitrile) (AIBN; Hayashi Pure Chemical Industries, Ltd.) of extra pure reagent grade was used as initiator without further purification.

Polymerization. Copolymerizations of MMA and St at the azeotropic composition (0.465 mole fraction of MMA) were carried out at 60 °C in 1-L four-neck Pyrex reactors. In order to change the rate of reaction and the molecular weights, four different AIBN concentrations were used to initiate the azeotropic copolymerization. Duplicate samples of about 20 mL each were taken, benzohydroquinone was quickly added to stop the reaction, and the samples were weighed. Each copolymer obtained was redissolved, reprecipitated, and dried under vacuum at 50 °C. The monomer conversion was determined by conventional gravimetry.

Analysis. Number-average molecular weights ($\bar{M}_n$) were mainly determined with a Waters Associates Model 440 ALC/GPC gel permeation chromatograph (GPC). A train of five μ-Styragel packed columns of 10^6, 10^5, 10^3, and 500 Å were used. The unit was operated with tetrahydrofuran (THF) as the carrier solvent at a flow rate of 0.8 cm^3/min.

Table I
Intensive Viscosity, Osmometry Molecular Weight, and Mark-Houwink Constants for Azeotropic MMA-St Copolymers

$10^3 \times$ [AIBN],[a] M	η	M_n	K	a
8.60	0.864	1.091×10^5	1.452	0.699
11.02	0.803	9.636×10^4	1.452	0.699
21.10	0.764	6.965×10^4	1.450	0.698
27.96	0.638	6.050×10^4	1.450	0.698
412.03	0.415	1.576×10^4	1.451	0.699
			1.451[b]	0.699[b]

[a] At 60 °C. [b] Average value.

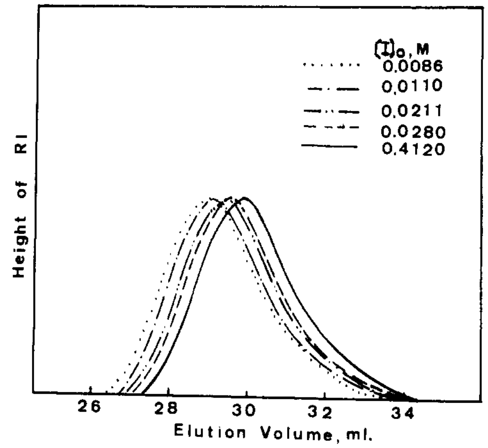

Figure 2. Gel permeation chromatograms of the azeotropic methyl methacrylate–styrene copolymers for determining the Mark–Houwink constants.

In the GPC analysis, we assume that the azeotropic MMA–St copolymers of THF solution follow the universal calibration curve proposed by Hamielec and Ouano.[14] A plot of $([\eta]M_n)_i$ vs. elution volume (Figure 1) was made, using narrow molecular weight distribution polystyrene provided by Waters Associates as a standard. Figure 1 and the Mark–Houwink equation are used to determine number molecular weights M_{ni} at each GPC count, and from these the number-average molecular weight $\bar{M}_n$ of the azeotropic MMA–St copolymers is determined. The Mark–Houwink constants K and a were estimated by Ambler's GPC technique.[15] In Ambler's technique, K and a are determined by the equations

$$[\eta] = K^{1/a+1}\sum w_i([\eta]M)_i^{a/a+1} \quad (23)$$

$$\bar{M}_n = K^{-1/a+1}/\sum w_i([\eta]M)_i^{-1/a+1} \quad (24)$$

In this work the intrinsic viscosity $[\eta]$ was measured with an Ubbelohde-type viscometer in THF at 30 ± 0.01 °C. $\bar{M}_n$ was measured with a Knauer membrane osmometer with a universal temperature recorder in THF at 30 ± 0.01 °C. The weight fraction of copolymer of *i*mer, w_i, was determined from the normalized GPC chromatogram.

