Parameter Estimation in Emulsion Copolymerization Using Reaction Calorimeter Data

MARÍA J. BARANDIARAN, LOURDES LÓPEZ DE ARBINA, JOSÉ C. DE LA CAL, LUIS M. GUGLIOTTA,* and JOSÉ M. ASUA[†]

Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco/Euskal Herriko Unibertsitatea, Apdo.1072, 20080 San Sebastián, Spain

SYNOPSIS

The feasibility of estimating the kinetic parameters of emulsion copolymerization using only calorimetric measurements was investigated by simulation. It was found that for the case in which the average number of radicals per particle exceeds 0.5 only two of the three estimable parameters (k_I, k_a, and k_t) could be estimated together provided that an accurate value for the third parameter is available from independent measurements. For systems with $\bar{n} < 0.5$, the three unknown parameters k_I, k_d, and k_a were accurately estimated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In spite of the importance of emulsion copolymerization, only a limited effort has been devoted to elucidate the mechanisms involved in emulsion copolymerization by estimating the corresponding kinetic parameters. Nomura[1] proposed an approach to determine kinetic parameters by using the steady-state portion of the conversion vs. time curves of seeded copolymerizations. The approach involves the use of $\bar{n}$ vs. α' relationships developed by Ugelstad and Hansen.[2] However, the method can only be safely applied if the termination in the aqueous phase is negligible.[3] De la Cal et al.[4] extended the method proposed by Asua et al.[3] for emulsion homopolymerization to the parameter estimation in emulsion copolymerization systems under zero–one conditions. The use of this method required data of the time evolution of the overall conversion and the copolymer composition during the approach to the steady state of the average number of radicals per particle. Overall conversion can be easily monitored by gravimetry. Copolymer composition can be measured by gas chromatography and NMR. However,

the frequency of the experimental measurements is often not enough to apply the specific strategy developed for parameter estimation in emulsion copolymerization systems.[4]

Reaction calorimetry offers the possibility of continuous and accurate monitoring of polymerization reactions. Moritz[5] reviewed the state of the art of isothermal bench-scale calorimeters and their application to polymerization reactions. Nilsson et al.[6] developed an isothermal calorimetric reactor system and studied the kinetics of the emulsion polymerization of vinyl chloride. Moritz[5] developed a microcomputer-controlled bench-scale polymerization calorimeter with on-line determination of polymerization rate and monomer conversion and studied the batch and semibatch emulsion polymerization of vinyl acetate. Varela[7] used an automated reactor calorimeter to carry out kinetic studies of polymerization of styrene with low and high solids contents.

However, one of the limitations of this kind of reactor is that only information related to overall conversion is directly available from the heat of reaction. Urretabizkaia et al.[8] developed an approach to estimate the evolution of the copolymer composition in batch emulsion copolymerization systems using calorimetric measurements. This method required knowledge of the reactivity ratios. Furthermore, the concentration of the monomers in the different phases were calculated, assuming that these

---

concentrations were at equilibrium. To carry out this calculation, either suitable partition coefficients or accurate values of the parameters of the thermodynamic equilibrium equations were required. In the present work, the feasibility of estimating the kinetic parameters of emulsion copolymerization systems using only calorimetric measurements was assessed by simulation.

THEORETICAL FRAMEWORK

Assuming that the cross-propagation heats $(-\Delta H_{ij})$ are equal to the heat of homopolymerization $(-\Delta H_i)$, the overall calorimetric conversion can be calculated as follows:[8]

$$X_{Tc} = \frac{M_{A0}X_A(-\Delta H_A) + M_{B0}X_B(-\Delta H_B)}{M_{A0}(-\Delta H_A) + M_{B0}(-\Delta H_B)} \quad (1)$$

where X_{Tc} is the overall calorimetric conversion; M_{i0}, the number of moles of monomer i per cm^3 of water initially charged into the reactor; and $(-\Delta H_i)$, the heat of homopolymerization of monomer i. The fractional conversions of monomers A and B, X_A and X_B, assuming that the contribution of aqueous phase polymerization to the conversion is negligible, are given by

$$\frac{dX_A}{dt} = (k_{pAA}P_A^P + k_{pBA}P_B^P)[A]_P \frac{\bar{n}N_T}{M_{A0}N_A} \quad (2)$$

