

# Kinetic Parameter Estimation for the MMA/MA Copolymerization System

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**ABSTRACT:** The mathematical model for a batch methyl methacrylate (MMA) and methyl acrylate (MA) copolymerization system was simplified by applying the pseudo-kinetic rate constant method and used for the estimation of parameters for various reaction rate constants. For this, the polymerization experiment was conducted under a variety of reaction conditions and the Levenberg-Marquardt method was employed. The state variables selected for the parameter estimation were the solid content and the number and weight average molecular weights. The validity of the estimated parameters was corroborated by conducting experiments under different reaction conditions and the newly estimated parameter values were found to be superior to the ones reported in the literature. Thus the kinetic parameters estimated in this study may be used to predict the properties of polymer product obtained by solution MMA/MA copolymerization. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2554–2564, 2000

**Key words:** batch; MMA/MA; copolymerization; kinetic parameters; estimation

## INTRODUCTION

Polymerization reactors are commonly encountered in process industries. Development of a rigorous mathematical model for a polymerization reactor makes it possible to predict not only the dynamics of the reactor but also the properties of polymer product. The reliability of the model, however, depends on the model parameters. Indeed, well-estimated model parameters can enhance the performance of computer simulation and control.

Parameters in bulk and solution polymerization reactor models are usually obtained from very careful measurements of conversion and molecular weights. The discrepancy between the predicted values and the actual measurements is generally attributed to inaccurate values for the kinetic parameters and other model parameters.

A number of publications have dealt with the problem of estimating such unknown parameters by minimizing the sum of squares of the differences between the measured and computed values of the output. Rosenbrock and Storey<sup>1</sup> described the method of minimizing such an objective function by integrating the differential equations and calculating the outputs at those points in time where measured values are available.

Investigating the kinetics and modeling of bulk styrene-acrylonitrile copolymerization, Garcia-Rubio et al.<sup>2</sup> employed the minimization of a weighted, nonlinear, least squares criterion involving molar conversion and residual monomer mole fraction. Bhattacharya and Hamielec<sup>3</sup> used a sixth-order Runge-Kutta differential equation solver within a Gauss-Marquardt optimization scheme to estimate parameters for the bulk thermal copolymerization of styrene-paramethyl styrene. The kinetic parameters of batch solution polymerization of MMA were estimated by Ponuswamy et al.<sup>4</sup> using the experimental data.

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**Table I Mechanism for Free-Radical Copolymerization**

<b>Initiation</b>	<b>Propagation</b>
$I \xrightarrow{k_d} 2\varphi \cdot$	$R_{m,n,1} \cdot + M_1 \xrightarrow{k_{11}} R_{m+1,n,1} \cdot$
$\varphi \cdot + M_1 \xrightarrow{k_{i1}} R_{1,0,1} \cdot$	$R_{m,n,1} \cdot + M_2 \xrightarrow{k_{12}} R_{m,n+1,2} \cdot$
$\varphi \cdot + M_2 \xrightarrow{k_{i2}} R_{0,1,2} \cdot$	$R_{m,n,2} \cdot + M_1 \xrightarrow{k_{21}} R_{m+1,n,1} \cdot$
$D \cdot + M_1 \xrightarrow{k_{iD2}} R_{1,0,1} \cdot$	$R_{m,n,2} \cdot + M_2 \xrightarrow{k_{22}} R_{m,n+1,2} \cdot$
$D \cdot + M_2 \xrightarrow{k_{iD2}} R_{0,1,2} \cdot$	
$S \cdot + M_1 \xrightarrow{k_{iS2}} R_{1,0,1} \cdot$	
$S \cdot + M_2 \xrightarrow{k_{iS2}} R_{0,1,2} \cdot$	
<b>Termination</b>	<b>Chain Transfer</b>
$R_{m,n,1} \cdot + R_{r,s,1} \cdot \xrightarrow{k_{td11}} P_{m,n} + P_{r,s}$	$R_{m,n,1} \cdot + M_1 \xrightarrow{k_{f11}} P_{m,n} + R_{1,0,1} \cdot$
$R_{m,n,1} \cdot + R_{r,s,1} \cdot \xrightarrow{k_{tc11}} P_{m+r,n+s}$	$R_{m,n,1} \cdot + M_2 \xrightarrow{k_{f12}} P_{m,n} + R_{0,1,2} \cdot$
$R_{m,n,1} \cdot + R_{r,s,2} \cdot \xrightarrow{k_{td12}} P_{m,n} + P_{r,s}$	$R_{m,n,2} \cdot + M_1 \xrightarrow{k_{f21}} P_{m,n} + R_{1,0,1} \cdot$
$R_{m,n,1} \cdot + R_{r,s,2} \cdot \xrightarrow{k_{tc12}} P_{m+r,n+s}$	$R_{m,n,2} \cdot + M_2 \xrightarrow{k_{f22}} P_{m,n} + R_{0,1,2} \cdot$
$R_{m,n,2} \cdot + R_{r,s,1} \cdot \xrightarrow{k_{td21}} P_{m,n} + P_{r,s}$	$R_{m,n,1} + D \xrightarrow{k_{f1D}} P_{m,n} + D \cdot$
$R_{m,n,2} \cdot + R_{r,s,1} \cdot \xrightarrow{k_{tc21}} P_{m+r,n+s}$	$R_{m,n,2} + D \xrightarrow{k_{f2D}} P_{m,n} + D \cdot$
$R_{m,n,2} \cdot + R_{r,s,2} \cdot \xrightarrow{k_{td22}} P_{m,n} + P_{r,s}$	$R_{m,n,1} + S \xrightarrow{k_{f1S}} P_{m,n} + S \cdot$
$R_{m,n,2} \cdot + R_{r,s,2} \cdot \xrightarrow{k_{tc22}} P_{m+r,n+s}$	$R_{m,n,2} + S \xrightarrow{k_{f2S}} P_{m,n} + S \cdot$

Hwang et al.<sup>5</sup> developed a mathematical model for a batch reactor in which binary free-radical copolymerization occurs. In particular, these authors formulated the chain-length-dependent termination rate constant by using the continuous probability function.

