

Modeling of the Copolymerization, with Depropagation, of α -Methyl Styrene and Methyl Methacrylate at an Elevated Temperature

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ABSTRACT: We propose a dynamic model for the copolymerization of α -methyl styrene (α -MS) and methyl methacrylate (MMA) in a batch reactor. The parameters are based on data from the literature and our own laboratories over the full conversion range. A two-parameter model with constant reactivity ratios shows the most reasonable results. The dynamic model depicts the reaction kinetics and reactor behavior more clearly. Termination occurs mainly by the

cross reaction of unlike radicals, and its rate increases with the molar ratio of α -MS to MMA. The model enables us to predict the instantaneous and cumulative properties of the copolymer and also provides us with a basic tool for the optimization and control of industrial reactors. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 261–270, 2004

Key words: kinetics (polym.); modeling; copolymerization

INTRODUCTION

The copolymerization of α -methyl styrene (α -MS) and methyl methacrylate (MMA) has been recently studied for higher temperature applications because the addition of α -MS (due to its high glass-transition temperature of 176°C) greatly improves the thermal stability of the copolymer.¹ α -MS is known to depropagate at high temperatures; this limits its conversion and molecular weight because of the low ceiling temperature (61°C). The depropagation of MMA should not be neglected at high temperatures because the equilibrium constant for the homopolymerization is not less than 0.1 above 100°C.² The reversibility of polymerization with both monomers makes the copolymerization reaction more complex. Measuring the molecular weight is not reliable because of its fluctuation in a low-value range caused by a reversible reaction at high temperatures. Reactivity ratio data (estimated at low temperatures at which the reversible reaction can be neglected^{2–9}) conflict in this high-temperature range.^{2–6} Developing a dynamic model including a reversible reaction, as well as validating it through experimental data, is challenging.

Martinet and Guillot^{7–9} predicted the kinetics and properties of an α -MS/MMA copolymer in bulk and toluene solutions, as well as an emulsion process. Their model assumed that the homopolymerization of

α -MS was reversible from 60 to 80°C. They observed almost constant reactivity ratios and a high value of the termination rate constant, which was reasonably validated through their experimental data. Palmer et al.^{5,6} investigated the properties of an α -MS/MMA system in bulk and solution at low conversions and over the full conversion range. The reactivity ratios were almost constant in a low-temperature range (<100°C) and almost the same as other published data.^{2–4,7–9} However, one of them (related to α -MS) greatly varied with the temperature in a high-temperature range, from about 1×10^{-2} to 0.5, and this was not reported in another article.² The experimental data over the full conversion range explained the effects of various operating conditions on the polymer properties, but the dynamics through an appropriate reaction model were not analyzed appropriately. Kang and O'Driscoll¹⁰ developed a method for calculating the molecular weight of the copolymer under conditions for which the reversibility of the propagation reaction must be considered. The method was tested experimentally with an α -MS/styrene copolymerization system. They explained the rapid reduction of the molecular weight with an increasing α -MS feed concentration by relating it to a progressive increase in the apparent termination rate constant (k_a).

α -MS does not homopolymerize above its ceiling temperature of 61°C. Few studies have dealt with the termination of MMA at high temperatures of up to 150°C.^{11,12} The reaction kinetics for the cross-termination of α -MS and MMA have not been well studied in a high-temperature range. Nevertheless, it has been recognized in a few published articles^{13,14} that the

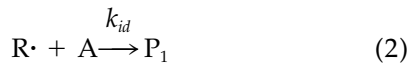
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termination reaction is strongly dependent on the feed composition but not on the molecular weight in a high-molecular-weight range. In general, the cross-termination reaction rate for the reaction between unlike radical chain ends is significantly larger than the two termination rate constants of the respective homopolymerization for many different pairs of comonomer systems.^{15–18}

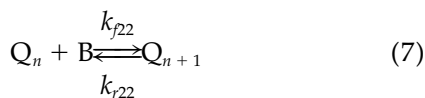
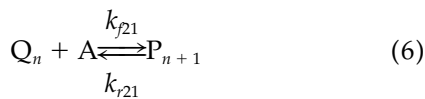
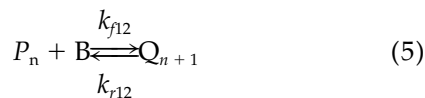
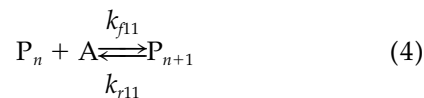
In this article, we develop a dynamic model for α -MS/MMA copolymerization and compare the results with our experimental data and published data, including the conversion, copolymer composition, and molecular weight. The reaction kinetics, especially for termination, are investigated together. The results obtained from the low-conversion experiments for the determination of the copolymer reactivity ratios are revisited with this model.

THEORY

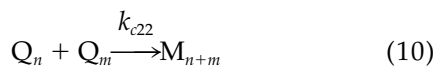
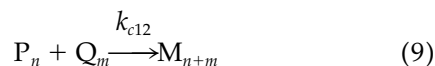
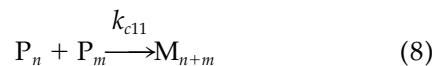
The reaction model is based on an analysis by Kang and O'Driscoll.¹⁰ The following simplifications are introduced: (1) the long-chain hypothesis is applied, (2) the quasi-steady-state assumption (QSSA) is made, and (3) interchain compositional heterogeneity is neglected. The composition of the copolymer is calculated from Kruger et al.'s¹⁹ equation. Copolymerization reversibility is considered in the propagation. We make use of the generating function technique to calculate the leading moments of the molecular weight distribution (MWD). The copolymerization of α -MS with MMA can be represented by the following mechanism. For initiation,