$$\frac{dX_B}{dt} = (k_{pAB}P_A^P + k_{pBB}P_B^P)[B]_P \frac{\bar{n}N_T}{M_{B0}N_A} \quad (3)$$

where $k_{p_{ij}}$ is the propagation rate constant; $[A]_P$ and $[B]_P$, the concentrations of monomers A and B, respectively, in the polymer particles; N_A, Avogadro's number; N_T, the number of polymer particles per cm^3 of water; and P_i^P, the time probability of finding a radical chain with ultimate unit of type i in the polymer particles. These probabilities can be obtained from the pseudo-steady-state assumption for the growing radicals as follows:[9]

$$P_A^P = \frac{k_{PBA}[A]_P}{k_{PBA}[A]_P + k_{PAB}[B]_P} \quad (4)$$

$$P_B^P = 1 - P_A^P. \quad (5)$$

The average number of radicals per particle, $\bar{n}$, is given by

$$\bar{n} = \frac{\sum\limits_{i=0}^{\infty} iN_i}{\sum\limits_{i=0}^{\infty} N_i} \quad (6)$$

where N_i is the number of particles containing i radicals, given by the following generalized population balance:

$$\frac{dN_i}{dt} = k_a[R]_w(N_{i-1} - N_i) + \bar{k}_d[(i + 1)N_{i+1} - iN_i]$$

$$+ \frac{\bar{k}_t}{v_pN_A}[(i + 2)(i + 1)N_{i+2} - i(i - 1)N_i]$$

$$\text{for} \quad i = 1, 2, \cdots \quad (7)$$

where k_a is the radical entry rate coefficient; $[R]_w$, the concentration of free radicals in the aqueous phase; $\bar{k}_d$, the overall rate coefficient for radical desorption; $\bar{k}_t$, the average termination rate coefficient in the polymer particles; and v_p, the volume of one monomer swollen particle.

For the case of particles with zero radicals, eq. (7) reduces to

$$\frac{dN_0}{dt} = -k_a[R]_wN_0 + \bar{k}_dN_1 + \frac{\bar{k}_t}{v_pN_A}2N_2. \quad (8)$$

If m is the maximum number of radicals that can coexist in a polymer particle without the occurrence of an instantaneous termination reaction, the population balances for N_m and N_{m-1} are as follows:

$$\frac{dN_m}{dt} = k_a[R]_w(N_{m-1} - N_m) - \bar{k}_dmN_m$$

$$- \frac{\bar{k}_t}{v_pN_A}m(m - 1)N_m \quad (9)$$

$$\frac{dN_{m-1}}{dt} = k_a[R]_w(N_{m-2} - N_{m-1})$$

$$+ \bar{k}_d[mN_m - (m - 1)N_{m-1}]$$

$$- \frac{\bar{k}_t}{v_pN_A}(m - 1)(m - 2)N_{m-1}$$

$$+ k_a[R]_wN_m. \quad (10)$$

Note that for a zero–one system $\bar{n}xN_T$ equals N_1.

In this case, the population balance for particles containing one radical is given by

$$\frac{dN_1}{dt} = k_a[R]_w(N_T - 2N_1) - \bar{k}_d N_1. \tag{11}$$

The concentration of free radicals in the aqueous phase can be calculated through the material balance for free radicals in the aqueous phase:

$$\frac{d[R]_w}{dt} = 2k_I[I_2] + \frac{\bar{k}_d \bar{n} N_T}{N_A} - \frac{k_a[R]_w N_T}{N_A}$$
$$- 2\bar{k}_{tw}[R]_w^2 = 0 \tag{12}$$

where k_I is the effective rate coefficient for initiator decomposition, which includes the efficiency factor; $[I_2]$, the number of moles of initiator per cm^3 of water; and $\bar{k}_{tw}$ the average termination rate coefficient in the aqueous phase. It has been demonstrated that the pseudo-steady-state assumption for the free-radical concentration in the aqueous phase can be safely used[1] and, hence, the left-hand side of eq. (12) equals zero.

