Kinetics of Radical Copolymerization between α-Methylstyrene and Methyl Methacrylate

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ABSTRACT: The theoretical treatment of copolymerization with propagation and depopagation is presented in order to estimate r_1, r_2, and K_{11} (the equilibrium constant for propagation and depropagation) in the copolymerization of α-methylstyrene (αMSt: M_1) and methyl methacrylate (MMA: M_2). The values of r_1, r_2, and K_{11} are found to be 0.48, 0.47, and 5.0, respectively. The termination rate constant in the copolymerization is estimated to be 3.3×10^7 regardless of monomer feed composition. This means that a φ-factor proposed by Walling is equal to unity.
   KEY WORDS   Copolymerization / Propagation / Depropagation / α-Methylstyrene / Methyl Methacrylate / Values of r_1, r_2 / Equilibrium Constant / Termination Rate /

In order to treat cross termination in radical copolymerization, Walling[1] used a φ-factor as $\phi = k_{t12}/(k_{t11}k_{t12})^{1/2}$. In the copolymerizations of methylmethacrylate (MMA) with vinylacetate[2] and styrene with α-methylmethacrylate (αMSt),[3] φ could be set up unity, since the rates are diffusion-controlled.[4] On the other hand, φ was larger than 10 in the copolymerization of styrene with some methacrylates.[1,5–7] Such larger values have been ascribed to polar effects which favor cross termination. Russo *et al.*[7] proposed a model based on the steric effect in terms of the penultimate unit. In the preceeding paper,[4] we showed that the Russo model could not be applied to the data on the copolymerization of dodecylmethacrylate (DMA) and MMA, in spite of the statement[8] that it is the best model. To examine the Russo model in more detatil, it is suitable to choose a monomer of which the steric hindrance of α-carbon atom is larger than that of styrene. Thus, in this article, a copolymerization system between αMSt and MMA is chosen. However, the kinetics of this system are more complex than those of the above, because depropagation cannot be neglected in the former but are negligible in the others. Thus, the kinetics for the copolymerization with propagation and depropagation are treated precisely, to estimate r_1, r_2, and K_{11}. Using these values, the termination rate is calculated and discussed.

THEORY

Polymerization scheme:

$$\sim M_1{}^\bullet + M_1 \rightleftarrows \sim M_1 M_1{}^\bullet \qquad (1)$$

$$\sim M_1{}^\bullet + M_2 \rightarrow \sim M_1 M_2{}^\bullet \qquad (2)$$

$$\sim M_2{}^\bullet + M_1 \rightarrow \sim M_2 M_1{}^\bullet \qquad (3)$$

$$\sim M_2{}^\bullet + M_2 \rightarrow \sim M_2 M_2{}^\bullet \qquad (4)$$

Wittmer[10] derived the following ratios:

$$F_2 = \frac{[M_1][M_2] + r_2[M_2]^2}{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)(1 - K_p)} \qquad (5)$$

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$$K_p = \frac{r_1 K_{11} \sigma [M_1]}{r_1 [M_1]^2 + 2[M_1][M_2] + r_2 [M_2]^2} \tag{6}$$

$$\sigma = \frac{r_1 [M_1] + [M_2] + r_1 K_{11} - [(r_1 [M_1] + [M_2] + r_1 K_{11})^2 - 4 r_1^2 K_{11} [M_1]]^{1/2}}{2 r_1 K_{11}} \tag{7}$$

The polymerization rate is written as:

$$
\begin{aligned}
R_p &= -\frac{d[M_1] + d[M_2]}{dt} \\
&= (k_{11}[M_1] + k_{12}[M_2])[N^1] + (k_{21}[M_1] + k_{22}[M_2])[N^2] - k_{\overline{11}}\sigma[N^2] \\
&= k_p (1 - K_p)(2 f k_d [C]/k_t)^{1/2}
\end{aligned}
\tag{8}
$$

$$k_p = \frac{k_{11} k_{22} (r_1 [M_1]^2 + 2[M_1][M_2] + r_2 [M_2]^2)}{r_1 k_{22} [M_1] + r_2 k_{11} [M_2]} \tag{9}$$

$$
\begin{aligned}
d[N_n]/dt &= (k_{11}[M_1] + k_{12}[M_2])([N_{n-1}^1] - [N_n^1]) + (k_{21}[M_1] + k_{22}[M_2])([N_{n-1}^2] - [N_2^2]) \\
&\quad + k_{\overline{11}}\sigma[N_{n+1}] - (k_{r11}[M_1] + k_{r12}[M_2])[N_n^1] - (k_{r12}[M_1] + k_{r22}[M_2])[N_n^2] = 0
\end{aligned}
\tag{10}
$$