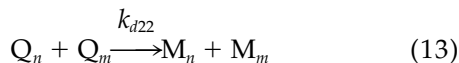
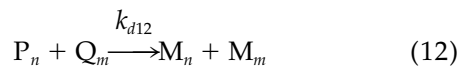
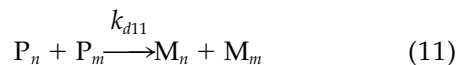
where I , $R \cdot$, A , and B denote the concentration of the initiator, primary radical, α -MS, and MMA, respectively, and P_i and Q_i denote an active polymer of length i ending in an A monomer unit and B monomer unit, respectively; k_d is the initiator decomposition rate constant (1/min), k_{iA} is the initiation rate constant for monomer A (L/mol min), and k_{iB} is the initiation rate constant for monomer B (L/mol min). For propagation and depropagation,



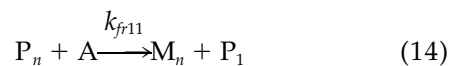
where k_{fij} is the propagation rate constant for a monomer of type i with a live polymer of type j (L/mol min, 1/min) and k_{rij} is the depropagation rate constant for a monomer of type i with a live polymer of type j (L/mol min, 1/min). For termination by combination,

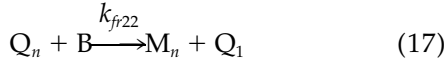
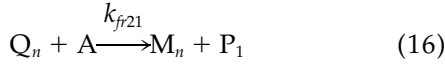
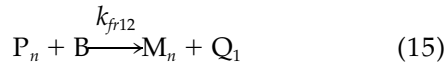


where k_{cij} is the combination termination rate constant (L/mol min). For termination by disproportionation,



where k_{dij} is the disproportionation termination rate constant (L/mol min). For chain transfer to the monomer,





where k_{frij} is the transfer reaction rate constant (L/mol min). The following are defined for the sake of simplicity:

$$P = \sum_{n=1}^{\infty} P_n$$

$$Q = \sum_{n=1}^{\infty} Q_n$$

where P is the total concentration of live polymer P_i species (mol/L) and Q is the total concentration of live polymer Q_i species (mol/L). The rate expressions for the initiator, monomers, and dead polymers are as follows.

$$-\frac{dI}{dt} = k_d I \quad (18)$$

$$-\frac{dA}{dt} = (k_{f11}P + k_{f21}Q)A - (k_{r11}\varepsilon_{11} + k_{r21}\varepsilon_{21})P + C_1 \quad (19)$$

$$-\frac{dB}{dt} = (k_{f22}Q + k_{f12}P)B - (k_{r22}\varepsilon_{22} + k_{r12}\varepsilon_{12})Q + D_1 \quad (20)$$

$$\begin{aligned} \frac{dM_n}{dt} = & \frac{1}{2}k_{c11} \sum_{r=1}^{n-1} P_r P_{n-r} + k_{c12} \sum_{r=1}^{n-1} P_r Q_{n-r} + \frac{1}{2}k_{c22} \sum_{r=1}^{n-1} Q_r Q_{n-r} \\ & + (k_{d11}P + k_{d12}Q + k_{fr11}A + k_{fr12}B)P_n + (k_{d22}Q \\ & + k_{d12}P + k_{fr21}A + k_{fr22}B)Q_n \quad (21) \end{aligned}$$

where M_n denotes the concentration of the dead polymer. ε_{ij} is the conditional probability of finding an A_i unit as the penultimate unit given that the chain end is occupied by an A_j unit. ε_{ij} is introduced to account for the penultimate unit effect on the depropagation step and can be calculated from Kang and O'Driscoll's²⁰ dyad model with known feed concentrations and var-

ious kinetic constants. C_1 and D_1 are given by the following equations:

$$C_1 = (k_{fr11}P + k_{fr21}Q)A + k_{iA}RA \approx (k_{fr11}P + k_{fr21}Q)A \quad (22)$$

$$D_1 = (k_{fr22}Q + k_{fr12}P)B + k_{iB}RB \approx (k_{fr22}Q + k_{fr12}P)B \quad (23)$$

P and Q can be obtained with the long-chain hypothesis and the QSSA:

$$P = \left[\frac{2f_i k_d I}{(k_{c11} + k_{d11}) + 2\beta(k_{c12} + k_{d12}) + \beta^2(k_{c22} + k_{d22})} \right]^2 = \left(\frac{2f_i k_d I}{k_a} \right)^2 \quad (24)$$

$$Q = \beta P \quad (25)$$

where f_i is the efficiency of the initiation reaction and β , the ratio of the total concentration of live polymer Q to that of live polymer P , can be calculated from Kang and O'Driscoll's²⁰ dyad model with known forward and reverse reaction rate constants and monomer concentrations. We introduce the generating function for the calculation of the molecular weight:

$$G(u) = \sum_{n=1}^{\infty} u^n P_n \quad (26)$$

$$J(u) = \sum_{n=1}^{\infty} u^n Q_n \quad (27)$$

$$H(u) = \sum_{n=1}^{\infty} u^n M_n \quad (28)$$

where $G(u)$, $Q(u)$, and $H(u)$ are generating functions of any variable, u , for the calculation of the molecular weight. The first and second moments of the MWD of live polymers can be obtained by the application of QSSA to the active polymer rate equations.²¹ They are used for the calculation of the molecular weight of the dead polymer. Suppose that R_n is the amount of the dead polymer produced per unit of volume of the reaction mixture during a very short time, Δt . Then, a mass balance for a batch reactor gives the following equation:

$$R_n = \Delta t \frac{dMn}{dt} = \Delta t \left[\frac{1}{2} k_{c11} \sum_{r=1}^{n-1} P_r P_{n-r} + k_{c12} \sum_{r=1}^{n-1} P_r Q_{n-r} + \frac{1}{2} k_{c22} \sum_{r=1}^{n-1} Q_r Q_{n-r} + (k_{d11}P + k_{d12}Q + k_{f11}A + k_{f12}B)P_n + (k_{d22}Q + k_{d12}P + k_{f21}A + k_{f22}B)Q_n \right] \quad (29)$$