Equations (2), (3), and (7)–(12) are a system of initial value stiff differential equations containing nine unknown parameters k_{pAA}, k_{pAB}, k_{pBA}, k_{pBB}, $\bar{k}_d$, k_I, k_a, $\bar{k}_t$, and $\bar{k}_{tw}$. k_{pAA} and k_{pBB} can be estimated by using the approach proposed by Asua et al.[3] for parameter estimation in emulsion homopolymerization systems. In addition, these authors demonstrated that k_a and k_{tw} are correlated and, hence, they cannot be unambiguously determined unless some independent measurement of the concentration of radicals in the aqueous phase is available. Furthermore, de la Cal et al.[4] found that the cross-propagation rate constant, k_{pBA}, with A being the most reactive monomer, cannot be estimated accurately even when the two fractional conversions are measured and they advised the use of the method proposed by de la Cal et al.[10] for estimation of the reactivity ratios from data obtained in emulsion polymerization to estimate the cross-propagation rate constants. Therefore, in the present work, $\bar{k}_d$, k_I, k_a, and $\bar{k}_t$ are the estimable parameters of the model for the case in which the average number of radicals per particle exceeds 0.5. For a zero–one system, the unknown parameters reduce to $\bar{k}_d$, k_I, and k_a.

The system of stiff differential equations can be rewritten in the following form:

$$\frac{d\mathbf{S}}{dt} = \mathbf{F}(t, \mathbf{S}, \mathbf{X}, \mathbf{K}) \tag{13}$$

where $\mathbf{S}$ is the vector of the state variables; $\mathbf{X}$, the vector of observable variables; and $\mathbf{K}$, the vector of adjustable parameters.

In a zero–one system,

$$\mathbf{S} = \{X_A, X_B, N_1\} \tag{14}$$

$$\mathbf{K} = \{\bar{k}_d, k_I, k_a\} \tag{15}$$

$$\mathbf{X} = \{X_{T_C}\}. \tag{16}$$

For the case in which $\bar{n} > 0.5$,

$$\mathbf{S} = \{X_A, X_B, N_0, N_1, \ldots, N_m\} \tag{17}$$

$$\mathbf{K} = \{\bar{k}_d, k_1, k_a, \bar{k}_t\} \tag{18}$$

$$\mathbf{X} = \{X_{T_C}\}. \tag{19}$$

In both cases, the overall calorimetric conversion is considered to be the only observable variable.

Parameter estimation involves the choice of an objective function to be minimized. In this work, the residual sum of squares was chosen:

$$\text{Sum} = \sum_{j=1}^{M} \sum_{i=1}^{G_j} (X_e - X_C^h)_{i,j}^2 \tag{20}$$

where M is the number of experiments; G_j, the number of experimental points in an experiment j; X_e, the measured conversion; and X_C^h, the model prediction using the set of parameters h.

The minimization of the residual sum of squares is carried out using the Levenberg–Marquardt method in which the vector of increments of the value of the parameters is given by

$$\Delta\mathbf{K}^{h+1} = [\mathbf{H}^h + \lambda\mathbf{I}]^{-1}$$
$$\times \sum_{j=1}^{M} \sum_{i=1}^{G_j} [\mathbf{J}^h]_{i,j}^T (X_e - X_C^h)_{i,j} \tag{21}$$

where $\mathbf{I}$ is the identity matrix; λ, a scalar; and $\mathbf{H}$, the Hessian matrix, given by

$$\mathbf{H}^h = \sum_{j=1}^{M} \sum_{i=1}^{G_j} [\mathbf{J}^h]_{i,j}^T \mathbf{J}_{i,j}^h \tag{22}$$

with

$$\mathbf{J}_{i,j}^h = \left(\frac{\partial X_C}{\partial[\mathbf{S}]}\right)_{i,j}^h \left(\frac{\partial[\mathbf{S}]}{\partial[\mathbf{K}]}\right)_{i,j}^h. \tag{23}$$

The matrix of the sensitivity coefficients is calculated as follows:

$$\frac{d(\partial[\mathbf{S}]/\partial[\mathbf{K}])}{dt} = \frac{\partial[\mathbf{F}]}{\partial[\mathbf{K}]} + \frac{\partial[\mathbf{F}]}{\partial[\mathbf{S}]}\frac{\partial[\mathbf{S}]}{\partial[\mathbf{K}]}. \qquad (24)$$

At $t = 0$, all the state variables have a constant value and, hence, the initial conditions for eq. (24) are $\partial[\mathbf{S}]/\partial[\mathbf{K}] = 0$. Details about the use of this algorithm are given in Ref. 3.

