

Free-Radical Copolymerization V. Rate Constants of Propagation and Termination for a Styrene/Methyl Methacrylate/Toluene System

Dedicated to the Memory of the late Professor Ichiro Sakurada

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ABSTRACT: The free-radical copolymerization of styrene and methyl methacrylate at 40°C in the presence of 50 wt% of toluene was critically examined by studying both the steady-state and nonsteady-state polymerizations and thus evaluating the rate constants of propagation and termination individually as a function of monomer composition. The results closely agree with those for the corresponding bulk system, establishing that the propagation step of this system, which the terminal model fails to describe, obeys the penultimate model rather than other alternatives which include the solvent fraction as one of the model parameters. Numerically, the experimental values of propagation constant are reproduced with sufficient accuracy by assuming that the homo-propagation rates decrease by a factor about 0.3, when the penultimate units are replaced by the foreign monomers. There is detected no apparent penultimate-unit effect on the composition curve in the solution as well as in bulk. The termination rate constants in the solution agree, within experimental error, with those in the bulk, showing no particular preference for the cross-termination reactions.

KEY WORDS Solution-Copolymerization / Rotating-Sector Method / Absolute Rate of Propagation / Terminal Model / Penultimate Model /

In previous papers,^{1,2} the bulk-copolymerizations of styrene (ST) and methyl methacrylate (MMA) and of *p*-chlorostyrene (pCS) and methyl acrylate (MA) were examined, and the rate constants of propagation and termination for each system were determined as a function of feed-monomer composition. The results indicate that the classical model, commonly termed the "terminal model",³ fails to describe the absolute rate of propagation for both systems. On the other hand, the observed values of termination rate constant of the two systems show, as opposed

to the prevailing view, no particular preference for the cross-termination reactions,⁴ indicating that the termination step of copolymerization is controlled by a rather simple rule. Clearly now, it is the propagation, rather than termination, step that need be reexamined for better understanding of free-radical copolymerization.

The mentioned two copolymerizations were carried out in bulk. In a bulk-copolymerization, the monomers play the role of solvents, and thus any change in the composition means a change in the reaction envi-

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ronment. In the field of homopolymerization, there is a considerable body of evidence showing that the propagation rate depends significantly on solvent in certain cases.⁵ Thus, it is logical to consider the possibility that an environmental factor may be responsible for the failure of the terminal model. Typical copolymerization models along this line include the monomer-monomer complex model,⁶ the radical-solvent (monomer) complex model,⁵ and the hot-radical model.⁷

An alternative possibility may be to assume participation of the penultimate (and higher-order) units in the propagation reaction. The penultimate model is distinguished from the above ones in that it includes no explicit environmental parameters, which the others do, other than the feed-monomer composition.

In this paper, we examine the solution-copolymerization of ST and MMA at 40°C with toluene (TOL) as a solvent. In this solvent, the propagation rate constants of both ST and MMA are nearly the same as in the bulk,⁸ as is expectable from the previous results^{5,9} with a similar type of solvents. In other words, the solvent is almost "inert" for the propagation step of both ST and MMA, which will simplify the situation. In the presence of a sufficient amount of such a solvent, the environmental change associated with a compositional change will be accordingly small so that comparison of the solution- and bulk-copolymerizations should allow us at least to choose between the two groups of models, *i.e.*, the penultimate (and higher-order) models *vs.* those others which include the solvent fraction as one of their model parameters. This is the main topic to be dealt with below.

EXPERIMENTAL

Materials

Commercial products of ST, MMA, 2,2'-azobis(isobutyronitrile) (AIBN), 2,2'-azobis(cyclohexane-1-carbonitrile) (ACN), and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy

(HTMPO) were purified as described previously.¹ Reagent-grade toluene (TOL) was fractionally distilled just prior to use.