In this study, we set up a mathematical model for a batch reactor in which solution free-radical methyl methacrylate (MMA)/methyl acrylate (MA) copolymerization takes place and simplify the rate expressions by using the pseudo-kinetic rate constant method. Experiments are then conducted under several reaction conditions and the results are used to estimate the kinetic parameters by employing the Levenberg-Marquardt method. The estimated parameters are validated by additional experiments.

## MATHEMATICAL MODELING

We consider the free radical copolymerization of MMA and MA, which is assumed to follow the reaction mechanism summarized in Table I. The initiator to be used here is 2,2' azobis-isobutyronitrile (AIBN).

The first step is the formation of free radicals  $\varphi$  by decomposition of initiator  $I$  with rate constant  $k_d$ , and then the free radical reacts with monomer to form primary radicals. For the propagation reaction, additions of monomers to free radicals  $R_{m,n,i} \cdot$  proceed with rate constant  $k_{ij}$ , where  $R_{m,n,i} \cdot$  represents the polymer radical whose terminal is monomer  $i$  with  $m$  units of monomer 1 and  $n$  units of monomer 2, respectively. Terminal model thus gives four distinct propagation rate

constants  $k_{11}$ ,  $k_{12}$ ,  $k_{21}$ , and  $k_{22}$ , where  $k_{ij}$  indicates the reactions of polymer radical  $i$  with monomer  $j$ . It is to be noted that the mechanism assumes a chain-length independent propagation rate constant. We also consider chain transfer reactions to monomers  $M_1$  and  $M_2$ , chain transfer agent  $D$  and solvent  $S$ . In the terminal model, there are two kinds of termination reactions: one by disproportionation and the other by combination.

By considering the elementary reactions discussed in the above, we can derive the rate expressions for the radical and polymer in the copolymerization reaction system. In order to reduce the complexity of the rate expressions, the pseudo-kinetic rate constant method (PKRCM), which was introduced by Hamielec et al.<sup>6</sup> and developed further by Tobita and Hamielec<sup>7</sup> and Hwang et al.,<sup>5</sup> is applied to the present copolymerization system. On the basis of the terminal model for free-radical copolymerization, the pseudo-kinetic rate constants for propagation, termination, and chain transfer reactions may be expressed by the following equations.<sup>5</sup>

$$\bar{k}_p = \sum_{i=1}^2 \sum_{j=1}^2 k_{ij} \Phi_i f_j \quad (1)$$

$$\bar{k}_t = \bar{k}_{td} + \bar{k}_{tc} = \sum_{i=1}^2 \sum_{j=1}^2 k_{tij} \Phi_i \Phi_j \quad (2)$$

$$\bar{k}_{fM} = \sum_{i=1}^2 \sum_{j=1}^2 k_{fij} \Phi_i f_j \quad (3)$$

$$\bar{k}_{fD} = \sum_{i=1}^2 k_{fDi} \Phi_i \quad (4)$$

$$\bar{k}_{fS} = \sum_{i=1}^2 k_{fSi} \Phi_i \quad (5)$$

where

$$\Phi_1 = \frac{[R_1 \cdot]}{[R_1 \cdot] + [R_2 \cdot]} \cong \frac{k_{21} f_1}{k_{21} f_1 + k_{12} f_2},$$

$$\Phi_2 = \frac{[R_2 \cdot]}{[R_1 \cdot] + [R_2 \cdot]} \cong \frac{k_{12} f_2}{k_{21} f_1 + k_{12} f_2}$$

$$[R_1 \cdot] = \sum_{m=1}^{\infty} \sum_{n=0}^{\infty} [R_{m,n,1} \cdot],$$

$$[R_2 \cdot] = \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} [R_{m,n,2} \cdot]$$

$$f_i = M_i/M, \quad M = M_1 + M_2$$

The model also contains the moment equations of the living and dead polymer concentrations defined as follows:

$$G_k = \sum_{r=1}^{\infty} r^k \{ [R_{r,1} \cdot] + [R_{r,2} \cdot] \} \quad (6)$$

$$H_k = \sum_{r=1}^{\infty} r^k [P_r] \quad (7)$$

where  $G_k$  and  $H_k$  represent the  $k$ -th moment of the living and dead polymer concentrations, respectively. Here,  $[R_{r,i} \cdot]$  denotes the concentration of living polymer with monomer  $i$  as the terminal and  $r$  units of monomer and  $[P_r]$  is the concentration of dead polymer with  $r$  units of monomer. The adoption of eqs. (1)–(7) reduces the complex kinetic rate expressions to simpler ones so that mass balances for various species in a batch MMA/MA copolymerization reactor give rise to the following equations.<sup>5</sup>

