New Approach for the Estimation of Kinetic Parameters in Emulsion Polymerization Systems. II. Homopolymerization Under Conditions where $\bar{n} > 0.5$

MARÍA J. BARANDIARAN,[1] MARY E. ADAMS,[2,†] JOSÉ C. DE LA CAL,[1] E. DAVID SUDOL,[1,‡] and JOSÉ M. ASUA[1,*]

[1]Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain, and [2]Emulsion Polymers Institute, Lehigh University, Mountaintop Campus, Building A, 111 Research Drive, Bethlehem, Pennsylvania 18015

SYNOPSIS

A new approach for the estimation of kinetic parameters in emulsion polymerization systems in which the average number of radicals per particle exceeds 0.5 is presented. The approach uses the time evolution of the conversion in chemically initiated systems and is based on a model that includes fundamental parameters such as the propagation rate constant, k_p, the termination rate constant in the polymer particles, k_t, the rate coefficient for initiator decomposition, k_I, and the entry, k_a, and exit, k_d, rate coefficients. It was found that k_p, k_t, k_I, k_a, and, under some circumstances, k_d can be accurately estimated provided that termination in the aqueous phase is significant. When the extent of the aqueous phase termination is negligible, only k_p, k_t, and k_I can be estimated. The effect of both the experimental noise level and the run-to-run irreproducibility on the accuracy of the estimates was studied. In addition, it was found that significant inaccuracies resulted from the poor determination of the exact time when polymerization begins. A method to circumvent this problem was proposed.

INTRODUCTION

The elucidation of the mechanisms involved in emulsion polymerization is a primary goal in the investigation of industrial polymerization processes. This requires the accurate determination of the kinetic parameters under well-defined experimental conditions. In the first paper of this series, a new method for the estimation of kinetic parameters in emulsion polymerization systems was presented.[1] In that paper homopolymerization under zero-one conditions was considered. The method was based on studies of the evolution of monomer conversion with time in chemically initiated seeded polymer-

ization systems. The conversion data can be obtained by swelling a seed of monodisperse polymer particles with monomer, heating the mixture to the desired temperature and then adding the water-soluble chemical initiator. The evolution of the conversion is followed by dilatometry.[2] The method[1] was based on a model that included the free radical balance in the aqueous phase and fundamental parameters such as the entry and exit rate coefficients, the termination rate constant in the aqueous phase and the rate coefficient for initiator decomposition. In order to estimate these parameters, as well as the propagation rate coefficient, an algorithm for parameter estimation in stiff differential equations was used. With the use of simulated experimental data, it was found that accurate values of all of the parameters of the model could be obtained through the proposed approach, provided that a minimum number of experiments were available. For the case studied, this minimum ranged between 9 and 12 experiments, and the use of 3 different values of the

number of particles was advised. Comparisons with previous approaches[2-5] showed that the proposed methodology offers advantages because it uses more fundamental parameters that can be readily used in mechanistic studies as well as in predictive mathematical models, and it estimates accurately all of the parameters of the model by using data obtained from a simple experimental design. Therefore, in the case of systems for which the zero-one assumption applies, the method does not depend on any parameter value taken from the literature.

The approach proposed by Asua et al.[1] was used to estimate the entry and exit rate coefficients in the emulsion polymerization of styrene,[6] using data of the time evolution of the conversion during the approach to steady-state values of $\bar{n}$ reported in the literature.[2,7] The dependence of these coefficients on the particle size was used in an attempt to discriminate between the models proposed for the entry and exit rate coefficients. The results obtained were found to be consistent with a model in which the entry of radicals into the polymer particles occurs by the propagational mechanism,[8] and the radicals desorb from the polymer particles by diffusion. de la Cal et al.[9] have extended this method to the parameter estimation in emulsion copolymerization under zero-one conditions. The mathematical model used by these authors included material balances for the monomers, population balances for particles containing one radical, and the free radical balance in the aqueous phase. Although the model involves seven estimable parameters, the propagation rate constants can be estimated using the approach for parameter estimation in emulsion homopolymerization.[1] In addition, 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 was advised.