CHECK OF THE PRESENT APPROACH

To check the present approach, data were generated by simulation using arbitrary but reasonable values of the rate coefficients (referred to as "exact" parameters). Then, the approach described previously was applied to estimate the parameters of the model. The closeness of the fit of the original data and the match of the estimated kinetic parameters to the rate coefficients used in the data generation were the criteria for deciding the usefulness of the method.

Data Simulation

The time evolution of the overall conversion of chemically initiated seeded emulsion copolymerizations during interval II of two different monomer systems were simulated by integrating eqs. (2)–(12) using a Gear algorithm.[11]

Parameter estimation in emulsion polymerization depends on the value of $\bar{n}$.[3,12] Therefore, two different systems were considered: The seeded batch emulsion copolymerization of methyl acrylate (A) and vinyl acetate (B) was simulated to study the case in which $\bar{n} < 0.5$. To evaluate a case in which $\bar{n}$ exceeds 0.5, the seeded batch emulsion copolymerization of methyl methacrylate (A) and butyl acrylate (B) was simulated.

Some parameters of the model depend on experimental conditions such as the particle size and the monomer molar ratio. Therefore, the dependency of the rate constant values with the experimental conditions was taken into account in the simulation of the data.

It was assumed that the entry of radicals into the polymer particles occurred by the diffusional mechanism.[1] Therefore, in this work, the dependency of the entry rate coefficient to the particle size was given by

$$k_a = k_a^* \cdot d_p \qquad (25)$$

where d_p is the diameter of the monomer swollen polymer particle and k_a^* is a constant.

Furthermore, assuming a diffusion mechanism and no additional resistance in the interphase, Nomura[13] proposed that the average desorption rate coefficient is inversely proportional to the second power of the particle size. Therefore, the average desorption rate coefficient was written as follows:

$$\bar{k}_d = k_d^*/d_p^2 \qquad (26)$$

where k_d^* is a constant.

The average termination rate constant in the polymer particle is given by

$$\bar{k}_t = k_{tAA}(P_A^P)^2 + 2k_{tAB}P_A^P P_B^P + k_{tBB}(P_B^P)^2 \qquad (27)$$

and the average termination rate constant in the aqueous phase is calculated in the following way:

$$\bar{k}_{tw} = k_{twAA}(P_A^w)^2 + 2k_{twAB}P_A^w P_B^w + k_{twBB}(P_B^w)^2 \qquad (28)$$

where k_{tij} and k_{twij} are the termination rate constant in the polymer particles and aqueous phase, respectively. P_i^w is the time-averaged probability of finding a radical with an ultimate unit of type i in the aqueous phase. These probabilities are given by

$$P_A^w = \frac{k_{pBA}[A]_w}{k_{pBA}[A]_w + k_{pAB}[B]_w} \qquad (29)$$

$$P_B^w = 1 - P_A^w \qquad (30)$$

Table I   Values of the Parameters Used for Data Generation: A = Methyl Acrylate; B = Vinyl Acetate (Ref. 4)

k_{PAA}	0.209×10^7 cm³ mol⁻¹ s⁻¹	k_{twAA}	0.950×10^{10} cm³ mol⁻¹ s⁻¹
k_{PAB}	0.232×10^6 cm³ mol⁻¹ s⁻¹	k_{twAB}	0.166×10^{11} cm³ mol⁻¹ s⁻¹
k_{PBA}	0.230×10^8 cm³ mol⁻¹ s⁻¹	k_{twBB}	0.290×10^{11} cm³ mol⁻¹ s⁻¹
k_{PBB}	0.230×10^7 cm³ mol⁻¹ s⁻¹		
k_I	0.1×10^{-5} s⁻¹		
m_{dAp}	14	m_{dBp}	28
m_{dAd}	20	m_{dBd}	42.5
m_{dwd}	0.1×10^{-2}		
k_a^*	0.1×10^{16}	k_d^*	0.15×10^{-12}
$d_{p\ seed}$	80 nm		