Results and Discussion

Table I shows the experimental data for the intrinsic viscosity and the osmometry number-average molecular weights of the azeotropic MMA–St copolymers. These copolymers are formed from the copolymerizations initiated by different levels of initiator concentrations at 60 °C. Figure 2 gives the normalized GPC chromatograms for these copolymers. Using Ambler's technique,[15] we estimated values of K and a as 1.451×10^{-4} and 0.699, respectively. Therefore, the Mark–Houwink equation for

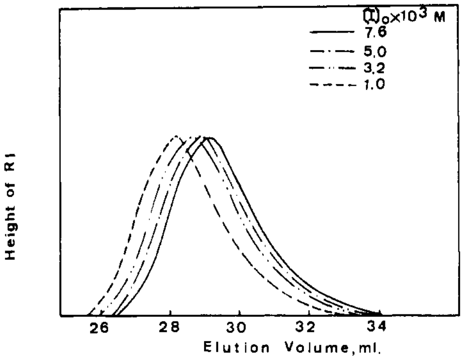

Figure 3. Gel permeation chromatograms of the azeotropic methyl methacrylate–styrene copolymers for determining the number-average molecular weights.

Table II
Summary of Experimental Data for the Azobis(isobutyronitrile)-Initiated Copolymerization of the Methyl Methacrylate–Styrene System at the Azeotropic Composition and 60 °C

10^3[AIBN], M	reaction time, min	X, %	$\bar{M}_n \times 10^{-5}$
1.0	20	0.280	3.199
	40	0.557	3.204
	60	0.832	3.208
	80	1.104	3.215
	100	1.374	3.216
	120	1.643	3.220
3.2	20	0.501	1.787
	40	0.994	1.786
	60	1.483	1.789
	80	1.966	1.790
	100	2.445	1.787
	120	2.919	1.789
5.0	20	0.626	1.430
	40	1.241	1.428
	60	1.850	1.427
	80	2.452	1.426
	100	3.047	1.427
	120	3.636	1.425
7.6	20	0.771	1.159
	40	1.528	1.157
	60	2.276	1.156
	80	3.014	1.154
	100	3.743	1.155
	120	4.463	1.151

the azeotropic MMA–St copolymers in THF solvent at 30 °C is

$$[\eta] = 1.451 \times 10^{-4} \bar{M}_n^{0.699} \qquad (25)$$

Figure 3 gives the normalized GPC chromatograms for those copolymerizations initiated by the AIBN concentrations shown in Table II. Substituting the w_i, $([\eta]M)_i$, a, and K values mentioned above into eq 24, we determined the number-average molecular weights for these copolymers and give them in Table II. The fitting of the data of Table II by eq 4 and 8 yields plots of R_{pi} vs. $(fk_dI)^{1/2}M_0$ (Figure 4) and $(M_0M_{\mathrm{av}}X/\bar{M}_n)/(I_0\alpha)^{1/2}$ vs. $f(1-\alpha)(I_0/\alpha)^{1/2}$ (Figure 5). $k_{\mathrm{pa}}^{\mathrm{az}}/(k_{\mathrm{ta}}^{\mathrm{az}})^{1/2}$, determined from the slope of Figure 4, is 0.253, and $k_df/k_{\mathrm{ta}}^{\mathrm{az}}$, estimated from the intercept of Figure 5, is 2.210×10^{-7}. If the value of k_df is taken to be 5.1×10^{-6} s^{-1}, then the absolute value of $k_{\mathrm{ta}}^{\mathrm{az}}$ is 10.45×10^7 L mol^{-1} s^{-1}; the absolute value of $k_{\mathrm{pa}}^{\mathrm{az}}$ obtained is 334.0 L mol^{-1} s^{-1}. Obviously, the values of $k_{\mathrm{pa}}^{\mathrm{az}}$ and $k_{\mathrm{ta}}^{\mathrm{az}}$ estimated are dependent on the value of k_df chosen. From the slope of Figure 5, we obtained $\beta = 0.682$. This result means that a fraction, 0.682, of the termination reaction occurs as a combination reaction.