In this work, systems in which $\bar{n} > 0.5$ are considered. Ballard et al.[11] proposed a method for parameter estimation in emulsion polymerization systems for which $\bar{n} > 0.5$. Their method uses both chemical initiation and γ-radiolytic initiation and is based on a model that includes the radical entry rate coefficient in the absence of desorption, ρ_A, and the fate parameter, α, as estimable parameters. The fate parameter accounts for the reentry of desorbed radicals into the particles. According to Ballard et al.[11] α lies between -1 and $+1$, being -1 if all desorbed radicals terminate in the aqueous phase and $+1$ if all desorbed radicals reenter the polymer particles. This approach was applied to the kinetic investigation of the seeded emulsion polymerization of methyl methacrylate.[11,12] For this system, how-

ever, low initiator concentrations result in an average number of radicals per particle lower than 0.5 and high initiator concentrations lead to $\bar{n} > 0.5$. The authors used the slope and intercept method[3] to analyze their data, concluding that chemically initiated data were not enough to determine the parameters of the model (even if k_p was previously known), and further information from γ-radiolysis experiments was needed. However, even with those additional data, the estimated parameters were subject to considerable uncertainty because they relied on assumed values of some parameters such as the desorption rate coefficient and the fate parameter for the chemically initiated systems, α_c.[11] More recently, Maxwell et al.[13] presented an improved method of data analysis and applied it to the study of the seeded emulsion polymerization of butyl acrylate. According to that approach,[13] both chemically initiated and γ-radiolytically initiated experiments are needed for estimation of the parameters of the model. This estimation is performed, in a rather complicated way, for arbitrary pairs of values of the propagation rate constant, k_p, and the fate parameter for the chemically initiated system, α_c. This results in different sets of values of the parameters of the model [one for each pair (k_p, α_c)]. The fit of the time dependence of the conversion in the relaxation experiments is the criterion for deciding between the different sets of parameter values. As a result, the method is highly dependent on the choice of the values of k_p and α_c made at the beginning of the estimation procedure. As a matter of fact, the final values of parameters are decided by the initial choice of k_p and α_c. The procedure is time consuming because there is theoretically no limitation for the number of pairs of values of k_p and α_c for which the rest of the parameters are estimated.

In addition, a single value of α_c was used to describe the kinetics of experiments in which the initiator concentration ranged over two orders of magnitude. However, it has been demonstrated[1] that α_c varies from values close to $+1$ at low initiator concentrations, to lower values at high initiator concentrations, and hence the reliability of the parameters estimated through this approach is questionable. Moreover, both the entry rate coefficient in the absence of desorption, ρ_A, and the fate parameter are not fundamental parameters of a particular system but depend upon individual experimental conditions such as initiator concentration and number of polymer particles. These estimated parameters have, therefore, only a limited application for mechanistic studies and predictive mathematical modeling.

In the present work, the methodology presented in the first paper of this series[1] is extended to the case in which the average number of radicals per particle exceeds 0.5. Although the methodology could be applied to both chemically initiated and γ-radiolytically initiated systems, the aim of this work is to estimate the parameters of the model using only chemically initiated seeded emulsion polymerizations. The approach was checked by using the same methodology employed in the previous work.[1] Data were generated by simulation using exact values of the rate coefficients and to make the data closer in character to experimental data both random errors and systematic errors were introduced. Two sources of random errors were considered: experimental noise and run-to-run irreproducibility. Poor determination of the initial polymerization time was considered to be the main systematic error. The present approach was then applied to the generated data in an attempt to estimate the rate coefficients. The fit of the data and a comparison of the estimated values of the rate parameters to those used in the data generation gave a measure of the usefulness of this method.