This is rewritten as:

$$d[N_n]/k_p dt = ([N_{n-1}] - [N_n]) + K_p[N_{n+1}] - 2 f k_d [C][N_n]/R_p - C_{tr}[N_n] = 0 \tag{11}$$

$$C_{tr} = \frac{r_1 C_{11:11}[M_1]^2 + (r_1 C_{12:11} + r_2 C_{21:22})[M_1][M_2] + r_2 C_{22:22})[M_2]^2}{r_1 [M_1]^2 + 2[M_1][M_2] + r_2 [M_2]^2} \tag{12}$$

$$[N_{n-1}] \simeq [N_n] - d[N_n]/dt \tag{13}$$

$$[N_{n+1}] \simeq [N_n] + d[N_n]/dt \tag{14}$$

$$d[N_n]/dn + \beta[N_n] \simeq 0 \tag{15}$$

$$\beta = 2 f k_d [C]/R_p + (C_{tr} - K_p)/(1 - K_p) \tag{16}$$

The solution is:

$$[N_n]/[N] = \beta \exp(-\beta_n) \tag{17}$$

Following the usual manner, the weight-average degree of polymerization is written as eq 18, when disproportionation predominates.

$$X_w(=2X_n) = 2/\beta \tag{18}$$

A linear relationship between $2/X_w$ and $[C]/R_p$ is given by:

$$2/X_w = (C_{tr} - K_p)/(1 - K_p) + 2 f k_d ([C]/R_p) \tag{19}$$

EXPERIMENTAL

Commercial αMSt and MMA were purified by a similar method as described before.[6] Azophenylethane (APE) was prepared by the method described previously.[9]

The monomers and APE in the ampoule were degassed at a vacuum of about 10^{-3} mmHg. The ampoule was maintained at $60.0 \pm 0.05°C$ for a given polymerization time. The polymer was precipitated by adding methanol, and purified using tetrahydrofuran and methanol when $[M_1]$ was less than 2.98 mol dm^{-3}. When larger than 2.98, the weight loss on the purification of the polymers was not negligible and, then, the conversion was estimated by liquid chromatography, using a Jasco TRI ROTOR high pressure liquid chromatogram with refractive index detector (RI) and ultraviolet one (UV). The mono- mer composition in the copolymer was es-

timated by elemental analysis and the above liquid chromatography. The later method is more suitable when $1 \gg F_1$, since ratio ($=$ 0.506) of RI of polyMMA to RI of polyαMSt is exceedingly larger than the ratio ($=0.027$) of absorptivity of polyMMA to that of poly-αMSt at 254 nm in UV. The weight-average degree of polymerization was measured by gel permeation chromatography, using a Toyo Soda HLC-802A with low angle light scattering detector. All units in terms of concentrations and rates are shown in mol, dm³, and s.

RESULTS AND DISCUSSION

Estimations of r_1, r_2, and K_{11}

Designating as $F_2 = G([M_2]: r_1, r_2, K_{11})$, a modification of Tidwell and Mortimer's method[11] along eq 6 was applied to the data in Table I and all Wittmer's data.[10] However, r_1, r_2, and K_{11} did not converge to the respective most probable values. Fortunately, the r_1 and r_2 converged to the respective most probable values at a given value of K_{11}. In this case, F_2 is written as $G([M_2]: r_1, r_2)$ where $K_{11} =$ constant. The values of r_1 and r_2 at the given value of K_{11} are shown in Figure 1, where the data in Table I are used. Wittmer estimated the r_1 and r_2 values, using $K_{11} = 7.1$ in anionic polymerization. In the present paper, we can obtain the value of K_{11} without the use of the results in the anionic polymerization. When $[M_1] \ll [M_2]$, eq 6 is reduced to:

$$d[M_1]/d[M_2] = (1/r_2)([M_1]/[M_2])$$

$$+ (r_1/r_2 - 1/r_2{}^2 - r_1{}^2 K_{11}/r_2)([M_1]/[M_2])^2 + \cdots$$

$$\simeq (1/r_2)([M_1]/[M_2]) \qquad (20)$$

A line based on eq 20 is obtained when $[M_1] \leq 1.49$ (Figure 2). From the slope of the line, r_2 is found to be 0.47. Using this value, the curves in Figure 2 give $r_1 = 0.48$ and $K_{11} = 5.0$. The $f_2 - F_2$ curve made using the above values fits well the experimental data (Figure 3). In the following section, the co-
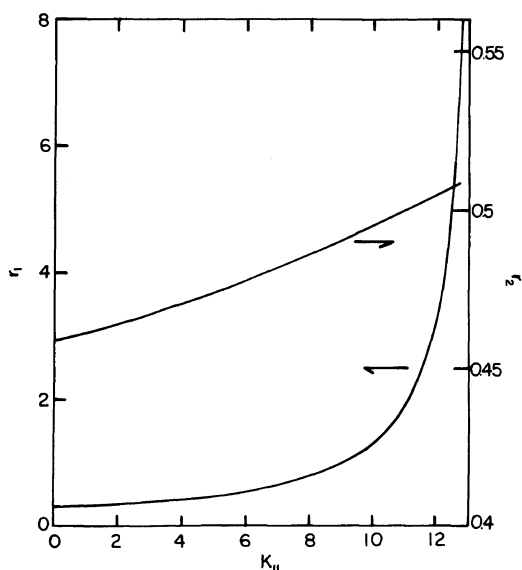

Figure 1. Relationship between r_1 and r_2 at given K_{11}, calculated using the data in Table I.

Table I. The monomer coposition in copolymers ([M₁]: α-MSt, [M₂]: MMA)

[M₁]	[M₂]	d[M₁]/d([M₁]+[M₂])	
0.0375	8.75	0.99107[a]	
0.0740	8.70	0.9824[a]	
0.120	8.65	0.9728[a]	
0.149	8.62	0.9681[a]	
0.373	8.35	0.9416[a]	0.940[b]
0.746	7.89	0.859[a]	0.862[b]
1.491	7.00	0.741[a]	0.725[b]
2.24	6.09	0.670[a]	0.638[b]
2.98	5.20	0.621[a]	0.601[b]
3.39	4.47		0.518[b]
5.97	1.59		0.340[b]

[a] By RI and UV.
[b] By elemental analysis.

polymerization rate is discussed on the basis of $r_1 = 0.48$, $r_2 = 0.47$, and $K_{11} = 5.0$.

Copolymerization Rate

Because of $X_w/X_n \simeq 2$ (Table II), disproportionation predominates[12] and eq 19 may be used. The values of $2fk_d$ and $k_t/k_p{}^2$ are found to be 3.36×10^{-7} (APE) and 70.3 at 60°C by the introduction of the values obtained in the homopolymerization of MMA
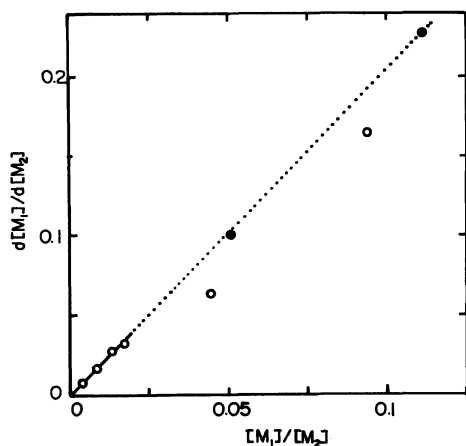
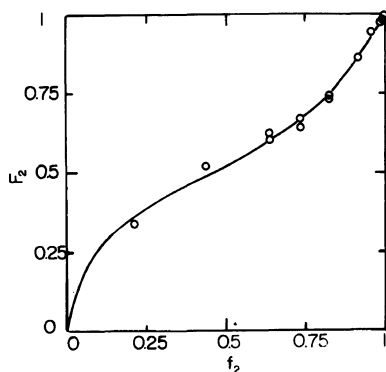**Figure 2.** Estimation of r_2 when $[M_1] \ll [M_2]$ ($\bigcirc$, the data in Table I; $\bullet$, Wittmer's data[10]).

Figure 4. Analysis of the kinetic data obtained when $f_1 = 0.27$ using eq 19.

Figure 3. Copolymerization curve ($\bigcirc$, experimental; ———, calculated when $r_1 = 0.48$, $r^2 = 0.47$, and $K_{11} = 5.0$.