By multiplying thus equation by u^n and summing, we get

$$H(u) = \Delta t \left[\frac{1}{2} k_{c11} G(u)^2 + k_{c12} G(u)J(u) + \frac{1}{2} k_{c22} J(u)^2 + (k_{d11}G(u) + k_{d12}J(u) + k_{f11}A + k_{f12}B)G(u) + (k_{d22}J(u) + k_{d12}G(u) + k_{f22}B + k_{f21}A)J(u) \right] \quad (30)$$

The number-average molecular weight (MW_n) and weight-average molecular weight (MW_w) are obtained by the differentiation of this equation with respect to u and by the substitution of 1 for u :

$$MW_n = W \left[\frac{dH(u)/du}{H(u)} \right]_{u=1} \quad (31)$$

$$MW_w = W \left[\frac{d^2H(u)/du^2}{dH(u)/du} + 1 \right]_{u=1} \quad (32)$$

where W is the average molecular weight of the monomer unit in the polymer. If the copolymer compositions (molar fraction) are denoted by a_1 and a_2 for monomer units A and B, respectively, and the molecular weights of monomers A and B are denoted by W_1 and W_2 , respectively, W can be expressed as follows:

$$W = a_1W_1 + a_2W_2 \quad (33)$$

The detailed procedure for calculating ε_{ij} , β , and the molecular weight is described in Kang and O'Driscoll.^{10,20}

To estimate the kinetic constants, we select k_{f12} , k_{f21} , k_{r21} , and k_a as adjustable parameters and minimize the following objective function (f), which is the sum of the relative errors of conversion, the molar fraction of α -MS in the copolymer ($X_{\alpha\text{-MS}}$), and MW_w between model and experimental data:

$$f = \sum_{i=1}^n \left[\frac{C(i)_{\text{model}} - C(i)_{\text{exp}}}{C(i)_{\text{model}}} \right]^2 + \left[\frac{X_{\alpha\text{-MS}}(i)_{\text{model}} - X_{\alpha\text{-MS}}(i)_{\text{exp}}}{X_{\alpha\text{-MS}}(i)_{\text{model}}} \right]^2 + \left[\frac{MW_w(i)_{\text{model}} - MW_w(i)_{\text{exp}}}{MW_w(i)_{\text{model}}} \right]^2 \quad (34)$$

where C is the conversion. We apply QSSA to the simplified rate expression for P live polymer species and obtain the following approximation for k_{r12} :

$$k_{r12} = \frac{1}{\varepsilon_{12}Q} (k_{f12}PB - k_{f21}QA + k_{r21}\varepsilon_{21}P) \quad (35)$$

RESULTS AND DISCUSSION

We used the experimental data of Palmer et al.^{5,6} and added new data (Dube²²) at 100°C obtained under the same experimental conditions. The weight fraction of α -MS ($w_{\alpha\text{-MS}}$) was 0.1 or 0.2 at 100°C and 0.45 at 115 or 140°C in our new data. The initiator was Trigonox B [di-*tert*-butyl peroxide (DTBP)], and its concentration was fixed at 2 wt %. All available kinetic data and references are listed in Table I. Unfortunately, we have found a great discrepancy in the absolute values of the cross-propagation rate constants (k_{f12} and k_{f21} , or reactivity ratios defined as ra_1 and ra_2 , respectively) at high temperatures. The values are constant or slightly changing with the temperature in the low-temperature range. However, in recent articles,^{5,6} k_{f12} has been reported to greatly decrease with the temperature in a high-temperature range. These values are crucial in developing a dynamic model. We define q_1 as k_{r21}/k_{f12} and q_2 as k_{r12}/k_{f21} to account for the reversibility of the cross-propagation reactions because we cannot neglect the reverse reaction of the cross-propagation at high temperatures. We take q_1 as another adjustable parameter. Then, one of the reverse cross-propagation rate constants (k_{r21}) can be obtained from q_1 . The other reverse cross-propagation rate constant (k_{r12}) can be calculated from eq. (35) if the relevant kinetic constants are given. k_a is not known well even though the homotermination rate constant is, which has been chosen as another adjustable parameter.

We have placed four adjustable parameters, k_{f12} , k_{f21} , q_1 , and k_a , in one model, which is called here a four-parameter model. In the other model, we have assumed that the reactivity ratios are constant. The Alfrey-Price Q-e scheme gives $ra_1 = 0.16$ and $ra_2 = 0.41$, which have been accepted as reasonable values by many researchers.^{2,4,8,20} Therefore, we have only two adjustable parameters, q_1 and k_a , which are called here a two-parameter model. We have applied both models to the reaction system and compared the results. The profiles of the conversion, copolymer composition, and weight-average molecular weight from the two models are shown and compared in Figures 1–3, respectively. The optimized parameters and function values obtained from both models are shown in Tables II and III, respectively.