$$\frac{1}{V} \frac{d(IV)}{dt} = -k_d I \quad (8)$$

$$\frac{1}{V} \frac{d(SV)}{dt} = -\bar{k}_{fS} S G_0 \quad (9)$$

$$\frac{1}{V} \frac{d(DV)}{dt} = -\bar{k}_{fD} D G_0 \quad (10)$$

$$\frac{1}{V} \frac{d(MV)}{dt} = -2fk_d I - (\bar{k}_p M + \bar{k}_{fM} M + \bar{k}_{fD} D + \bar{k}_{fS} S) G_0 \quad (11)$$

$$\frac{1}{V} \frac{d(G_0 V)}{dt} = 2fk_d I - \bar{k}_t G_0^2 \quad (12)$$

$$\frac{1}{V} \frac{d(G_1V)}{dt} = 2fk_dI + \overline{k_p}MG_0 - \overline{k_t}G_0G_1 + (\overline{k_{fM}}M + \overline{k_{fD}}D + \overline{k_{fS}}S)(G_0 - G_1) \quad (13)$$

$$\frac{1}{V} \frac{d(G_2V)}{dt} = 2fk_dI + \overline{k_p}M(G_0 + 2G_1) - \overline{k_t}G_0G_2 + (\overline{k_{fM}}M + \overline{k_{fD}}D + \overline{k_{fS}}S)(G_0 - G_2) \quad (14)$$

$$\frac{1}{V} \frac{d(H_0V)}{dt} = \left( \overline{k_{td}} + \frac{1}{2} \overline{k_{tc}} \right) G_0^2 + (\overline{k_{fM}}M + \overline{k_{fD}}D + \overline{k_{fS}}S)G_0 \quad (15)$$

$$\frac{1}{V} \frac{d(H_1V)}{dt} = (\overline{k_t}G_0 + \overline{k_{fM}}M + \overline{k_{fD}}D + \overline{k_{fS}}S)G_1 \quad (16)$$

$$\frac{1}{V} \frac{d(H_2V)}{dt} = (\overline{k_t}G_0 + \overline{k_{fM}}M + \overline{k_{fD}}D + \overline{k_{fS}}S)G_2 + \overline{k_{tc}}G_1^2 \quad (17)$$

As the monomer is converted to the polymer, the density of the reaction mixture increases and the volume of the reaction mixture  $V$  shrinks. Rearranging the total mass balance equation, one can obtain the following equation that can be used to calculate the change in the volume of the reaction mixture<sup>8</sup>; that is,

$$\frac{dV_p}{dt} = -\frac{1}{\rho_p} \left[ W_{M_1} \frac{d(M_1V)}{dt} + W_{M_2} \frac{d(M_2V)}{dt} + W_s \frac{d(SV)}{dt} \right] \quad (18)$$

$$V_{M_1} = (M_1V) \frac{W_{M_1}}{\rho_{M_1}}, \quad V_{M_2} = (M_2V) \frac{W_{M_2}}{\rho_{M_2}},$$

$$V_s = (SV) \frac{W_s}{\rho_s} \quad (19)$$

where  $W_j$  and  $V_j$  represent the weight and volume fractions, respectively, of species  $j$ .

Average molecular weights of polymers are determined in the same manner as homopolymerization except that the molecular weight of monomer is used in the form of instantaneous average molecular weight,  $M_{av}(t) = M_1F_1 + M_2F_2$ , where  $F_i$  represents the instantaneous copolymer composition. Then the number and weight aver-

age molecular weights can be calculated by the following equations:

$$M_n = \frac{\int_0^t \left\{ \frac{d(G_1V)}{V dt} + \frac{d(H_1V)}{V dt} \right\} M_{av}(t) dt}{\int_0^t \left\{ \frac{d(G_0V)}{V dt} + \frac{d(H_0V)}{V dt} \right\} dt} \quad (20)$$

$$M_w = \frac{\int_0^t \left\{ \frac{d(G_2V)}{V dt} + \frac{d(H_2V)}{V dt} \right\} M_{av}^2(t) dt}{\int_0^t \left\{ \frac{d(G_1V)}{V dt} + \frac{d(H_1V)}{V dt} \right\} M_{av}(t) dt} \quad (21)$$

Table II shows the rate constants and reactivity ratios available in the literature for the experimental conditions of this study. In regard to the termination rate constants,  $k_{t11}$  and  $k_{t22}$  are the same as those used in the homopolymerization system and, for  $k_{t12}$  and  $k_{t21}$ , Atherton and North<sup>9</sup> suggested the following relationship:

$$k_{t12} = k_{t21} = F_1k_{t11} + F_2k_{t22} \quad (22)$$

In this study, the changes in the densities of reactants and product with the reaction temperature are considered. Physical properties of reactants and product are listed in Table III.