Volume Contraction Factor

The volume contraction factor Γ^0 for an *incipient* copolymerization of two monomers (1 and 2) in the presence of a solvent (3) is defined as the decrease in the system volume (in ml) per unit mole of the monomers polymerized. Simple extension of the previous treatments of the solvent-free system^{10,11} gives the following expression for Γ^0 :

$$\begin{aligned} \Gamma^0 = & (F_1\Gamma_1^0 + F_2\Gamma_2^0) \\ & \times (1 - a_{12}x_1x_2 - a_{13}x_1x_3 - a_{23}x_2x_3) \\ & - F_{12}\Delta V_{12} + x_2F_1(a_{12}V_1 + \tilde{V}_{1,1}^0 - \tilde{V}_{1,2}^0) \\ & + x_3F_1(a_{13}V_1 + \tilde{V}_{1,1}^0 - \tilde{V}_{1,3}^0) \\ & + x_1F_2(a_{12}V_2 + \tilde{V}_{2,2}^0 - \tilde{V}_{2,1}^0) \\ & + x_3F_2(a_{23}V_2 + \tilde{V}_{2,2}^0 - \tilde{V}_{2,3}^0) \end{aligned} \quad (1)$$

$$\Gamma_1^0 = V_1 - \tilde{V}_{1,1}^0 \quad \text{and} \quad \Gamma_2^0 = V_2 - \tilde{V}_{2,2}^0 \quad (2)$$

Equation 1 should be sufficiently accurate for the present purpose, even though it does not take account of 1-2-3 ternary interactions.¹⁰ Here x_i represents the volume fraction of component *i* before mixing ($x_1 + x_2 + x_3 = 1$), and the significances of other symbols are the same as or analogous to those appearing in the previous paper¹: For example, a_{13} describes the volume change upon mixing 1 and 3, $\tilde{V}_{1,3}^0$ is the partial molar volume of polymer 1 in solvent 3, F_i is the composition of the copolymer, and F_{12} is the population of the 1-2 alternating linkages in the copolymer. Values of the volumetric parameters were determined by measuring the densities of appropriate solutions^{8,11} and are listed in Table I.

Rates of Polymerization and Initiation

A known amount of AIBN, ST, MMA and TOL were charged in a pyrex tube to which two pyrex dilatometers were connected. The

Table I. Values of the volumetric parameters for ST(1)/MMA(2)/TOL(3)/40°C system^a

Parameter	ST (<i>i</i> =1)	MMA (<i>i</i> =2)
V_i	117.04	108.61
$\bar{V}_{i,1}^\circ$	96.51	80.90
$\bar{V}_{i,2}^\circ$	96.41	81.20
$\bar{V}_{i,3}^\circ$	96.29	81.48
ΔV_{i2}	-1.42	—
A_{i2}	-2.9	—
B_{i2}	-3.2	—
A_{i3}	-3.1	0.5
B_{i3}	2.6	3.2

^a See eq 1 and 2; V 's and ΔV are in ml mol^{-1} ; $10^3 a_{ij} \equiv A_{ij} + B_{ij}(x_i - x_j)$ with $x_i + x_j = 1$ ($i, j = 1, 2$ or 3 ; $i \neq j$); Data from ref 1 and 8.

solution, thoroughly degassed with freezing-and-thawing cycles and sealed off under vacuum, was poured into the dilatometer to a predetermined level. The mixture was allowed to polymerize at 40.0°C in a double water bath thermo-regulated to the order of 10^{-3} °C. The course of polymerization was dilatometrically followed with the image sensor system described previously,¹ which permitted automatic determination of the meniscus-migration rate with unusually high precision.

The rate of initiation was determined for ST/MMA/TOL/AIBN systems with approximately the same compositions as those used for the polymerization-rate experiments. An appropriate amount of HTMPO was added to each system, as an inhibitor. In all cases, a well-defined inhibition time was observed as in the bulk case.¹

Radical Lifetime

The lifetime was determined by the rotating-sector method with ACN used as a photosensitizer. Details have been described.¹ For an optimum value of lifetime τ_L , raw data were fitted on a microcomputer to the theoretical relation¹