At 115 and 140°C, both models are in good agreement with the experimental data. However, at 100°C, both models show a slight deviation in predicting the

TABLE I
Parameters Used for the Modeling of α -MS/MMA Copolymerization at 100°C

	k_p (L mol ⁻¹ s ⁻¹) ^a	E_a (kcal mol ⁻¹)	k_t (L mol ⁻¹ s ⁻¹)	E_a (kcal mol ⁻¹)
Propagation and termination rate constants ^a				
α -MS	390	13	8.3×10^{11}	2
MMA	1340	6	2.3×10^9	0.7
		100°C	115°C	140°C
Equilibrium constants ^b				
K_1		22.9	0.119	54
K_2		32	0.22	0.45
		100°C	115°C	140°C
Transfer constants ($C_1 \times 10^4$, $C_f = k_{fij}/k_{fij}$)				
$C_{\alpha\text{-MS}-\alpha\text{-MS}}^c$		2.1	3.5	8
$C_{\alpha\text{-MS}-\text{MMA}}^c$		1.5	2.5	5
$C_{\text{MMA}-\text{MMA}}^d$		0.8	1.4	3.0
		k_d (s ⁻¹)	E_a (kcal/mol)	Efficiency
Initiator DTBP ^e		1.17×10^{-6}	35.01	0.5

k_p = propagation rate constant; k_t = termination rate constants; E_a = activation energy.

^a Martinet and Guillot.⁷

^b Wittmer.²

^c Brandrup and Immergut.⁴

^d Kang and O'Driscoll.¹⁰

^e Hoppe and Renken.¹²

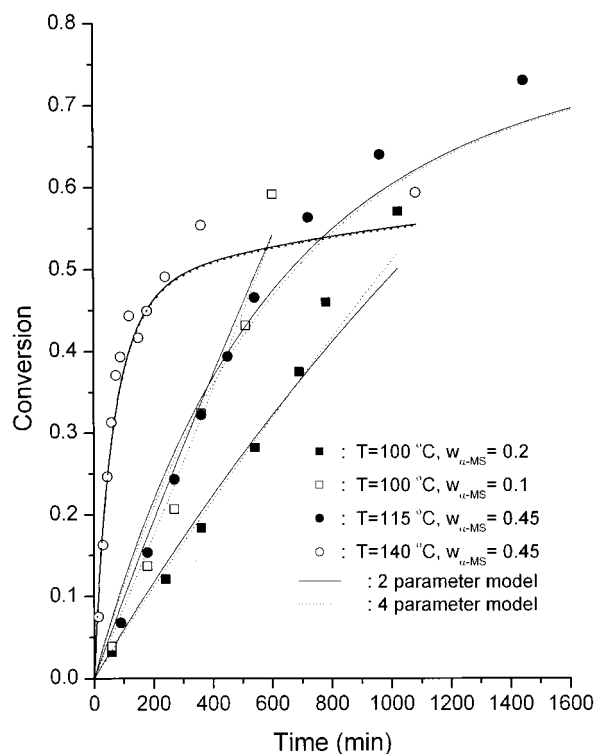


Figure 1 Comparison of the two models with experimental data for the conversion versus the time at 100°C and $w_{\alpha\text{-MS}} = 0.1$ or 0.2 and at 115 or 140°C and $w_{\alpha\text{-MS}} = 0.45$.

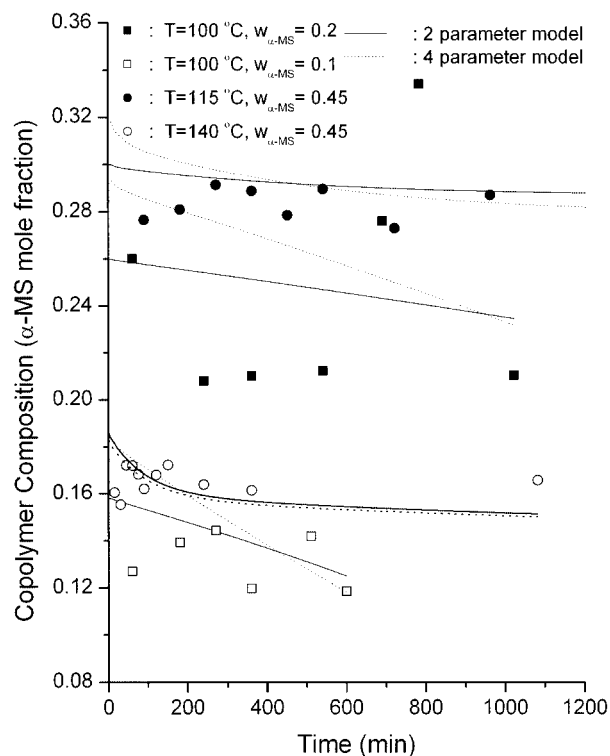


Figure 2 Comparison of the two models with experimental data for the copolymer composition versus the time at 100°C and $w_{\alpha\text{-MS}} = 0.1$ or 0.2 and at 115 and 140°C and $w_{\alpha\text{-MS}} = 0.45$.

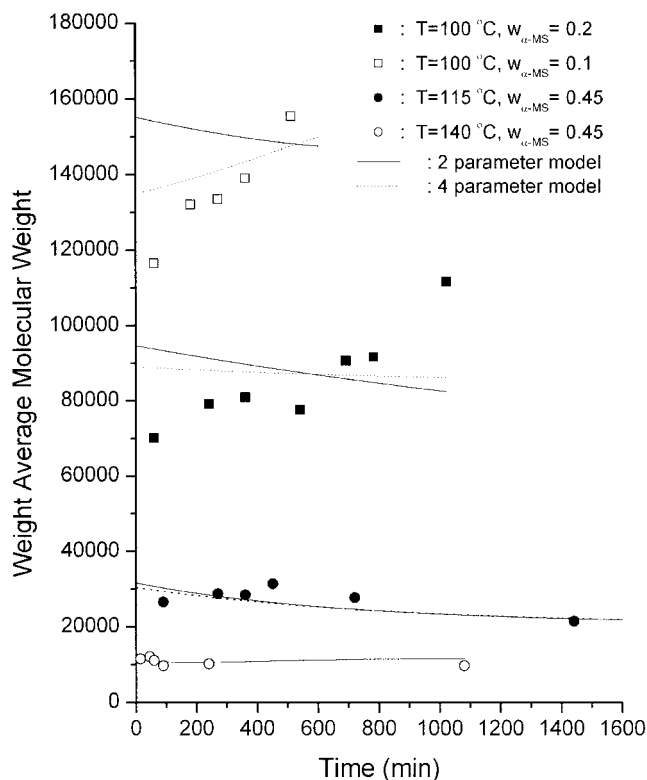


Figure 3 Comparison of the two models with experimental data for the weight-average molecular weight versus the time at 100°C and $w_{\alpha\text{-MS}} = 0.1$ or 0.2 and at 115 and 140°C and $w_{\alpha\text{-MS}} = 0.45$.