Gel effect is an important phenomenon in free-radical polymerization that occurs at high monomer conversion. For MMA homopolymerization, this is taken into account by introducing the following correlations for the gel and glass effects, suggested by Ross and Laurence<sup>12</sup>:

$$k_{11} = g_{p1}(k_{11})_0 \quad (23)$$

$$k_{t11} = g_{t1}(k_{t11})_0 \quad (24)$$

where subscript 0 denotes the value at zero conversion and  $g_{p1}$  and  $g_{t1}$  represent the gel effect correlations for propagation and termination, respectively. For MMA homopolymerization, these are expressed as follows:

$$g_{p1} = \begin{cases} 1.0 & V_f > V_{fpc} \\ 7.1 \times 10^{-5} \exp(171.53V_f) & V_f \leq V_{fpc} \end{cases} \quad (25)$$

$$V_{fpc} = 0.05$$

**Table II** Reaction Rate Constants Available in the Literature ( $T$  in [K])

Rate Constants [L/mol · s]	Symbol	Correlation Equations	Reference
Initiation	$k_d^a$	$5.88 \times 10^{15} \exp(-31,788/RT)$	10
Propagation	$(k_{11})_0$	$4.77 \times 10^7 \exp(-7,478/RT)$	12
	$(k_{22})_0$	$2.656 \times 10^8 \exp(-7,100/RT)$	15
Reactivity ratio	$r_1$	2.15	13
	$r_2$	0.4	13
Termination <sup>b</sup>	$(k_{t11})_0$	$6.58 \times 10^{10} \exp(-5,043/RT)$	10
	$(k_{t22})_0$	$9.850 \times 10^{10} \exp(-5,290/RT)$	15
Chain transfer to monomer	$k_{f11}$	$2.00 \times 10^{-4} \times k_{11}$	11
	$k_{f22}$	$1.25 \times 10^{-4} \times k_{22}$	11
Chain transfer to solvent	$k_{f1S}$	$8.293 \times 10^{-4} \times k_{11}$	17
	$k_{f2S}$	$2.7 \times 10^{-4} \times k_{22}$	16
Chain transfer to chain transfer agent	$k_{f1D}$	$0.6 \times k_{11}$	11
	$k_{2fD}$	$0.4 \times k_{22}$	11

<sup>a</sup> Unit in [1/s].<sup>b</sup>  $k_\lambda = k_{td}/k_t = 34.81 \exp(-2,913.6/RT)$ .<sup>10</sup> $g_{t1}$ 

$$= \begin{cases} 0.10575 \exp(17.15V_f - 0.01715T)V_f > V_{frc} \\ 2.3 \times 10^{-6} \exp(75.0V_f) & V_f \leq V_{frc} \end{cases} \quad (26)$$

$$V_{frc} = 0.1856 - 2.956 \times 10^{-4}T$$

where  $T$  is the reactor temperature ([°C]), and  $V_{fpc}$  and  $V_{frc}$  are the critical free volumes for propagation and termination ([Å<sup>3</sup>/molecule]), respectively.  $V_f$  denotes the free volume of the reaction mixture and defined as follows:

$$V_f = \phi_{M_1}V_{f,M_1} + \phi_{M_2}V_{f,M_2} + \phi_S V_{f,S} + \phi_P V_{f,P} \quad (27)$$

$$V_{f,M_1} = 0.025 + 1.0 \times 10^{-3}(T - T_{g,M_1}) \quad (28)$$

$$V_{f,M_2} = 0.025 + 1.0 \times 10^{-3}(T - T_{g,M_2}) \quad (29)$$

$$V_{f,S} = 0.025 + 1.0 \times 10^{-3}(T - T_{g,S}) \quad (30)$$

$$V_{f,P} = 0.025 + 4.8 \times 10^{-4}(T - T_{g,P}) \quad (31)$$

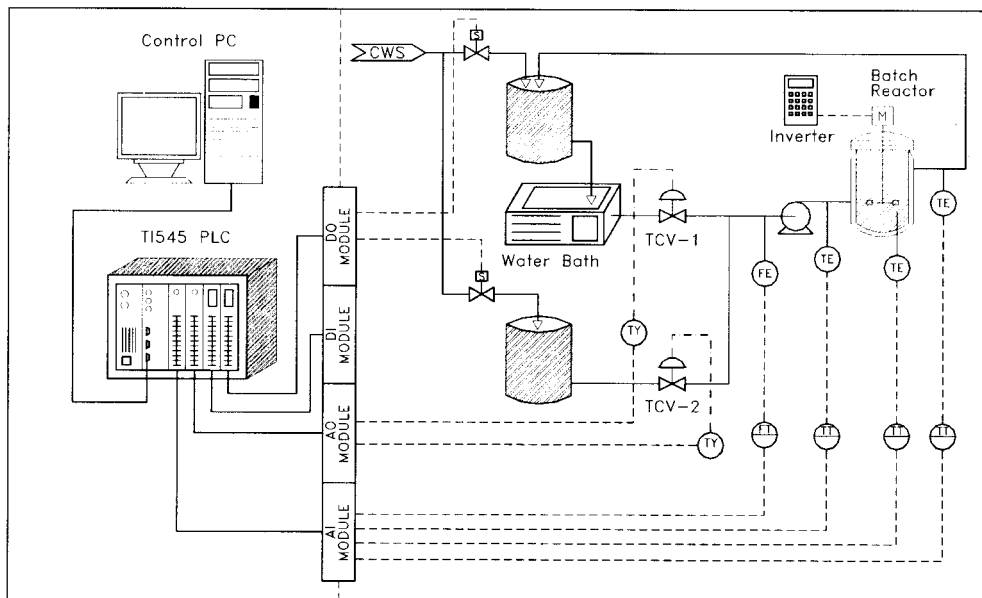
where  $T_{g,M_1}$ ,  $T_{g,M_2}$ ,  $T_{g,S}$  and  $T_{g,P}$  are the glass transition temperatures for monomer 1, monomer 2, solvent and polymer, respectively, whose values are given in Table III. For the glass transition temperature for the copolymer, the Gordon-Taylor-Wood equation is used:

$$T_g = T_{g,PMMA} - (1/k)(T_g - T_{g,PMA})(1 - w_{MMA})/w_{MMA} \quad (32)$$

where  $T_{g,PMMA}$  and  $T_{g,PMA}$  are the glass transition temperatures for MMA and MA homopolymers, respectively, and  $w_{MMA}$  denotes the weight fraction of MMA. The parameter  $k$  can be determined in terms of the thermal expansion coefficient