$$\bar{R}_p/R_{pL} = (s+1)[sy + 1 + b^{-1} \ln(Z/8y)] \quad (3)$$

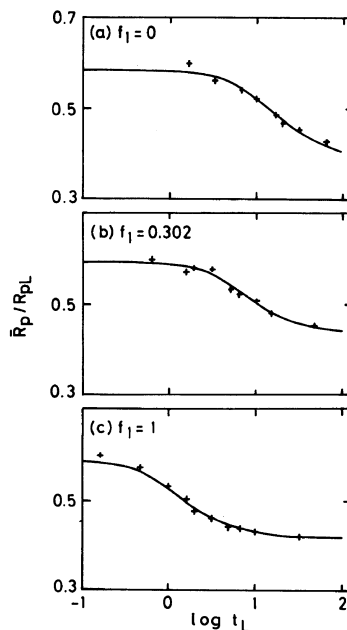


Figure 1. Plot of \bar{R}_p/R_{pL} vs. $\log t_L$ for ST/MMA/TOL/ACN/40°C systems ($s=2$, and ca. 50 wt% of TOL): (a) $f_1=0$, $10^3[\text{ACN}]=0.709 \text{ mol l}^{-1}$, $y=R_{pD}/R_{pL}=0.081$ (solid curve, for $\tau_L=4.85 \text{ s}$); (b) $f_1=0.302$, $10^3[\text{ACN}]=0.858$, $y=0.151$ ($\tau_L=2.88$); (c) $f_1=1$, $10^3[\text{ACN}]=2.00$, $y=0.126$ ($\tau_L=0.486$).

$$Z = (1 + A_1 A_2)(1 + y)^2 - (A_1 + A_2)(1 - y)^2 + \{[(1 + A_1 A_2)(1 + y)^2 - (A_1 + A_2)(1 - y)^2]^2 - 64 A_1 A_2 y^2\}^{1/2} \quad (4)$$

$$A_1 = \exp(-2b) \quad \text{and} \quad A_2 = A_1^{sy} \quad (5)$$

where \bar{R}_p is the average polymerization rate under intermittent illumination with light time t_L and dark time t_D ($s=t_D/t_L=2$ in our case), $b=t_L/\tau_L$, and $y=R_{pD}/R_{pL}$ is the ratio of the polymerization rate R_{pD} in the dark to the rate R_{pL} in the light. Examples of the \bar{R}_p/R_{pL} vs. t_L plot are given in Figure 1.

RESULTS AND DISCUSSION

The rate constants of propagation, k_p , and termination, k_t , for a copolymerization in the presence or absence of solvent(s) are defined by formally the same equations as for

Table II. Steady-state polymerization data for ST(1)/MMA(2)/TOL/40°C

f_1	[M] mol l ⁻¹	10 ² [AIBN] mol l ⁻¹	10 ⁵ R_p mol l ⁻¹ s ⁻¹	10 ⁶ (2 f' k_d) ^a s ⁻¹	F_1^b	10 ² $k_p/k_t^{1/2}$ l ^{1/2} mol ^{-1/2} s ^{-1/2}
0 ^c	4.60			0.575	0	6.48
0.046	4.43	2.07	1.536	0.580	0.112	3.17
0.169	4.79	1.89	0.941	0.577	0.276	1.88
0.193	4.56	1.99		0.579	0.291	
0.378	4.63	1.93	0.569	0.570	0.447	1.17
0.453	4.74	1.87	0.616	0.574	0.493	1.25
0.455	4.58	1.94	0.596	0.575	0.499	1.23
0.591	4.66	1.89	0.524	0.587	0.573	1.06
0.662	4.52	1.94	0.529	0.597	0.631	1.09
0.795	4.27	2.09	0.536	0.606	0.742	1.13
0.903	4.50	1.97	0.490	0.623	0.852	0.98
1 ^c	4.27			0.630	1	1.12

^a Average value determined with HTMPO used as inhibitor. Typical HTMPO concentrations were between 4×10^{-4} and 8×10^{-4} mol l⁻¹.

^b Mole fraction of ST in copolymer, determined by combustion analysis for carbon.