composition and molecular weight. We can also see this more clearly from the results given in Tables II and III. The final column in both tables represents the objective function value at the optimum point. The function values are almost the same at 115 and 140°C in both models. However, at 100°C, the value is almost double those at 115 and 140°C, even though it is a little more improved with the four-parameter model.

More importantly, in the case of the four-parameter model, the temperature dependence of the rate constants does not agree well with the Arrhenius equation, as shown by the values of k_{f12} and k_{f21} in Table II. In Palmer et al.'s⁵ work, k_{f12} increased (or ra_1 decreased) sharply with the temperature; it was obtained from low-conversion data. They admitted that many different solutions gave almost identical residuals. We

TABLE III
Kinetic Constants Obtained from Two-Parameter Optimization

Temperature (°C)	$w_{\alpha\text{-MS}}$	$q_2 (q_1)$	$k_a \times 10^{14}$	f
100	0.1	0.13	0.132	0.74
	0.2	0.01	0.11	0.58
115	0.45	8.2	0.23	0.33
140	0.45	19.1 (1.27)	0.8	0.24

f = function value of eq. (34) at the optimum point.

also observed that there was a broad plateau around the optimum point, which made it difficult to follow the right path toward the global optimum point. However, in the case of the two-parameter model, the data agree well with the Arrhenius equation, and there was no problem in finding the optimum path. On the basis of these considerations, we have chosen the two-parameter model instead of the four-parameter model.

Walling and Briggs²³ reported that the thermal polymerization of MMA could not be far from negligible at about 150°C. Palmer et al.'s⁵ reactivity ratio data showed that thermal initiation at 140°C could not be neglected. We have assumed that the thermal initiation rate (R_i) is third-order with respect to the monomer concentration, as assumed in many cases. We applied the two-parameter model with the set of parameters that we obtained. Here we substituted 28.3 instead of 19.1 for q_1 . The reason is discussed later. Palmer et al.'s experimental data were used to correlate R_i with the monomer concentration. We obtained the following R_i equation:

$$R_i = 1.32 \times 10^{-9}A^3 + 2.5 \times 10^{-9}B^3(\text{Lmol}^{-1}\text{s}^{-1}) \quad (36)$$

Figure 4 shows the model prediction for the copolymer composition and conversion with the feed monomer molar fraction in the case of purely thermally initiated copolymerization. The model shows a slight deviation for the conversion in the low-feed-composition region and the copolymer composition in the high-feed-composition region. However, the model prediction is good in the intermediate region, in which the experiment for thermal initiation [temperature = 140°C; $w_{\alpha\text{-MS}} = 0.45$; molar fraction of $\alpha\text{-MS}$ in the monomer ($x_{\alpha\text{-MS}} = 0.41$); molar ratio of $\alpha\text{-MS}$ to MMA

TABLE II
Kinetic Constants Obtained from Four-Parameter Optimization

Temperature (°C)	$w_{\alpha\text{-MS}}$	$k_{f12} \times 10^6$	$k_{f21} \times 10^6$	$q_1 (q_2)$	$k_a \times 10^{14}$	f
100	0.1	0.41	1.0	25.8	1.0	0.57
	0.2	0.45	1.054	22.5	0.91	0.51
115	0.45	0.351	1.076	39.8	0.33	0.30
140	0.45	1.28	0.41	18.3 (1.3)	2.15	0.23

f = function value of eq. (34) at the optimum point.

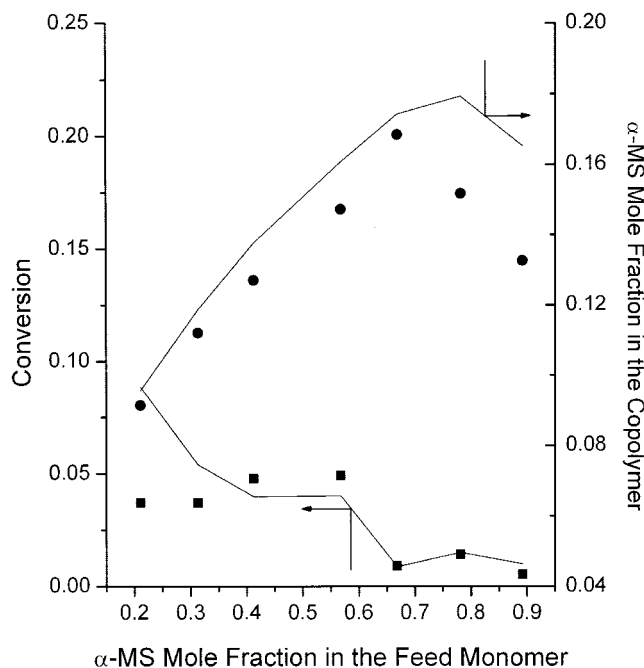


Figure 4 Prediction of the two-parameter model for the conversion and copolymer composition in the case of thermally initiated copolymerization at 140°C.