**Table III** Physical Properties of Various Species ( $T$  in [°C])

	Density [g/L]	Glass Transition Temperature [°C]
MMA	$965.4 - 1.090T - 9.7 \times 10^{-4}T^2$	-106.0
MA	$976.5 - 1.15T$	-106.0
Toluene	$888.32 - 9.824 \times 10^{-4}T$	-92.0
Copolymer	$1195 - 1.0583 \times 10^{-1}T - 8.2093 \times 10^{-3}T^2$	—
PMMA	—	105.0
PMA	—	6.0



**Figure 1** Schematic diagram of the experimental set-up for batch MMA/MA copolymerization.

coefficients of the homopolymers in the liquid and in the glassy state,  $\alpha^l$  and  $\alpha^g$ , where  $\alpha = dv/dT$  and  $v$  is the specific volume. From the experimental data, Garcia et al.<sup>13</sup> determined the value of  $k$  as 0.43, and this value was used in eq. (32).

For MA homopolymerization, the gel effect is considered by introducing the correlations suggested by Pinto and Ray.<sup>14</sup>

$$g_{p2} = 1 \quad (33)$$

$$g_{t2} = \exp(-0.4407x - 6.7530x^2 - 0.3495x^3) \quad (34)$$

where  $x$  is the monomer conversion.

## EXPERIMENTAL

The jacketed pyrex reactor has a capacity of 1 L and contains a turbine-type stirrer for effective mixing of reactants. The stirring speed is kept constant at 150 rpm throughout the course of the reaction by a linked inverter.

Heating or cooling of the reaction mixture is carried out by heating and cooling water passing through the jacket. The valve positions of the hot and cold water lines are adjusted, in a cascade control configuration, in such a way that the jacket inlet temperature is kept equal to the desired value specified by the master controller. A

conventional PI controller supported by the control software FIX-DMACS (Intellution, Boston, MA) is used as the slave controller.

The temperatures of the reaction mixture, jacket inlet and outlet flows, and hot and cold water streams are measured by resistance temperature detector (RTD) and the resulting 4–20 mA analog signals through a transmitter are used for data acquisition and control by the computer. A IT 505 PLC is used to convert analog signals to digital ones, and vice versa. Figure 1 illustrates the schematic diagram of the batch MMA/MA copolymerization system.

Toluene, AIBN, MMA, and MA were used as solvent, initiator, monomer 1, and monomer 2, respectively. First, the monomers and the solvent were charged into the reactor and the reactor temperature was raised to the desired starting temperature. Subsequently, the purified initiator dissolved in solvent was fed to the reactor.

The reaction mixture was sampled every 30 min and the solid content was calculated by the following equations:

$$X = W_p/W_{m0} \quad (35)$$

$$W_p = \frac{W_{p,sample}}{W_{mix,sample}} W_{mix} \quad (36)$$

where  $W_p$ ,  $W_{m0}$ , and  $W_{mix}$  denote the weights of the polymer, the initially charged monomers, and

**Table IV Reference Conditions for the Batch MMA/MA Copolymerization System**

Chemicals	Initial Charge (g)	Reaction Temperature (°C)
MMA	440.15	80
MA	58.55	80
Toluene	500.00	80
AIBN	0.30	80
n-DDM	0.00	80
Total	1000.00	80

the reaction mixture, respectively. For the measurement of number and weight average molecular weights of polymer, we used gel permeation chromatography (GPC) with the Waters Ultra-styragel Linear column.

Table IV shows the reference conditions for the batch MMA/MA copolymerization reactor. To ensure the reproducibility of experimental results, we conducted several experiments under the reference conditions with the total reaction time of 7 hours. Also, we carried out a number of experiments with various combinations of the concentrations of the initiator (AIBN) and the chain transfer agent (n-DDM), and the reactor temperature. Reaction conditions are listed in Table V.