THEORETICAL FRAMEWORK

Assuming that the contribution of aqueous phase polymerization to the overall conversion is negligible, the monomer material balance is as follows:

$$\frac{dx}{dt} = \frac{k_p[M]_p \bar{n} N_T}{M_0 N_A} \quad (1)$$

where x is the fractional conversion of the monomer, k_p the propagation rate constant, $[M]_p$ the concentration of the monomer in the polymer particles, M_0 the initial number of moles of monomer per dm^3 of water, N_A Avogadro's number, and N_T the number of polymer particles per dm^3 of water. The average number of radicals per particle, $\bar{n}$, is given by

$$\bar{n} = \frac{\sum\limits_{i=0}^{\infty} i N_i}{\sum\limits_{i=0}^{\infty} N_i} \quad (2)$$

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

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

$$+ \frac{k_t}{v_p N_A}[(i+2)(i+1)N_{i+2} - i(i-1)N_i]$$

$$\text{for } i = 1, 2, \cdots \quad (3)$$

where k_a is the radical entry rate coefficient, $[R]_w$ the concentration of free radicals in the aqueous phase, k_d the rate coefficient for radical desorption, k_t the termination rate coefficient in the polymer particles, and v_p the volume of a monomer swollen polymer particle.

For the case of particles with zero radicals, Eq. (3) reduces to

$$\frac{dN_0}{dt} = -k_a[R]_w N_0 + k_d N_1 + \frac{k_t}{v_p N_A}2N_2 \quad (4)$$

Although there is no theoretical limitation for the value of i in Eq. (3), in practice the series has to be truncated at a large enough value of the number of radicals $(i = m)$.

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

$$- \frac{k_t}{v_p N_A} m(m-1)N_m \quad (5)$$

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

$$+ k_d[m N_m - (m-1)N_{m-1}] - \frac{k_t}{v_p N_A}(m-1)$$

$$\times (m-2)N_{m-1} + k_a[R]_w N_m \quad (6)$$

where m is the maximum number of radicals that can coexist in a polymer particle without the occurrence of an instantaneous termination reaction.

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

$$\frac{d[R]_w}{dt} = \frac{2k_I[I_2]}{\phi_w} + \frac{k_d \bar{n} N_T}{N_A}$$

$$- \frac{k_a[R]_w N_T}{N_A} - \frac{2k_{tw}[R]_w^2}{\phi_w} = 0 \quad (7)$$

where the left-hand side represents the accumulation of free radicals in the aqueous phase. It has been demonstrated[1] that the pseudo steady-state as-

sumption can be safely used, and hence Eq. (7) can be converted into an algebraic equation by making the accumulation term equal to zero. The first term of the right-hand side accounts for the generation of radicals through initiator decomposition, the second for the desorption of radicals from latex particles, the third for the entry of radicals into the polymer particles, and the fourth for the consumption of radicals by bimolecular termination. k_{tw} is the termination rate constant in the aqueous phase and ϕ_w the volume fraction of water in the aqueous phase that can be less than 1.0 because of the monomer dissolved in the aqueous phase.

For chemically initiated systems, the initial conditions for Eqs. (1) to (7) are

$$t = 0 \quad x = 0 \quad [R]_w = 0 \quad N_i = 0 \quad i \neq 0 \quad (8)$$

Equations (1)–(7) are a system of initial-value stiff differential equations containing six unknown parameters k_a, k_t, k_I, k_d, k_{tw}, and k_p.

Equations (1)–(6) can be rewritten in the following form:

$$\frac{dS}{dt} = F(t, S, X, K) \quad (9)$$

where S is the vector of the state variables, X the vector of observable variables, and K the vector of adjustable parameters:

$$S = \{x, N_0, N_1, \ldots, N_m\} \quad (10)$$

$$K = \{k_p, k_t, k_I, k_a, k_d, k_{tw}\} \quad (11)$$

$$X = \{x\} \quad (12)$$

In the present case, the conversion is the only observable variable. Parameter estimation involves the choice of an objective function to be minimized. In this paper, the residual sum of squares was chosen:

$$\text{Sum} = \sum_{j=1}^{M} \sum_{i=1}^{G_j} (x_e - x_c^h)_{i,j}^2 \quad (13)$$