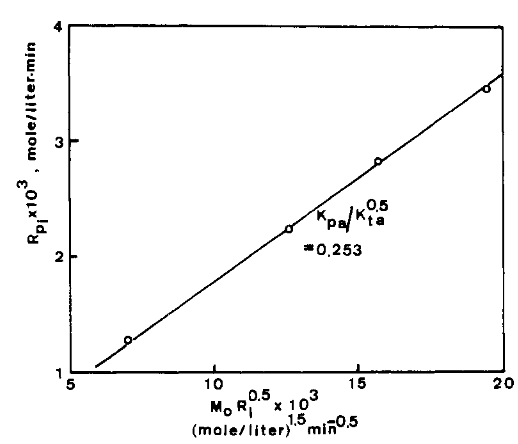

Figure 4. Plot of R_{pi} vs. $M_0R_i^{0.5}$ for determining $K_{\mathrm{pa}}/K_{\mathrm{ta}}^{0.5}$ for the azeotropic copolymerization of methyl methacrylate and styrene at 60 °C.

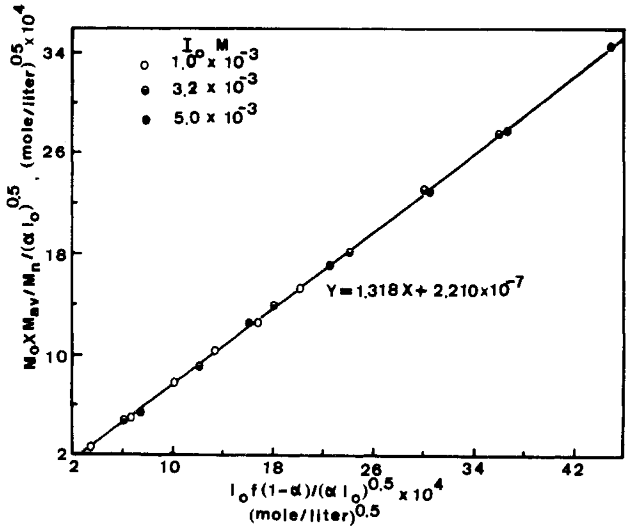

Figure 5. Plot for determining the absolute rate constant of termination and the relative importance of combination in the overall termination process for the low-conversion azeotropic methyl methacrylate–styrene system at 60 °C.

Table III
Absolute Rate Constants[a]

k_{11} = 705 L mol^{-1} s^{-1}; k_{22} = 145 L mol^{-1} s^{-1}
k_{12} = 1533 L mol^{-1} s^{-1}; k_{21} = 279 L mol^{-1} s^{-1}
k_{t1} = 2.55 × 10^7 L mol^{-1} s^{-1}
k_{t2} = 2.90 × 10^7 L mol^{-1} s^{-1}

[a] At 60 °C; ref 15 and 16. The subindices 1 and 2 denote MMA and St, respectively.

As described in the theory section, $k_{\mathrm{pa}}^{\mathrm{az}}$ may be calculated by using eq 17 if the kinetics of propagation is known. The data of Table III, which are collected from the literature,[16,17] show k_{ij} values for propagation. The k_{ti} and k_{tij} values for termination are also listed in the table. We substitute these k_{ij} values into eq 17 and obtain the apparent rate constant $k_{\mathrm{pa}}^{\mathrm{az}}$ as 333.6 L mol^{-1} s^{-1}. Within experimental error, the observed value of $k_{\mathrm{pa}}^{\mathrm{az}}$ agrees with the predicted one.