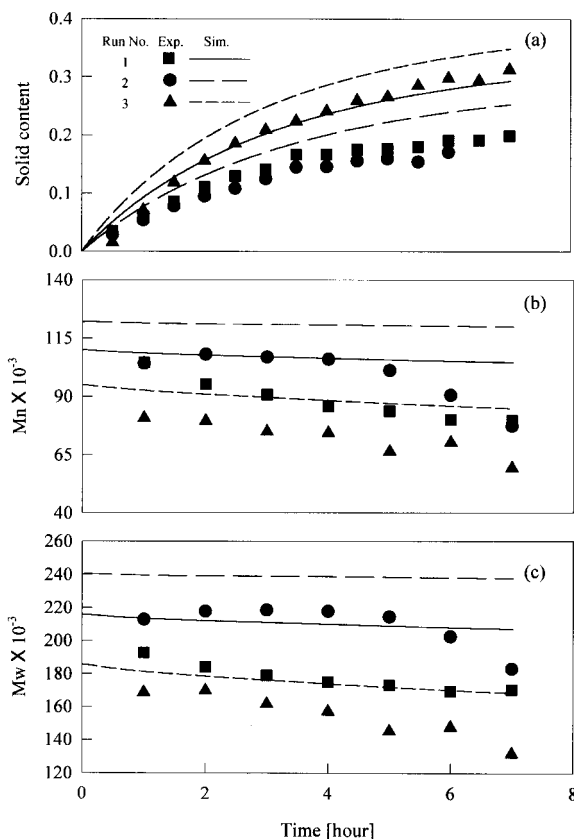
## PARAMETER ESTIMATION

The reaction rate equations contain a number of rate constants, most of which are based on the homopolymerization reaction rate constants. Var-

**Table V Reaction Conditions for Various Runs of Experiment<sup>a</sup>**

Run	AIBN (g)	n-DDM (g)	Reactor Temp. (°C)	Remark
1	0.3	0.00	80	Reference condition
2	0.2	0.00	80	—
3	0.5	0.00	80	—
4	0.3	0.00	90	Higher temp.
5	0.3	0.98	80	With n-DDM
6	0.3	1.96	80	With n-DDM
7	0.5	1.96	80	—
8	0.5	0.00	90	Higher temp.

<sup>a</sup> Other conditions are the same as the reference conditions.



**Figure 2** Comparison between the simulation results calculated by using the rate constants available in the literature and the corresponding experimental data. The results were obtained under the conditions for Runs 1, 2, and 3.

ious reaction rate constants for MMA homopolymerization are available in the literature. For MA homopolymerization, however, there are no reaction rate constants suitable for our experimental conditions in the form of Arrhenius equation and hence the reaction rate constants were obtained by linear regression using several values available in the literature.<sup>11,15</sup>

First, the simulation results were obtained by using the literature values for the reaction rate constants in the model under three different reaction conditions listed in Table V; that is, Runs 1 (reference), 2, and 3. These results are presented in Figure 2 in comparison with the experimental data measured under the corresponding reaction conditions. In all of the three diagrams showing the time histories of the solid content and the number and weight average molecular weights, respectively, it is clearly seen that the simulation results consistently overestimate the experimen-

tal data. This implies that especially the propagation rate constants taken from the literature may be much larger than the actual values.

Evidently, there is a necessity to re-estimate at least some of the rate constants. For this purpose we employed the Levenberg-Marquardt method (also called Marquardt method), which is used for varying smoothly between the extremes of the inverse-Hessian method and the steepest descent method.

By using the Levenberg-Marquardt method, we estimated (1) the kinetic parameters for the initiation; (2) the kinetic parameters for the propagation and termination for MA homopolymerization; (3) the fraction ( $k_\lambda$ ) of disproportionation in the termination reaction; and (4) the kinetic parameters for chain transfer to solvent. For the propagation and termination reaction rate constants of MMA homopolymerization, those reported in the literature were used because these appear to be fairly well estimated. The reason why we decided to modify the fraction of disproportionation in the termination reaction is that it exercises a considerable influence on the average molecular weights of the polymer products because each termination reaction gives rise to different molecular weights.

It is well known that the values of the pre-exponential factor ( $A_j$ ) and the activation energy ( $E_j$ ) are considerably different in the order of magnitude. Hence, it is necessary to re-parameterize the Arrhenius equation around the reference temperature of the experimental runs and we used the following equation.<sup>3</sup>

$$k_j(T) = k_j(T_0) \exp \left[ -\frac{E_j}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right],$$

$$j = d, 22, t22, \lambda \quad (37)$$

where  $k_j(T_0) = A_j \exp(-E_j/RT_0)$ . In this study the reference temperature  $T_0$  was taken as 343 K. The total number of parameters to be estimated is 10. For the parameter estimation, we used the experimental data of Runs 1, 2, 3, and 4 with the objective function defined as follows:

$$J(\mathbf{a}) = \sum_{i=1}^n (\mathbf{y}_{mi} - \mathbf{y}_{pi})^T W_i (\mathbf{y}_{mi} - \mathbf{y}_{pi}) \quad (38)$$

where  $W = \text{diag}(1.0, 1 \times 10^{-10}, 1 \times 10^{-10})$ ,  $\mathbf{a}$  is the parameter vector,  $n$  is the number of data,

**Table VI Kinetic Parameters Estimated in This Study**

Parameter	Unit	Estimated Value
$A_d$	1/s	$1.157 \times 10^{18}$
$E_d$	cal/mol	35764.9
$(A_{22})_0$	L/mol · s	$1.3866 \times 10^{20}$
$E_{22}$	cal/mol	26914.5
$(A_{t22})_0$	L/mol · s	$1.2396 \times 10^{10}$
$E_{t22}$	cal/mol	103.5
$A_\lambda$	—	11.187
$E_\lambda$	cal/mol	2005.4
$C_{f1S}^a$	—	$1.021 \times 10^{-4}$
$C_{f2S}^a$	—	$6.015 \times 10^{-3}$

$$^a k_{f1S} = C_{f1S} \times k_{11} \text{ and } k_{f2S} = C_{f2S} \times k_{22}.$$

$\mathbf{y}_{mi}$  is the measured value,  $\mathbf{y}_{pi}$  is the calculated value, and  $\mathbf{y}_i = (\text{solid content}, M_n, M_w)$ .