($f_{\alpha\text{-MS}} = 0.69$) and the full-conversion experiment were carried out. Therefore, we neglected this deviation and used this equation because R_i is not so large in comparison with the chemical initiation. We added this equation to the main program and updated the optimization routine. The optimum point for the adjustable parameters did not change, but the objective function value changed slightly. Further simulation trials showed that a slight difference in the R_i equation did not change the results of the optimization.

Many interesting phenomena of reversible polymerization reactions were analyzed by Palmer et al.^{5,6} A more detailed investigation (Fig. 3) reveals that the model prediction of the molecular weight is in good agreement with the experimental data at 115 and 140°C, but the model shows the opposite trend against the experimental data at 100°C. The experimental data show a slight increase in the molecular weight with time, whereas the two-parameter model shows a slight decrease with time as expected. An increase in the molecular weight with time is not expected in free-radical polymerization under normal circumstances. For a better appreciation of the experimental data for the molecular weight, we show the polydispersity indices and the weight-average molecular weights versus the conversion in Table IV. The polydispersity indices are lower than 1.5 in most cases, although from a theoretical point of view, they should exceed 1.5. This is more pronounced in the low-molecular-weight range. The same phenomena have been observed in other experimental results.⁸ It is possible

TABLE IV
Weight-Average Molecular Weight (M_w) and Polydispersity Index (PDI) with Conversion at 100, 115, and 140°C

Temperature (°C)	$w_{\alpha\text{-MS}}$	Conversion	M_w	PDI
100	0.1	0.039	116,606	1.45
		0.137	132,065	1.48
		0.207	133,574	1.47
		0.324	139,096	1.48
		0.432	155,486	1.58
		0.592	236,334	1.95
	0.2	0.032	70,099	1.44
		0.121	79,208	1.37
		0.184	81,000	1.41
		0.282	77,624	1.52
		0.375	90,638	1.43
		0.46	91,668	1.44
		0.571	111,666	1.47
		0.694	145,486	1.95
115	0.45	0.068	26,550	1.29
		0.243	28,800	1.27
		0.322	28,440	1.33
		0.394	31,420	1.45
		0.563	27,750	1.49
		0.730	21,510	1.81
140	0.45	0.075	11,520	1.35
		0.247	12,090	1.30
		0.313	11,130	1.41
		0.383	9,756	1.44
		0.491	10,210	1.48
		0.594	9,695	1.64

that this is due to errors from the gel permeation chromatography analysis inherent in the low-molecular-weight regime.

Considering now that the polydispersity index is about 1.5 in the temperature range tested, we can assume that radicals terminate predominantly via combination. A large value of the cross-termination factor ϕ (see eq 37) is an indication that cross-termination is greatly favored. Therefore, we can assume that termination takes place predominantly via a combination of unlike radicals.

We can calculate the cross-termination rate constant and ϕ , which is defined as the ratio of the cross-termination rate constant to the geometric mean of the

TABLE V
Cross-Termination Reaction Rate Constants (k_{t12} 's) and Cross-Termination Factors (Φ 's) at Different Weight Fractions at 100, 115, and 140°C

Temperature (°C)	$w_{\alpha\text{-MS}}$	$f_{\alpha\text{-MS}}$	$k_{t12} \times 10^{13}$	Φ
100	0.1	0.094	0.060	103
	0.2	0.21	0.127	227
115	0.45	0.69	0.255	422
115 (4 wt % initiator) ^{*a}	0.45	0.69	0.242	400
140	0.45	0.69	0.340	505
140 ^{*a}	0.29	0.35	0.170	255

^a Data from Palmer et al.^{5,6}

two homotermination rate constants, with the following equation:

$$\phi = \frac{k_{t12}}{\sqrt{k_{t11}k_{t22}}} \quad (37)$$

We show the results from the two-parameter model in Table V. The tendency toward cross-termination parallels the tendency toward cross-propagation, in that ϕ increases as the product of ra_1 and ra_2 approaches zero. In the case of favorable cross-propagation, ϕ is very large.^{16,17} ϕ varies from 2 to 60 in the range of 60–80°C for α -MS/MMA copolymerization.⁸ Furthermore, it has been reported that ϕ depends on the monomer feed composition.^{15,16} We have plotted ϕ with the feed molar ratio of α -MS to MMA in Figure 5. ϕ increases almost linearly with the feed molar ratio of α -MS to MMA, although the experimental data were obtained under different temperatures and initiator concentrations. This effect is ascribed to the influence of the penultimate unit in the copolymer unit. In a mixture with a high ratio of MMA to α -MS, the penultimate units of the radicals ending with α -MS are predominantly MMA. The cross-termination is hindered by the repulsion between the penultimate unit of this radical and the MMA end of the other radical.^{15,16} Furthermore, the absolute values of ϕ in our system are much larger than those in other systems that favor cross-termination. For example, ϕ ranges

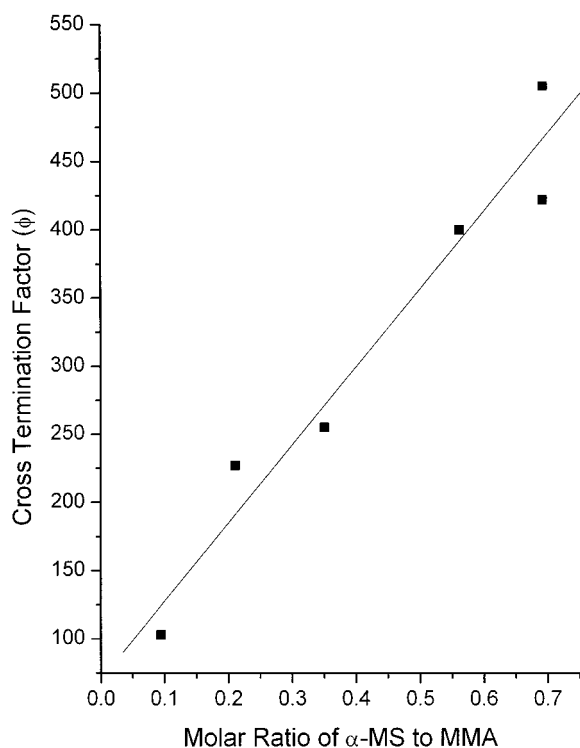


Figure 5 Correlation between ϕ and the feed molar ratio of α -MS to MMA.