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

Equation (13) is nonlinear with respect to the parameters, and therefore the search for the set of values of the parameters is carried out in an iterative

way. Given a set h of values of the parameters, a new set, $h + 1$, of values of the parameters that gives a smaller value of the residual sum of squares is calculated as follows:

$$K^{h+1} = K^h + \Delta K^{h+1} \quad (14)$$

where, according to the Levenberg–Marquardt method, the vector of increments of the values of the parameters is given by

$$\Delta K^{h+1} = [H^h + \lambda I]^{-1} \sum_{j=1}^{M} \sum_{i=1}^{G_j} [J^h]_{i,j}^T (x_e - x_c^h)_{i,j}$$

$$(15)$$

where I is the identity matrix, λ is a scalar, and

$$H^h = \sum_{j=1}^{M} \sum_{i=1}^{G_j} [J^h]_{i,j}^T J_{i,j}^h \quad (16)$$

and

$$J_{i,j}^h = \left(\frac{\partial x_c}{\partial [S]}\right)_{i,j}^h \left(\frac{\partial [S]}{\partial [K]}\right)_{i,j}^h \quad (17)$$

In order to calculate $\partial[S]/\partial[K]$, the following equation, obtained by differentiating Eq. (9), is used:

$$\frac{d(\partial[S]/\partial[K])}{dt} = \frac{\partial[F]}{\partial[K]} + \frac{\partial[F]}{\partial[S]} \frac{\partial[S]}{\partial[K]} \quad (18)$$

At $t = 0$, all the state variables have a constant value, and hence the initial conditions for Eq. (18) are $\partial[S]/\partial[K] = 0$. Based on these equations, the algorithm presented in Appendix I was developed. The algorithm can be applied to a set of M experiments carried out under different experimental conditions with G_j experimental points measured in experiment j.

CHECK OF THE PRESENT APPROACH

Data was generated by integration of Eqs. (1)–(7) using a given set of parameters that will be referred to as the exact parameters. Then, the present approach was used to estimate the parameters of the model. The criteria for deciding the usefulness of the methodology are the closeness of the fit of the original data as well as the match of the estimated kinetic parameters to the exact values of the parameters.

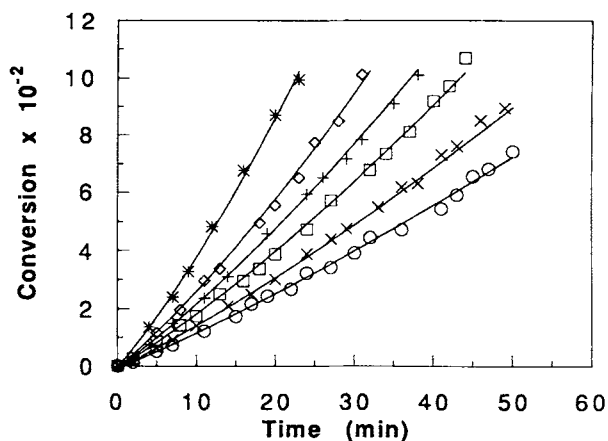**Table I   Values of the Parameters Used for Data Generation**

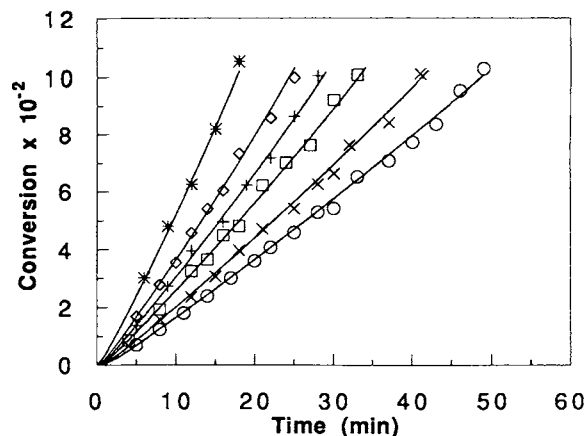|		
$k_p{}^a$	170	$dm^3\ mol^{-1}\ s^{-1}$
$k_t{}^a$	3400	$dm^3\ mol^{-1}\ s^{-1}$
k_I	1×10^{-6}	s^{-1}
k_a	4×10^6	$dm^3\ mol^{-1}\ s^{-1}$
k_d	3×10^{-3}	s^{-1}
$k_{tw}{}^a$	3400	$dm^3\ mol^{-1}\ s^{-1}$