If the termination process is chemically controlled, eq 22 may be employed to evaluate the rate constant of the cross-termination k_{t12} and the Φ factor. Here we substitute $k_{\mathrm{ta}}^{\mathrm{az}} = 10.45 \times 10^7$ L mol^{-1} s^{-1} and the k_{ti}'s and k_{tij}'s given in Table III into eq 22 and obtain $k_{t12} = 6.86 \times 10^8$ L mol^{-1} s^{-1} and $\phi = 15$. The ϕ value obtained here is close to that reported by Walling,[5] Fukui et al.,[7] and Bevington et al.[6]

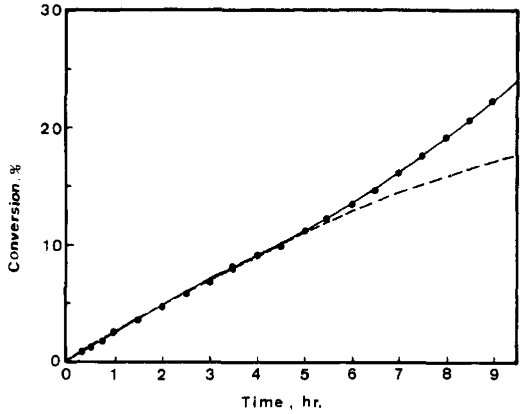

Figure 6. Experimental and theoretical isothermal conversion–time data for the azeotropic methyl methacrylate–styrene system at 60 °C (initiated by 7.60×10^{-3} mol/L AIBN): (●) experimental data; (---) predicted by chemical control; (—) predicted by correlation of k_{ta}.

It is interesting to note the k_{ta}^{az} obtained here is different from that computed with $k_{t12}^{az} = F_1^{az}k_{t1} + F_2^{az}k_{t2}$. It means this simple form of North's model cannot satisfactorily be used for description of the azeotropic MMA–St copolymerization.

We substitute the values of k_{pa}^{az} and k_{ta}^{az} from above into integrated form of eq 4

$$\ln(1 - X) = 2(k_{pa}^{az}/(k_{ta}^{az})^{1/2})(fI_0/k_d)^{1/2}\{1 - \exp(-k_d t/2)\} \quad (4')$$

and construct the monomer conversion vs. reaction time curve; this is shown as the dotted line in Figure 6. The solid circles in the figure are experimental results. We find the chemically-controlled model can only fit up to 11% by mole monomer conversion. Beyond this conversion, deviation takes place. This phenomena may be attributed to the Norrish–Trommsdorff effect.

Hamielec's equation[18] is used for corelation of k_{ta}

$$k_{ta} = \frac{k_{ta0}}{(1 - X)^2} \exp\{2(b_1X + b_2X^2)\} \quad (26)$$

where b_1 and b_2, the temperature dependence parameters, are experimentally determined and k_{ta0} denotes the apparent rate constant of termination at zero monomer conversion. Here k_{ta0} has already been determined to be 10.45×10^7 L mol^{-1} s^{-1} for the azeotropic MMA–St copolymerization, while b_1 and b_2 are determined as follows. Substitution of eq 26 into eq 4 gives

$$R_p = BI^{1/2}\{\exp[-(b_1X + b_2X^2)]\}(1 - X)^2$$

where $B = k_{pa}(fk_d/k_{ta0})^{1/2}$. Rearranging this equation and then taking the natural logarithm we get

$$-\frac{1}{X} \ln \frac{R_p}{BI^{1/2}(1 - X)^2} = b_1 + b_2X \quad (27)$$

b_1 and b_2 can be separately evaluated from the intercept and slope of a plot of $(1/X) \ln (R_p/BI^{1/2}(1 - X)^2)$ vs. X. Here X and R_p are obtained from Figure 6, and I is obtained from $I = I_0 \exp(-k_d t)$. b_1 and b_2 are thus determined to be 0.206 and −6.250, respectively. Consequently, k_{ta} is

$$k_{ta} = \frac{10.45 \times 10^7}{(1 - X)^2} \exp(0.412X - 12.50X^2) \quad (28)$$

k_{pa} and k_{ta} in eq 4 are replaced by 334.0 L mol^{-1} s^{-1} and eq 28, respectively. Then, eq 4 is numerically integrated by the conventional Runge–Kutta–Gills method to yield monomer conversions at each reaction time (given as the solid line in Figure 6). This predicted monomer conversion–time line is in very good agreement with the experimental data in the range of monomer conversion investigated. Therefore, we conclude that the termination reaction of azeotropic MMA–St copolymerization is preferred to be the diffusion-controlled process.

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