Table II. Kinetic data

1000 [C$_1$]	[M$_1$]	[M$_2$]	$10^6 R_p$	X_n	X_w
0.20	5.97	1.59	1.20		
0.20	3.39	4.47	2.41		
0.20	2.98	5.26	3.98		
0.20	2.24	6.09	8.73		235
0.10	2.27	6.21	6.56	160	332
0.050	2.29	6.26	5.14	220	457
0.025	2.30	6.29	4.04	350	708
0.0125	2.30	6.30	2.84	480	1000
0.20	1.491	7.00	9.00	400	780
0.20	0.746	7.89	13.0	500	1059
0.20	0.373	8.35	26.0		
0.20	0.149	8.62	48.0		
0.20	0.0740	8.70	75.0		
0.20	0.0375	8.75	110		
0.20	0	8.80	272	3885	7731

(Table II) and a value of $C_{22:22} = 1.0 \times 10^{-5}$ (ref 13) into eqs 8 and 19. The former value is in good agreement with 3.28×10^{-7} obtained previously.[14] The later value is in good agreement with 72.9 which is calculated from $k_t = 3.40 \times 10^7$ and $k_{22} = 683$.[15] In the copolymerization, $2fk_d$ is found to be 3.50×10^{-7} from the slope of the line in Figure 4. This value is also in good agreement with both the above values obtained in the homopolymerizations. Accordingly, the initiation rate may be invariant when $[C] =$ constant. Here, an average value as $2fk_d = 3.43 \times 10^{-7}$ among the above values are used. From the intercept of the line in Figure 4, $C_{11:11}$ and $(r_1 C_{12:11} + r_2 C_{21:22})$ are found to both the above values obtained in the homopolymerizations. Accordingly, the initiation rate may be invariant when $[C] =$ constant. Here, an average value as $2fk_d = 3.43 \times 10^{-7}$ among the above values is used. From the intercept of the line in Figure 4, $C_{11:11}$ and $(r_1 C_{12:11} + r_2 C_{21:22})$ are found to be 0.07 and 0.02, respectively, where the data when $[M_1] = 1.491$ in Table II and $C_{22:22} = 1.0 \times 10^{-5}$ are used.

Polymerization rate in homopolymerization of αMSt was so slow that a valid value of k_t/k_{11}^2 could not be obtaind from the data on the homopolymerization. Here, such a

value is estimated by eq 22 of which eq 8 is rewritten.

$$U = (r_1 k_t^{1/2}/k_{11})([M_1]/[M_2]) \qquad (21)$$

where the value of U is calculated as:

$$U = \frac{(2fk_d)^{1/2}(1-K_p)(r_1-K_p)(r_1[M_1]^2+2[M_1][M_2]+r_2[M_2]^2)}{(\eta/\eta_2)^{1/2}R_p[M_2]} - \frac{r_2 k_t^{1/2}}{k_{22}} \qquad (22)$$

Table III. Kinetic data on the modification of polymerization rate as $[R_p/(1-K_p)][\eta/\eta_2]^{1/2}$ [a]

$[M_1]$	$[M_2]$	η/η_2	$10^4 K_p$	$\dfrac{10^6[R_p/(1-K_p)]}{[\eta/\eta_2]^{1/2}}$
0	8.80	1	0	272
0.0375	8.75	1.001	0.038	110
0.0740	8.70	1.006	0.149	74.8
0.149	8.62	1.013	0.598	47.2
0.373	8.35	1.032	3.60	25.6
0.746	7.89	1.058	14.8	12.8
1.491	7.00	1.100	55.8	8.63
2.24	6.09	1.140	129	8.27
2.98	5.20	1.190	241	3.76
3.39	4.47	1.280	357	2.21
5.97	1.59	1.380	1920	1.15

[a] $[C] = 0.20$. K_p = calculated when $r_1 = 0.48$, $r_2 = 0.47$, and $K_{11} = 5.0$.

On the assumption that $k_t \eta =$ constant,[4] this equation is modified. The ratio as (η/η_2) is shown in Table III. The slope of the line in Figure 5 gives $k_t^{1/2}/k_{11} = 2300$. On the assumption that k_t is invariable, k_{11} is found to be 2.5, using $k_t = 3.28 \times 10^7$. This assumption may be accepted, because eq 8 is applicable to all the data shown in Table III (Fiure 6).