Table II Values of the Parameters Used for Data Generation: A = Methyl Methacrylate; B = Butyl Acrylate (Ref. 14)

k_{PAA}	0.116×10^7 cm^3 mol^{-1} s^{-1}		
k_{PAB}	0.439×10^6 cm^3 mol^{-1} s^{-1}		
k_{PBA}	0.740×10^6 cm^3 mol^{-1} s^{-1}		
k_{PBB}	0.234×10^6 cm^3 mol^{-1} s^{-1}		
k_{tAA}	0.203×10^{11} cm^3 mol^{-1} s^{-1}	k_{twAA}	0.203×10^{11} cm^3 mol^{-1} s^{-1}
k_{tAB}	0.270×10^9 cm^3 mol^{-1} s^{-1}	k_{twAB}	0.270×10^9 cm^3 mol^{-1} s^{-1}
k_{tBB}	0.36×10^7 cm^3 mol^{-1} s^{-1}	k_{twBB}	0.36×10^7 cm^3 mol^{-1} s^{-1}
a_1	-5.08	b_1	-0.76
k_I	0.2×10^{-4} s^{-1}		
m_{dAp}	40	m_{dBp}	464
m_{dAd}	91	m_{dBd}	714
m_{dwd}	0.1×10^{-2}		
k_a^*	0.1×10^{16}	k_d^*	0.35×10^{-12}
$d_{p\,seed}$	140 nm		

where $[A]_w$ and $[B]_w$ are the concentrations of monomers A and B, respectively, in the aqueous phase.

To account for the gel effect, the following average gel effect factor was used to calculate the average termination rate constant in the polymer particle:[14]

$$\bar{k}_t = \overline{k_{t0}}\exp[a_1\phi_p^p + b_1\phi_P^P]^2 \tag{31}$$

where $\bar{k}_{t0}$ is the average termination rate constant in the polymer particles at zero polymer content, a_1 and b_1 are constants, and ϕ_P^P is the volume fraction of polymer in the polymer particles.

The values of the parameters used in the simulation of seeded batch emulsion copolymerization of

methyl acrylate (A)/vinyl acetate (B) are given in Table I. Three levels of numbers of particles $(N_T = 3 \times 10^{13}, 5 \times 10^{13},$ and 7×10^{13} particles/cm^3 of water) and four of initiator concentrations $(I = 1 \times 10^{-7}, 5 \times 10^{-7}, 1 \times 10^{-6},$ and 2×10^{-6} mol/cm^3 of water) were simulated.

Table II lists the values of the parameters used for data simulation for the methyl methacrylate (A)/butyl acrylate (B) batch seeded emulsion copolymerization. The set of "experiments" included 12 kinetic runs, where three levels of number of particles $(N_T = 1 \times 10^{13}, 3 \times 10^{13},$ and 5×10^{13} particles/cm^3 of water) and four levels of initiator concentrations $(I = 1 \times 10^{-6}, 2 \times 10^{-6}, 3 \times 10^{-6},$ and 4×10^{-6} mol/cm^3 of water) were used. The concentrations of the monomers in the different phases were calculated using the partition coefficients.

Parameter Estimation

Emulsion Copolymerization of Methyl Acrylate and Vinyl Acetate ($\bar{n} < 0.5$)

In the previous section, it was seen that for emulsion copolymerization under conditions where the zero-one assumption applies the estimable parameters of the model are $\bar{k}_d$, k_I, and k_a. However, due to the dependency of the particle diameter on the entry and exit rate coefficients [eqs. (25) and (26)], the constants k_d^* and k_a^* were used instead of the variables $\bar{k}_d$ and k_a as the adjustable parameters.

To enhance the convergence of the algorithm, the kinetic parameters were reparameterized in such a way that they all have similar values:

$$k_I' = k_I \times 10^5 = 0.1$$

$$k_a^{*\prime} = k_a^* \times 10^{-16} = 0.1$$

$$k_d^{*\prime} = k_d^* \times 10^{11} = 0.15.$$

Table III summarizes the effect of different initial guesses on the values of the estimated parameters

Table III Estimation of k_I, k_a^*, and k_d^* when $\bar{n} < 0.5$; Perfect Data; Monomer Molar Ratio = 50/50; $d_{p\,seed}$ = 80 nm

Initial Guess			Estimated Parameters			
k_I'	$k_a^{*\prime}$	$k_d^{*\prime}$	k_I'	$k_a^{*\prime}$	$k_d^{*\prime}$	Error
0.5	0.5	0.05	0.106	0.091	0.158	1.16×10^{-6}
0.05	0.8	0.5	0.106	0.091	0.158	1.21×10^{-6}