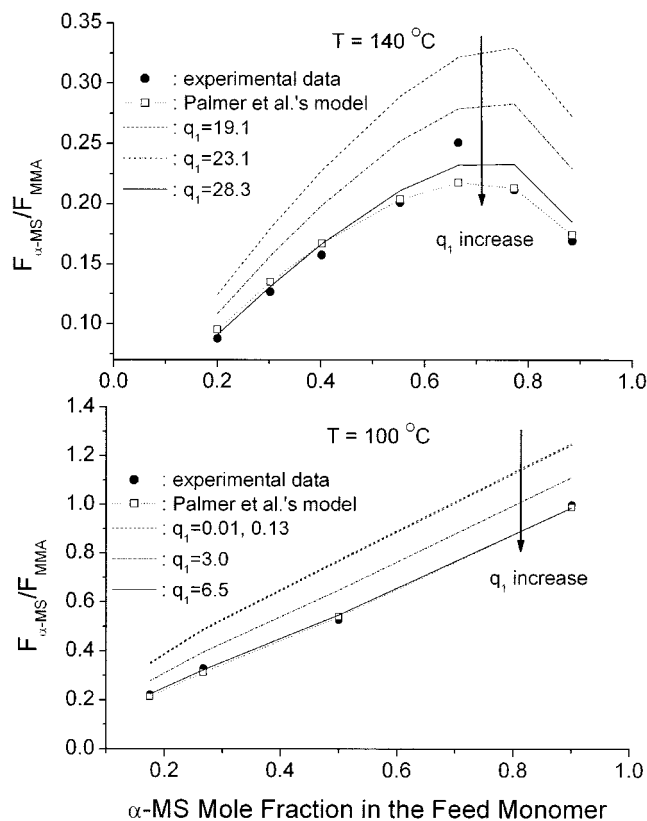


Figure 6 Effects of the variation of q_1 on the correlation between the copolymer composition and the monomer composition at 100 and 140°C.

from 10 to 150 for the copolymerization of styrene with some methacrylates,^{16,17} whereas it ranges from 150 to 500 in our case. This is attributed to the larger steric hindrance of the α -carbon atom in α -MS in comparison with that of styrene.¹⁵

Subsequently, we calculated Kruger et al.'s¹⁹ copolymer composition equation with a set of reactivity ratios obtained from the two-parameter model, and we compare the results with Palmer et al.'s⁵ experimental data at low conversions and the predictions of their model in Figure 6. The long dashed line represents results calculated with the two-parameter model. Although it shows the same trends with the experimental data, there is a discrepancy between the model predictions and the experimental data. Through some trials, we found that a slight increase in the q_1 parameter without changes in the other parameters would improve the model prediction. We finally obtained new optimum values for q_1 from low-conversion data: 28.3 at 140°C, 14.2 at 115°C, and 6.5 at 100°C. The solid line in Figure 6 represents the results calculated from the modified model with the new q_1 values, which agree quite well with the experimental data. In reactivity ratio experiments, the conversion was kept below 5%. This means that a large q_1 value goes well with the experimental data of low conver-

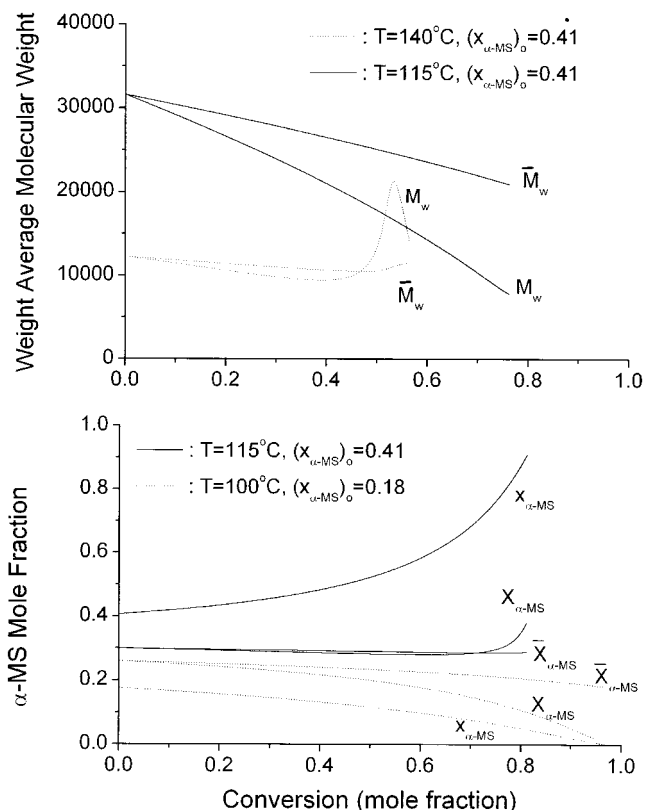


Figure 7 Profiles of the copolymer composition and weight-average molecular weight with the conversion (M_{w0} = instantaneous weight-average molecular weight; \bar{M}_w = cumulative weight-average molecular weight, $x_{\alpha\text{-MS}}$ = instantaneous molar fraction of α -MS in the monomer; $X_{\alpha\text{-MS}}$ = instantaneous molar fraction of α -MS in the polymer; $\bar{X}_{\alpha\text{-MS}}$ = cumulative molar fraction of α -MS in the polymer).

sions, whereas a small q_1 value goes well with the experimental data of high conversions. The reverse reaction of cross-propagation is probably retarded at high conversions. In full-conversion experiments, the conversion increases with time, and the copolymer molecular weight is over 10,000, so the reaction mixture is quite viscous even though the viscosity is still low enough not to cause a significant gel effect. One expects that the high viscosity would retard the reverse reaction to a certain degree. For thermal initiation, we applied 28.1 instead of 19.1 for q_1 because a high value of q_1 fits the real system well.