^c From ref 8.

homopolymerization:

$$R_p = k_p[P\cdot][M] \quad (6)$$

$$R_t = k_t[P\cdot]^2 \quad (7)$$

where R_p and R_t are the rates of propagation and termination, respectively, and $[P\cdot]$ and $[M]$ are the *total* concentrations of the polymeric radicals and the monomers, respectively. In the steady state in which $[P\cdot]$ becomes constant, the initiation rate R_i equals R_t , thus

$$R_p = (k_p/k_t^{1/2})R_i^{1/2}[M] \quad (8)$$

$$R_i = 2f'k_d[I] \quad (9)$$

where $[I]$ is the concentration of the initiator with a decomposition rate constant k_d and efficiency f' . Similarly, the radical lifetime τ associated with the steady-state rate R_p reads

$$\tau = (k_p/k_t)[M]/R_p \quad (10)$$

Thus, if one measures R_p , R_i , and τ at a given composition of the feed mixture, one can determine the individual values of k_p and k_t defined for that composition, just as in the case of homopolymerization. The only requirements specific to copolymerization are con-

stancy of the feed composition and sufficiently high degrees of polymerization.¹

The ST/MMA/TOL/40°C system was studied at a fixed weight-fraction of TOL of *ca.* 50% (actual values of x_3 , the volume fraction of TOL, ranged from 0.48 to 0.53). All copolymerization runs were carried out in a conversion range not exceeding 3% so that composition drifts with conversion may be neglected. Typical values of the number-average degrees of polymerization of the recovered polymers were 1×10^3 or larger, apparently large enough for the long-chain approximation to be applicable. Results of the steady-state runs and the rotating-sector runs are summarized in Tables II and III, respectively.

Figure 2 shows the plot of the copolymer composition F_1 against the feed-monomer composition f_1 . The data were fitted to the Mayo-Lewis-Sakurada equation³

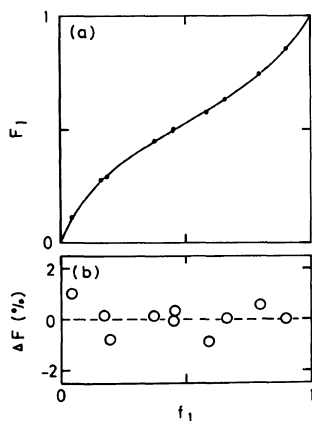
$$F_2/F_1 = (r_2f_2^2 + f_1f_2)/(r_1f_1^2 + f_1f_2) \quad (11)$$

$$r_1 = k_{11}/k_{12} \quad \text{and} \quad r_2 = k_{22}/k_{21} \quad (12)$$

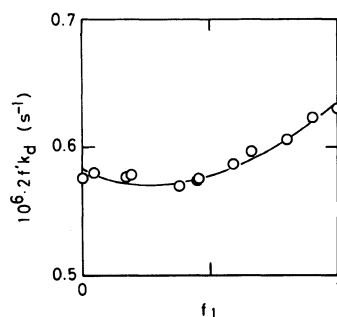
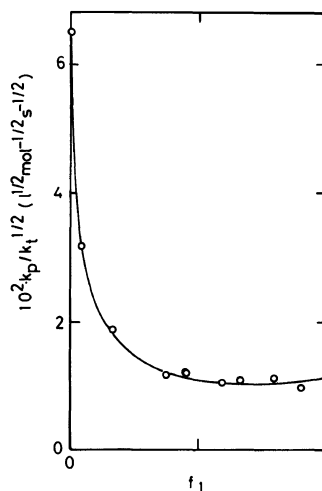
An optimum fit was obtained for values of the

Table III. Summary of the rotating-sector experiments for ST(1)/MMA(2)/TOL/40°C (50 wt% of TOL^a)

f_1	$10^3[\text{ACN}]$	$10^5\langle R_{pL}\rangle^b$	$R_{pD}/\langle R_{pL}\rangle^b$	τ_L
	mol l^{-1}	$\text{mol l}^{-1}\text{s}^{-1}$		
0.049	0.919	0.751	0.144	3.19
0.111	0.338	0.291	0.142	3.97
0.141	3.504	0.736	0.143	1.98
0.249	8.028	0.813	0.144	1.04
0.302	0.858	0.257	0.151	2.88
0.393	12.81	0.630	0.142	0.95
0.499	8.070	0.576	0.147	1.25
0.599	14.24	0.585	0.203	0.91

^a $[\text{M}] = 4.5 \pm 0.2 \text{ mol l}^{-1}$.^b An average value of R_{pL} (see ref 1 for detail).**Figure 2.** (a) Plot of F_1 vs. f_1 for the ST-MMA copolymers: the solid curve is the Mayo-Lewis-Sakurada equation³ with $r_1=0.534$, and $r_2=0.393$; (b) plot of $\Delta F = F_{1,\text{obsd}}$ vs. $F_{1,\text{calcd}}$ vs. f_1 .