Table IV Estimation of k_I, k_a^*, and k_d^* when $\bar{n} < 0.5$; Data with Random Errors; Monomer Molar Ratio $A/B = 50/50$; $d_{p\ seed} = 80$ nm

Initial Guess			Estimated Parameters			
k_I'	$k_a^{*\prime}$	$k_d^{*\prime}$	k_I'	$k_a^{*\prime}$	$k_d^{*\prime}$	Error
0.5	0.5	0.05	0.101	0.122	0.148	4.66×10^{-4}
0.05	0.8	0.5	0.101	0.121	0.148	4.67×10^{-4}

for an initial monomer molar ratio of 50/50 and a seeded particle diameter of 80 nm, when "perfect" simulated data were used. It can be seen that good estimates of all the parameters were obtained irrespective of the initial guess.

To evaluate the approach with data closer in character to experimental data, a random error, determined using a Gaussian random number generator, was added to each conversion point. A standard deviation equal to 0.04 was used to generate this error. Table IV shows the results obtained for different initial guesses. Again, good estimates of the parameters are obtained.

From this analysis, it can be concluded that it is possible to estimate the kinetic parameters k_I, k_a, and $\bar{k}_d$ of the model of emulsion copolymerization under conditions in which $\bar{n} < 0.5$ using only calorimetric measurements.

Emulsion Copolymerization of Methyl Methacrylate and Butyl Acrylate ($\bar{n} > 0.5$)

There are many copolymerization systems that under a wide range of experimental conditions have an average number of radicals per particle greater than 0.5. One of these copolymerization systems is methyl methacrylate (A)/butyl acrylate (B). The aim of this part of the work was to determine how many kinetic parameters can be estimated accurately with

the overall calorimetric conversion data as a unique observable variable under conditions in which $\bar{n} > 0.5$.

As discussed previously, the kinetic parameters to be estimated are k_I, k_a, $\bar{k}_d$, and $\bar{k}_t$. However, Barandiaran et al.[12] found that k_a can only be estimated in systems in which termination in the aqueous phase is significant. The methyl methacrylate has a rather high termination rate constant, whereas the termination rate constant of the butyl acrylate is small. In addition, methyl methacrylate is much more soluble in the aqueous phase than is butyl acrylate. Therefore, the average aqueous phase termination rate constant is expected to be closer to the value of methyl methacrylate, and, hence, k_a can, in principle, be estimated. Furthermore, under those conditions, only a rough estimation of the exit rate coefficient is achieved.[12] Consequently, the kinetic parameters to be estimated were k_I, k_a, and $\bar{k}_t$. The kinetic parameters were reparameterized as follows:

$$k_I' = k_I \times 10^4 = 0.2$$

$$k_a^{*\prime} = k_a^* \times 10^{-16} = 0.1$$

$$\bar{k}_t' = \bar{k}_t \times 10^{-9}.$$

Table V presents the results obtained for different initial guesses when the perfect simulated data were used. It can be seen that different sets of parameters

Table V Estimation of k_I, k_a^*, and $\bar{k}_t$ when $\bar{n} > 0.5$; Perfect Data; Monomer Molar Ratio $A/B = 50/50$; $d_{p\ seed} = 140$ nm

Initial Guess			Estimated Parameters			
k_I'	$k_a^{*\prime}$	k_t'	k_I'	$k_a^{*\prime}$	k_t'	Error
0.2	0.1	0.537	0.195	0.102	0.538	0.956×10^{-5}
0.4	0.5	0.2	0.271	0.120	0.745	0.775×10^{-5}
0.1	0.15	0.7	0.244	0.114	0.672	0.872×10^{-5}

Table VI Estimation of k_I, k_a^*, and $\bar{k}_t$ when $\bar{n} > 0.5$; Data Simulated with $\bar{k}_t = 0.537 \times 10^9$ cm^3 mol^{-1} s^{-1}; Monomer Molar Ratio $A/B = 50/50$; $d_{p\,seed} = 140$ nm