[a] From Ref. 15.

Data Simulation

The conversion versus time profiles of chemically initiated seeded emulsion polymerizations of butyl acrylate, during Interval II were simulated by integrating Eqs. (1)–(7) using a Gear algorithm.[14] Table I lists the values of the rate constants used for the "perfect" data simulation.[15] As a first approximation, constancy of the rate parameters was assumed over the whole range of experimental conditions. In addition, a constant monomer concentration in the particles of 3.2 mol dm^{-3} was used throughout the calculations.[2]

In order to make the simulated points closer in character to actual experimental data, a random error, determined using a Gaussian random number generator, was added to each perfect fractional conversion data point. A standard deviation equal to 0.02, which yielded maximum errors of ±6%, was used. These data, referred to as "experimental" data,

Figure 2   Comparison between perfect data (solid lines) and experimental data. $N_T = 4 \times 10^{16}$ particles dm^{-3}; (○) $[I_2] = 2 \times 10^{-4}$ mol dm^{-3}; (×) $[I_2] = 3 \times 10^{-4}$ mol dm^{-3}; (□) $[I_2] = 5 \times 10^{-4}$ mol dm^{-3}; (+) $[I_2] = 7 \times 10^{-4}$ mol dm^{-3}; (◇) $[I_2] = 1 \times 10^{-3}$ mol dm^{-3}; (∗) $[I_2] = 2 \times 10^{-3}$ mol dm^{-3}.

were used in the estimation of the parameters. Figures 1–3 show the comparison between perfect and experimental data, for three levels of number of particles ($N_T = 2 \times 10^{16}$, 4×10^{16}, and 6×10^{16} particles dm^{-3} of water) and six levels of initiator concentration ($I = 2 \times 10^{-4}$, 3×10^{-4}, 5×10^{-4}, 7×10^{-4}, 1×10^{-3}, and 2×10^{-3} mol dm^{-3} of water).

For this system, the termination in the aqueous phase is negligible because of the small termination rate constant in the aqueous phase, k_{tw}. As shown
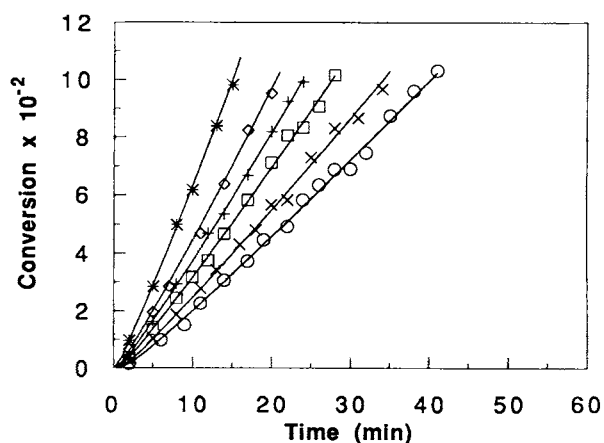
Figure 1   Comparison between perfect data (solid lines) and experimental data. $N_T = 2 \times 10^{16}$ particles dm^{-3}; (○) $[I_2] = 2 \times 10^{-4}$ mol dm^{-3}; (×) $[I_2] = 3 \times 10^{-4}$ mol dm^{-3}; (□) $[I_2] = 5 \times 10^{-4}$ mol dm^{-3}; (+) $[I_2] = 7 \times 10^{-4}$ mol dm^{-3}; (◇) $[I_2] = 1 \times 10^{-3}$ mol dm^{-3}; (∗) $[I_2] = 2 \times 10^{-3}$ mol dm^{-3}.