The Levenberg-Marquardt method was used to minimize above objective function. Here, it is important to choose the initial guess so as not to reach local minima, which is one of the main difficulties associated with minimizing  $J(\mathbf{a})$  in a highly nonlinear model. The results obtained by the parameter estimation are listed in Table VI.

The n-dodecyl mercaptane (n-DDM) used to regulate the average molecular weights in the commercial polymerization process produces dead polymer by reacting with living polymer and makes the average molecular weights of polymer decrease. In this study, we also estimated the reaction rate constants for the chain transfer between living polymer and transfer agent by using the experimental data of Runs 5 and 6. The results are expressed in the form

$$k_{f1D} = 0.3043k_{11}, k_{f2D} = 6.1397k_{22}$$

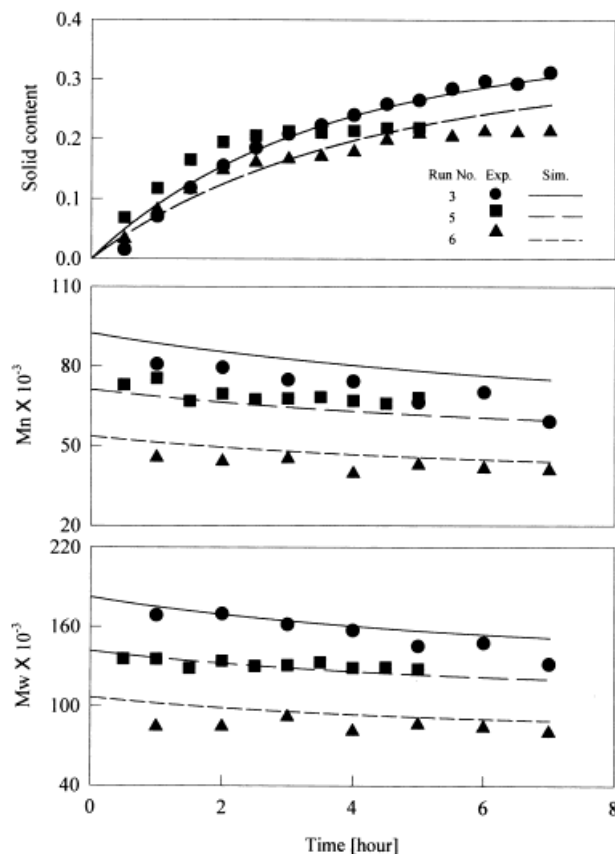
These expressions are to be compared with those reported in the literature<sup>11</sup>:

$$k_{f1D} = 0.6k_{11}, k_{f2D} = 0.4k_{22}$$

## VALIDATION

The results listed in Table VI show that the propagation rate constant for MA has a high activation energy that makes the reaction sensitive to the reaction temperature, whereas the termina-





**Figure 3** Comparison between the simulation results calculated by using the kinetic parameters estimated in this study and the corresponding experimental data. The results were obtained under the conditions for Runs 3, 5, and 6.

tion rate constant has a low activation energy that makes the reaction rather insensitive to the reaction temperature. Due to the characteristics of the Levenberg-Marquardt method, there is a possibility that one may end up with a suboptimal solution and obtain peculiar results. Therefore, it is necessary to corroborate the validity of the estimated parameters. For this purpose, additional reaction experiments were conducted under the conditions for Runs 7 and 8 of Table V. The newly estimated parameters were then used in the mathematical model under the conditions of Runs 3, 5, and 6, respectively, to obtain the simulation results presented in Figure 3. In all the three diagrams the simulation results turn out to be in reasonably good agreement with the corresponding experimental data. It is noticed that the charge of the chain transfer agent does not affect the reaction rate but the average molecular weights. This feature can be observed from the

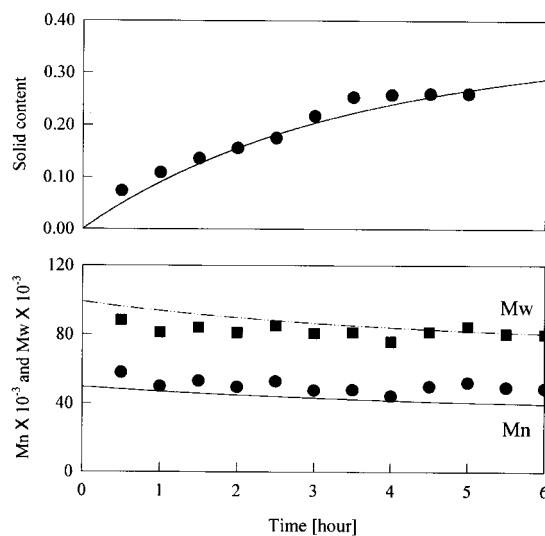
fact that between Runs 5 and 6 the solid content obtains the same result whereas the average molecular weights exhibit considerable differences.