Initial Guess			Estimated Parameters			
k_I'	$k_a^{*\prime}$	k_t'	k_I'	$k_a^{*\prime}$	k_t'	Error
0.4	0.5	0.2	0.279	0.117	0.745	0.482×10^{-5}
0.1	0.15	0.7	0.250	0.117	0.671	0.301×10^{-5}

led to different values of the estimated parameters but all of them fitted the data in a similar way. One of the reasons for this result could be the fact that in the estimation $\bar{k}_t$ was assumed to be constant during the polymerization, whereas, actually, $\bar{k}_t$ varies during polymerization. In the range of experimental conditions studied, $\bar{k}_t$ varied between 0.545 $\times 10^9$ and 0.530×10^9 cm^3 mol^{-1} s^{-1}. Although the variation is small, in order to determine all factors that can affect the estimation, it is worthwhile to establish the influence of these phenomena in the parameter estimation. Therefore, new data were simulated considering $\bar{k}_t$ as a constant and equal to 0.537×10^9 cm^3 mol^{-1} s^{-1}. Table VI summarizes the estimated values of k_I, k_a^*, and $\bar{k}_t$ for different initial guesses. It can be seen that different initial guesses let to different estimated parameters with similar data fitting. Therefore, the variation of $\bar{k}_t$ was not the origin of the difficulties for estimation of the three parameters.

The estimation was then restricted to two parameters: First, the estimation of k_a^* and $\bar{k}_t$ was attempted using data generated taking into account the variation of $\bar{k}_t$ due to the gel effect [eq. (31)]. Table VII shows that accurate values of the estimates were obtained for perfect data. Table VIII shows that an accurate parameter estimation was possible when noisy data were used. Similar results were obtained when k_I and $\bar{k}_t$ or k_a^* and k_I were chosen as adjustable parameters.

CONCLUSIONS

The feasibility of estimating the kinetic parameters of emulsion copolymerization systems using only calorimetric measurements was assessed by simulation. Because parameter estimation in emulsion polymerization systems depends on the value of $\bar{n}$, two different batch seeded emulsion copolymerization systems were considered. The first was the emulsion copolymerization of methyl acrylate and vinyl acetate, which gives values of $\bar{n}$ lower than 0.5; the second system was the emulsion copolymerization of methyl methacrylate and butyl acrylate for which $\bar{n} > 0.5$. Data were generated using arbitrary but reasonable values of the rate coefficients and random error was introduced to make the simulated data closer in character to real data. The kinetic parameters were estimated and the closeness of the fit of the data and the match of the estimated parameters to those used in the data generation were used as criteria to assess the feasibility of the estimation.

For $\bar{n} < 0.5$, it was found that $\bar{k}_d$, k_I, and k_a can be accurately estimated. On the other hand, for $\bar{n} > 0.5$, only two parameters of the three estimable parameters (k_I, $\bar{k}_t$, and k_a) can be estimated together provided that an accurate value for the third is available. It has to be pointed out that the present approach can be applied to other sources of data such as densitometry.

Table VII Estimation of k_a^*, and $\bar{k}_t$ when $\bar{n} > 0.5$; Perfect Data; Monomer Molar Ratio $A/B = 50/50$; $d_{p\,seed} = 140$ nm

Initial Guess		Estimated Value		
$k_a^{*\prime}$	k_t'	$k_a^{*\prime}$	k_t'	Error
0.2	0.7	0.103	0.551	0.886×10^{-5}
0.5	0.2	0.103	0.551	0.879×10^{-5}

Table VIII Estimation of k_a^*, and $\bar{k}_t$ when $\bar{n} > 0.5$; Data with Random Errors; Monomer Molar Ratio $= 50/50$; $d_{p\,seed} = 140$ nm

Initial Guess		Estimated Parameters		
$k_a^{*\prime}$	k_t'	$k_a^{*\prime}$	k_t'	Error
0.1	0.537	0.104	0.554	0.805×10^{-3}
0.5	0.2	0.104	0.554	0.805×10^{-3}