The main objective of developing a dynamic model is to investigate the dynamic behavior of the reaction system under various operating conditions and to determine optimized process conditions. Both the molecular weight and the composition are important properties in determining copolymer applications. Particularly in a batch process, it is very important to keep these properties constant in the copolymer throughout the whole conversion range. We present the typical dynamic behavior of these properties in a batch reactor in Figure 7. The overbar represents the

cumulative property, and the subscript zero stands for the initial state. The upper portion of Figure 7 shows the instantaneous and cumulative weight-average molecular weights as a function of the conversion at 115 and 140°C. At 140°C, the instantaneous molecular weight changes greatly with the conversion. During the initial stages, the instantaneous molecular weight decreases because the monomer concentration decreases with conversion, but it turns back and increases sharply as the initiator is slowly depleted with conversion. As the initiator is almost depleted, thermal initiation dominates, and so the instantaneous molecular weight decreases again. Nevertheless, the cumulative molecular weight is almost constant throughout the whole conversion range. However, at 115°C, both the instantaneous and cumulative molecular weights decrease monotonically with conversion. The initiator is not depleted throughout the reaction. As expected, the molecular weight decreases with temperature. The lower portion of Figure 7 shows the instantaneous and cumulative copolymer compositions of α -MS as a function of the conversion under two different reaction conditions. At 100°C and an α -MS molar fraction of 0.18 in the feed, the copolymer is richer in MMA than the monomer because MMA in the monomer is consumed faster. The reaction goes to completion at 100°C. At 115°C and an α -MS molar fraction of 0.41, the copolymerization behavior is different. The copolymer composition is almost constant because the instantaneous copolymer composition is constant throughout most of the conversion range. Although the instantaneous copolymer composition increases after 75% conversion, the copolymer composition stays almost constant because the reaction does not proceed further on account of equilibrium.

CONCLUSIONS

The kinetic parameters for a dynamic model for the copolymerization of α -MS and MMA at high temperatures have been estimated and validated through full-conversion experimental data. The values for the reactivity ratios obtained from a Q-e scheme are reasonable. By the application of this model, we have determined the following:

1. The cross-termination reaction rate constant is large in a high-temperature range.
2. ϕ increases almost linearly with the molar ratio of α -MS to MMA.
3. The termination reaction proceeds dominantly via a combination of unlike radicals.

This model may provide the basis for an understanding of the dynamic behavior of batch reactors for copolymerization with depropagation and the basis

for theoretical and experimental investigations for the optimization and control of industrial reactors.

NOMENCLATURE

A	concentration of α -MS (mol/L)
a_1	copolymer composition (molar fraction) of monomer unit A
a_2	copolymer composition (molar fraction) of monomer unit B
β	ratio of the total concentration of live polymer Q species to that of live polymer P species
B	concentration of MMA (mol/L)
C	conversion
Δt	reaction time
ε_{ij}	conditional probability of an A_i unit ending with penultimate unit A_j
ϕ	cross-termination factor
f	objective function
$f_{\alpha\text{-MS}}$	molar ratio of α -MS to MMA
f_i	efficiency of initiation reaction
$G(u)$	generating function for the calculation of the molecular weight
$H(u)$	generating function for the calculation of the molecular weight
I	concentration of the initiator (mol/L)
k_a	apparent termination rate constant (L/mol min)
k_{cij}	combination termination rate constant (L/mol min)
k_d	initiator decomposition rate constant (1/min)
k_{dij}	disproportionation termination rate constant (L/mol min)
k_{fij}	propagation rate constant for a monomer of type i with a live polymer of type j (L/mol min)
k_{frij}	transfer reaction rate constant (L/mol min)
k_{iA}	initiation rate constant for monomer A (L/mol min)
k_{iB}	initiation rate constant for monomer B (L/mol min)
k_{rij}	depropagation rate constant for a monomer of type i with a live polymer of type j (1/min)
M_n	concentration of the dead polymer (mol/L)
MW_n	number-average molecular weight
MW_w	weight-average molecular weight
P	total concentration of live polymer P_i species (mol/L)

P_i	concentration of active polymer of length i ending in monomer unit A (mol/L)
Q	total concentration of live polymer Q_i species (mol/L)
q_1	k_{r21}/k_{f12}
q_2	k_{r12}/k_{f21}
Q_i	concentration of active polymer of length i ending in monomer unit B (mol/L)
$Q(u)$	generating function for the calculation of the molecular weight
$R\cdot$	concentration of primary radical
R_i	thermal initiation rate (mol/L min)
R_n	amount of the dead polymer produced per unit of volume of the reaction mixture during a very short time (Δt)
W	average molecular weight of the monomer unit in the polymer
W_1	molecular weight of monomer A
W_2	molecular weight of monomer B
$w_{\alpha\text{-MS}}$	weight fraction of α -MS
$x_{\alpha\text{-MS}}$	molar fraction of α -MS in the monomer
$X_{\alpha\text{-MS}}$	molar fraction of α -MS in the copolymer

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