In the preceding paper,[4] the termination rate in copolymerization of DMA and MMA was explained in view of the hydrodynamic properties of the polymers. These properties have strong effect on the termination rate, because the hydrodynamic properties of poly-DMA differ markedly from those of poly-MMA. However, those of polyαMSt are approximated to those of polyMMA, since the former is similar to those of polystyrene[13] approximated to the later.[15,16] These approximations are consistent with the assump-
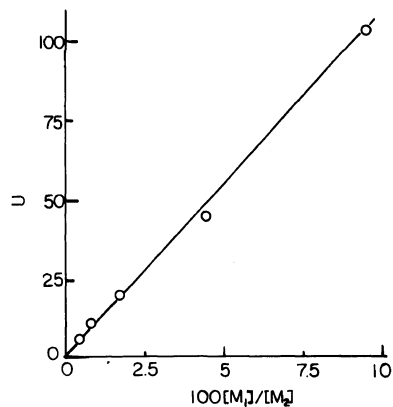
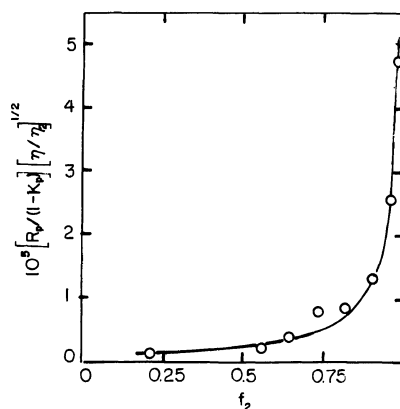

Figure 5. Estimation of k_2/K_{11}^2.

Figure 6. Relationship between polymerization rate and monomer feed composition (○, experimental; ——, calculated when $r_1 = 0.48$, $r_2 = 0.47$, $K_{11} = 5.0$, $k_{22} = 683$, and $k_t = 3.28 \times 10^7$).

tion that k_t is invariable.

Application of Russo *et al.*'s treatment of the present data gave $\delta_{BA}/\delta_A = -0.54$ and $(k_{t21:21}/k_{t11:11}) = 0.084$ (using their terminology). A negative value is physically unrealistic. Further, although these relative values could be obtained by the least square

method, δ_A did not converge to the most probable value. Especially, $[M_1] < 1$, the Russo model has completely no effect. It is concluded that the Russo model cannot describe the present copolymerization nor the copolymerization between DMA and MMA.

Fukuda et al.[17] showed that the termination rate constant in the copolymerization between styrene and MMA is close to the composition average of the termination rate constants of homopolymerizations or ϕ is close to unity. The present result is consistent with the Fukuda et al. result. Following their treatment, k_{11} and k_{22} are written as (using their terminology):

$$k_{11} = k_{111}(r_1 f_1 + f_2)/(r_1 f_1 + f_2/s_1) \quad (23a)$$

$$k_{22} = k_{222}(r_2 f_2 + f_1)/(r_2 f_2 + f_1/s_2) \quad (23b)$$

Along eq 23, the present data yield $s_1 = 1.0$ and $s_2 = 1.0$. In the copolymerization of styrene and MMA, $s_1 = 0.30$ and $s_2 = 0.53$ were obtained. If their treatment is realistic, the difference between $s_{\alpha MSt:MMA}$ and $s_{styrene:MMA}$ must be explained by only a difference between hydrogen and methyl group on α-carbon. This is quite interesting and will be discussed in the near future following more experimental work.

NOMENCLATURE

$[M_i]$ = concentration of monomer M_i

$f_i = [M_i]/([M_1] + [M_2])$

$F_i = d[M_i]/(d[M_1] + d[M_2])$

k_{ij} = propagation rate constant of radical $\sim M_i^{\cdot}$ to M_j

$k_{\overline{ij}}$ = depropagation rate constant of radical $\sim M_i M_j^{\cdot}$

k_t = termination rate constant

k_{tij} = termination rate constant between $\sim M_i^{\cdot}$ and $\sim M_j^{\cdot}$

k_{rij} = transfer rate constant of $\sim M_i^{\cdot}$ to M_j

$C_{ij:ss} = k_{rij}/k_{ss}$

$r_i = k_{ii}/k_{ij}$

$K_{ij} = k_{ij}/k_{\overline{ij}}$

$[N]$ = total concentration of polymer radicals

$[N_n^i]$ = concentration of $\sim M_i^{\cdot}$ with degree of polymerization n

R_p = polymerization rate

$[C]$ = initiator concentration

f = initiator efficiency

k_d = decomposition rate constant of initiator

X_n = number-average degree of polymerization

X_w = weight-average degree of polymerization

η = solvent viscosity of copolymerization solution

η_i = solvent viscosity of homopolymerization solution of M_i

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