NOMENCLATURE

$[A]_j$, $[B]_j$	concentration of monomer A and B, respectively, in the phase j (mol cm^{-3})
d_p	diameter of the monomer swollen polymer particle (cm)
$\mathbf{F}$	vector of functions [eq. (13)]
G_j	number of experimental points in experiment j
$\mathbf{H}$	Hessian matrix defined by eq. (22)
$(-\Delta H_i)$	heat of homopolymerization of monomer i (kcal/mol)
$[I_2]$	initiator concentration (mol cm^{-3})
$\mathbf{J}$	vector defined by eq. (23)
$\mathbf{K}$	vector of adjustable parameters [eqs. (15) and (18)]
$\Delta\mathbf{K}$	vector of increments of adjustable parameters [eq. (21)]
k_a	rate coefficient for radical entry (cm^3 mol^{-1} s^{-1})
k_a^*	parameter given by eq. (25)
$k_a^{*\prime}$	reparameterized k_a^*
$\bar{k}_d$	overall desorption rate coefficient (s^{-1})
k_d^*	parameter defined by eq. (26)
$k_d^{*\prime}$	reparameterized k_d^*
k_I	effective rate constant for generation of polymerizing free radicals from initiator decomposition (s^{-1})
k_I'	reparameterized rate constant for generation of polymerizing free radicals from initiator decomposition (s^{-1})
$k_{p_{ij}}$	propagation rate constant (cm^3 mol^{-1} s^{-1})
$\bar{k}_t$	average termination rate constant in the polymer particles (cm^3 mol^{-1} s^{-1}).
k_t'	reparameterized average termination rate constant in the polymer particles (cm^3 mol^{-1} s^{-1})
$\bar{k}_{tw}$	average termination rate constant in the aqueous phase (cm^3 mol^{-1} s^{-1})
M	number of experiments
M_{i0}	initial number of moles of monomer i per cm^3 of water
m_{did}	partition coefficient of monomer i or radicals of type i between monomer droplets and aqueous phase
m_{dip}	partition coefficient of monomer i or radicals of type i between polymer particles and aqueous phase
m_{dwd}	partition coefficient of water between monomer droplets and aqueous phase
$\bar{n}$	average number of radicals per particle
N_A	Avogadro's number
N_i	number of particles containing i radicals per cm^3 of water
N_T	number of polymer particles per cm^3 of water
P_i^j	time-averaged probability of finding a radical with ultimate unit of type i in the phase j
$[R]_w$	concentration of radicals in the aqueous phase (mol cm^{-3})
$\mathbf{S}$	vector of state variables [eqs. (14) and (17)]
Sum	residual sum of squares
t	time
v_p	volume of monomer swollen polymer particle (cm^3)
$\mathbf{X}$	vector of observable variables
X_A, X_B	conversions of monomers A and B, respectively
X_C	conversion predicted by the model
X_e	"measured" conversion
X_{Tc}	overall calorimetric conversion

Superscripts

h	values calculated using a particular set of experiments
T	transposed matrix

REFERENCES

1. M. Nomura, *Makromol. Chem. Suppl.*, **10/11**, 25 (1985).
2. J. Ugelstad and F. K. Hansen, *Rubber Chem. Technol.*, **49**, 536 (1976).
3. J. M. Asua, M. E. Adams, and E. D. Sudol, *J. Appl. Polym. Sci.*, **39**, 1183 (1990).
4. J. C. de la Cal, M. E. Adams, and J. M. Asua, *Makromol. Chem. Macromol. Symp.*, **35/36**, 23 (1990).
5. H. U. Moritz, in *Polymer Reaction Engineering*, K. H.

Reichert and W. Geiseler, Eds., VCH Verlag, Weinheim, Germany, 1989.

6. H. Nilsson, C. Silvegren, and B. Tòrnell, *Chem. Scr.,* **19,** 164 (1982).
7. L. Varela, M.S. Report, Lehigh University, 1991.
8. A. Urretabizkaia, E. D. Sudol, M. S. El-Aasser, and J. M. Asua, *J. Polym. Sci. Polym. Chem. Ed.,* **31,** 2907 (1993).
9. G. Arzamendi, J. C. de la Cal, and J. M. Asua, *Angew. Makromol. Chem.,* **194,** 47 (1992).
10. J. C. de la Cal, J. R. Leiza, and J. M. Asua, *J. Polym. Sci. Part A Polym. Chem. Ed.,* **29,** 155 (1991).
11. C. W. Gear, *Numerical Initial Value Problems in Or-dinary Differential Equations,* Prentice-Hall, New York, 1971.
12. M. J. Barandiaran, M. E. Adams, J. C. de la Cal, E. D. Sudol, and J. M. Asua, *J. Appl. Polym. Sci.,* **45,** 2187 (1992).
13. M. Nomura, in *Emulsion Polymerization,* I. Piirma, Ed., Academic Press, New York, 1982.
14. A. Urretabizkaia, G. Arzamendi, and J. M. Asua, *Chem. Eng. Sci.,* **47,** 2579 (1992).