The simulation results for Run 7 with 1.96 g of n-DDM added is shown in Figure 4 in comparison with the corresponding experimental data. The agreement between the two sets of data is remarkably good not only for the solid content but also for the average molecular weights. The feature observed from Figure 5, which shows the result for Run 8 at a higher temperature (90°C), is the acceleration of the decomposition rate of the initiator. The fixed value of the solid content and sluggish increase of the average molecular weights in the latter part (after 1.5 hours) of Figure 5 indicates that all of the initiator have decomposed.

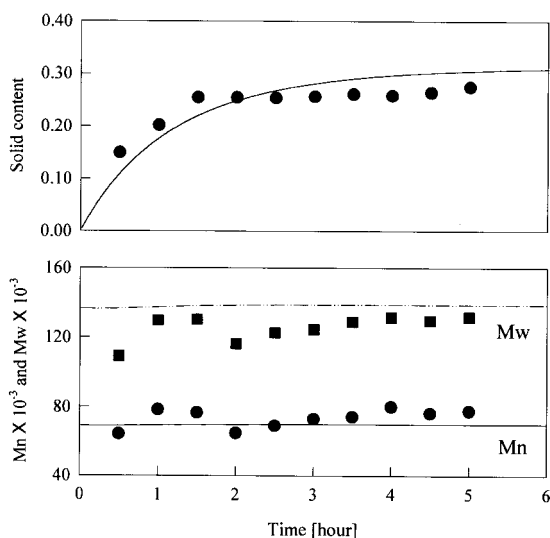
Putting the above discussions together, one can conclude that the kinetic parameters estimated in this study are reasonably good and may be used in the mathematical model presented here to predict the dynamic features of MMA/MA copolymerization reactors and the properties of the polymer product. The model with the estimated parameters may also be employed for the purpose of the optimization and control of MMA/MA copolymerization processes.

## CONCLUSIONS

Kinetic parameters for the reaction rate constants appearing in MMA/MA copolymerization



**Figure 4** Comparison between the experimental data and the simulation results calculated by using the rate constants estimated in this study. The results were obtained under the conditions for Run 7.



**Figure 5** Comparison between the experimental data and the simulation results calculated by using the rate constants estimated in this study. The results were obtained under the conditions for Run 8.

system have been estimated by applying the Levenberg-Marquardt method with the experimental data for the solid content and the average molecular weights obtained under various reaction conditions. The newly estimated parameters were validated by conducting additional experiments with or without the chain transfer agent n-DDM. It is clearly demonstrated that the parameters estimated in this study may be used in the mathematical model for the purpose of dynamic study of MMA/MA copolymerization reactors and predicting the properties of polymer product.

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## NOMENCLATURE

<b>a</b>	parameter vector
$A_j$	pre-exponential factor
$D$	n-DDM or its concentration [mol/L]
$E_j$	activation energy [cal/mol]
$F_i$	instantaneous copolymer composition for monomer $i$
$f_i$	fraction of monomer $i$
$g_p, g_t$	gel effect correlation for propagation and termination
$G_k$	$k$ -th moment of living polymer concentration, $k = 0, 1, 2$

$H_k$	$k$ -th moment of dead polymer concentration, $k = 0, 1, 2$
$I$	initiator or its concentration [mol/L]
$J$	objective function
$k_d$	decomposition rate constants [1/s]
$k_{ij}$	propagation reaction rate constants between living polymer with monomer $i$ as a terminal and monomer $j$ [L/mol · s]
$k_{fi,j}$	chain transfer reaction rate constants between living polymer with monomer $i$ as a terminal and monomer $j$ [L/mol · s]
$k_{fi,D}$	chain transfer reaction rate constants between living polymer with monomer $i$ as a terminal and transfer agent [L/mol · s]
$k_{fi,S}$	chain transfer reaction rate constants between living polymer with monomer $i$ as a terminal and solvent [L/mol · s]
$k_{t,ij}$	termination reaction rate constants between living polymer with monomer $i$ as a terminal and that with monomer $j$ as a terminal [L/mol · s]
$M_1$	MMA or its concentration [mol/L]
$M_2$	MA or its concentration [mol/L]
$M_{av}$	instantaneous average molecular weight
$M_n$	accumulated number average molecular weight
$M_w$	accumulated weight average molecular weight
$P_{m,n}$	dead polymer with $m$ units of monomer 1 and $n$ units of monomer 2
$[P_r]$	concentration of dead polymer with $r$ units of monomer
$R$	gas constant [cal/mol · K]
$[R_i \cdot]$	concentration of all living polymers whose terminals are monomer $i$
$R_{m,n,i} \cdot$	living polymer whose terminal is monomer $i$ with $m$ units of monomer 1 and $n$ units of monomer 2
$[R_{r,i} \cdot]$	concentration of living polymer whose terminal is monomer $i$ with $r$ units of monomer
$r_i$	reactivity ratio ( $r_i = k_{ii}/k_{ij}$ )
$S$	solvent or its concentration [mol/L]
$T_{g,i}$	glass transition temperature of component $i$
$T$	temperature [K]
$v$	specific volume
$V$	volume of reaction mixture [L]
$V_{f,i}$	free volume of component $i$
$w_{MMA}$	weight fraction of MMA
$W_i$	weight of component $i$ [g]
$x$	molar conversion
$X$	solid content
<b>y</b>	output vector

**Greek Letters**

- $\varphi$  free radical produced by the decomposition of initiator  
 $\rho$  density  
 $\Phi_i$  fraction of living polymer with monomer  $i$  as a terminal

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