monomer reactivity ratios of $r_1=0.534$ and $r_2=0.393$ with a standard deviation of 0.55%. This deviation is about what would be expected from the analytical accuracy (about $\pm 1\%$ per each run), which means that the composition curve of this system obeys the terminal model within experimental error. This is the same conclusion as we have reached for the bulk system,¹ but the r_1, r_2 values disagree (for the bulk have been obtained $r_1=0.523$ and $r_2=0.460^1$). At the present time, we are unable to comment on the origin of the difference in

**Figure 3.** Plot of $2f'k_d$ vs. f_1 for the ST/MMA/TOL/AIBN/40°C system.**Figure 4.** Plot of $k_p/k_t^{1/2}$ vs. f_1 for the ST/MMA/TOL/40°C system: the solid curve is the best-fit representation of the experimental points.

r_1, r_2 values, which we believe substantial. Differing r_1, r_2 values have been observed for ST/MMA/solvent systems notably between those with polar and nonpolar solvents.^{12,13}

Figure 3 shows the plot of $2f'k_d$ vs. f_1 . It may be seen that $2f'k_d$ depends nonlinearly, but less significantly than in the bulk,¹ on the monomer composition.

In Figure 4 is plotted against f_1 the steady-state polymerization parameter $k_p/k_t^{1/2}$ computed with the data in Table II. The solid curve in the figure, the best-fit representation of the data, will be used for the following analysis.

Table IV. Values of k_p and k_t for ST(1)/MMA(2)/TOL/40°C (50 wt%-TOL)

f_1	$10^2 k_p/k_t^{1/2}$ ^a	$10^6 k_p$ ^b	k_p	$10^{-7} k_t$
	$1^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$	k_t	$1 \text{ mol}^{-1} \text{ s}^{-1}$	$1 \text{ mol}^{-1} \text{ s}^{-1}$
0°	6.48	11.0	381	3.5
0.049	3.05	5.21	179	3.4
0.111	2.26	2.49	205	8.2
0.141	2.04	3.18	131	4.1
0.249	1.55	1.86	129	6.9
0.302	1.37	1.71	110	6.4
0.393	1.25	1.39	112	8.1
0.499	1.16	1.63	83	5.1
0.599	1.10	1.24	98	7.9
1°	1.12	1.08	116	10.8

^a Value read from the solid curve in Figure 4.^b From Table III.^c From ref 8.

The radical lifetime was measured for 10 different values of f_1 including $f_1=0$ and 1, and the value of k_p/k_t determined for each f_1 was combined with the value of $k_p/k_t^{1/2}$ from Figure 4 to obtain the individual values of k_p and k_t (Table IV). The rate constant values are expected to be correct to about 20% for k_p and about 40% for k_t , for all values of f_1 .

We now have a complete set of data to discuss our problems. The expression for k_p based on the terminal model is¹

$$k_p = \frac{r_1 f_1^2 + r_2 f_2^2 + 2f_1 f_2}{(r_1 f_1/k_{11}) + (r_2 f_2/k_{22})} \quad (13)$$

where k_{11} and k_{22} are identified with the k_p 's for the homopolymerizations. In Figure 5, the observed values of k_p are compared with eq 13 (the curve designated as $s=1$, in the figure), which shows that the terminal model is unable to describe our system. More importantly, the values of k_p for the present 50% TOL system almost agree with those for the bulk system¹. In other words, the conformity between the theory and experiment has not been at all improved by the addition of the solvent (in fact, some systematic deviations may seem to exist between the solution- and the bulk data,

but are within experimental uncertainty in any case, too small to be considered substantial). This result along with the arguments given in the first section may lead to the conclusion that the failure of the terminal model for the ST/MMA system should be ascribed not to an environmental effect but to a penultimate- (or higher-) unit effect.

Since we see no detectable deviation in composition between the terminal model and experiment, we may consider r_1 and r_2 to be invariant with f_1 . In this case, the penultimate-model expression for k_p reads as the eq 13 with the k_{11} and k_{22} replaced with the following functions:

$$k_{11} = k_{111}(r_1 f_1 + f_2)/(r_1 f_1 + s_1^{-1} f_2) \quad (14)$$

$$k_{22} = k_{222}(r_2 f_2 + f_1)/(r_2 f_2 + s_2^{-1} f_1) \quad (15)$$

$$s_1 = k_{211}/k_{111} \quad \text{and} \quad s_2 = k_{122}/k_{222} \quad (16)$$

where k_{ijm} is the rate constant for the terminal radical j with a penultimate unit i to add to a monomer m , and k_{111} and k_{222} refer to the homopolymerizations. As Figure 5 shows, the observed values of k_p can be described, with sufficient accuracy, by this model with $s_1 = s_2 (=s) = 0.34$ for the bulk case and $s = 0.27$ for the solution case. This means that the homo-propagation velocity, k_{pi} , decreases by a factor about 0.3, when the penultimate unit is replaced by the comonomer j ($\neq i$). In this analysis, we have assumed that $s_1 = s_2$. Indeed, a slightly better curve-fit would be obtained by allowing s_1 and s_2 independently different values. However, because of the relatively large uncertainty in experimental values of k_p , the question as to whether they are actually different or not would remain unanswered. This problem will be discussed elsewhere in more detail.¹⁴ At this time, we should emphasize that the above analysis is only semi-quantitative.

Figure 6 shows the plot of k_t vs. f_1 . The solution- and the bulk-data agree with each other within experimental error. Both sets of data show that k_t for copolymerization is

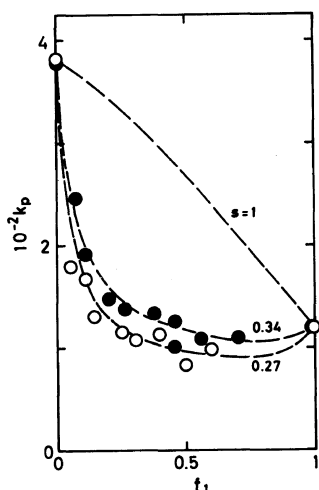


Figure 5. Plot of k_p vs. f_1 for the ST/MMA/TOL/40°C system (open circles): the filled circles are for the bulk system,¹ and the curves were calculated with the penultimate model with the indicated values of $s(=s_1=s_2)$; clearly, the curve with $s=1$ corresponds to the terminal model.

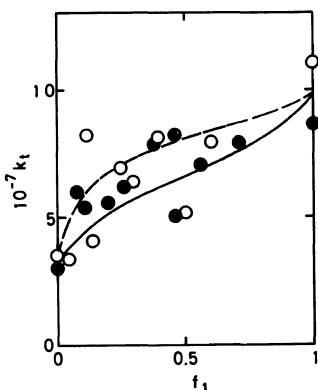


Figure 6. Plot of k_t vs. f_1 for the ST/MMA/TOL/40°C system (open circles): the filled circles are for the bulk system,¹ and the solid and the broken curves represent the North model¹⁶ and the chemical model with $\phi=1$,¹⁵ respectively.

between those for the homopolymerizations, which means that there is no particular preference for the cross-termination reactions, or in terms of the Walling ϕ factor,¹⁵ it is nearly unity. The experimental data are equally well described by the Atherton-North "ideal diffusion model"¹⁶ (see Figure 6). On the basis of

these data alone, it is thus difficult to answer the question as to whether the termination is chemically controlled or diffusion-controlled. However, according to our recent analysis on the pCS/MA system, the diffusion model is clearly favored over the chemical model.¹⁴

CONCLUDING REMARKS

The absolute rate of propagation in ST/MMA copolymerization should be understood by assuming the participation, in some way or other, of the penultimate (or higher) units in the propagation reactions. Numerically, the penultimate model with $s_1 \cong s_2 \cong 0.3$ reproduces the experimental values of k_p with sufficient accuracy. No apparent penultimate-unit effect is detected in the composition curve of the system.

The origin of the penultimate-unit (or higher-order) effect is not necessarily clear at this moment. Insofar as the present system is concerned, any model or mechanism to be proposed should simultaneously explain the two main features of the system, *i.e.*, a marked penultimate-unit effect in absolute rate but its apparent absence in composition curve. We will elsewhere propose one model meeting these requirements.¹⁴

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