Figure 3   Comparison between perfect data (solid lines) and experimental data. $N_T = 6 \times 10^{16}$ particles dm^{-3}; (○) $[I_2] = 2 \times 10^{-4}$ mol dm^{-3}; (×) $[I_2] = 3 \times 10^{-4}$ mol dm^{-3}; (□) $[I_2] = 5 \times 10^{-4}$ mol dm^{-3}; (+) $[I_2] = 7 \times 10^{-4}$ mol dm^{-3}; (◇) $[I_2] = 1 \times 10^{-3}$ mol dm^{-3}; (∗) $[I_2] = 2 \times 10^{-3}$ mol dm^{-3}.

later, a negligible aqueous phase termination makes it impossible to estimate the entry rate coefficient. Because the main goal of this paper is to check the usefulness of the approach for the estimation of kinetic parameters for systems with $\bar{n} > 0.5$, it would be interesting to evaluate the method for systems where k_a could be estimated. These systems should involve significant aqueous phase termination. Therefore, data for such a systems were also simulated. A large value of the termination rate constant in the aqueous phase was used in the simulation of these data ($k_{tw} = 7 \times 10^7\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$). The values of the rest of the parameters were the same as in Table I. Note that these values of the parameters do not correspond to an actual polymerization system, but it allows the potential of the approach to be illustrated. Random errors were included in the same way as for the butyl acrylate simulated system.

Parameter Estimation

The model considered for emulsion homopolymerization under conditions where $\bar{n} > 0.5$ contains six parameters: k_p, k_t, k_I, k_a, k_d, and k_{tw}. The goal of any parameter estimation approach is to estimate as many parameters as possible. However, prior to a brute force use of the parameter estimation approach one should analyze which parameters can realistically be estimated. Several reasons can make it impossible to unambiguously estimate some of the parameters: (i) correlation between the parameters, (ii) poor experimental design, and (iii) insensitivity of the model to the values of the parameters.

It has been demonstrated[1] 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. This conclusion is not restricted to this particular type of experiment but holds for any experimental design based on a property related to the polymer particles (conversion, molecular weight distribution, or particle size distribution).[1] Therefore, in the present work the value of k_{tw} was not estimated.

The experimental design should be chosen to maximize the sensitivity of the model to the values of the parameters. In practice, this is achieved by using a wide range of experimental conditions. For the type of experiments used in this work, the lower limit of $[I_2]$ should be high enough to safely neglect the thermal initiation component. Its upper limit, as well as the lower limit of N_T, are fixed by the onset of secondary nucleation. The upper limit of

N_T, and sometimes the upper limit of $[I_2]$, are controlled by the colloidal stability of the system.

Sometimes the model is not sensitive to the values of the parameters even though a wide range of experimental conditions are used. An example of this situation is the emulsion polymerization of butyl acrylate. The termination rate constant of this monomer is very low,[15] and hence the rate of termination in the aqueous phase is negligible. Under these circumstances, for reasonable values of k_a, nearly all of the radicals generated in the aqueous phase enter the polymer particles irrespective of the value of k_a, i.e., the behavior of the system is not sensitive to the value of k_a. Consequently, k_a cannot be estimated. In addition, Ugelstad and Hansen[16] showed that, for $\bar{n} > 0.5$, the average number of radicals per particle, and therefore the polymerization rate, is insensitive to the values of k_d when the termination rate in the aqueous phase is negligible ($Y = 0$ in the Ugelstad–Hansen plots). Therefore, for the butyl acrylate emulsion polymerization system only k_p, k_t, and k_I can be estimated. Nevertheless, it should be pointed out that in this case the kinetics of the process are independent of the values of k_a and k_d, and hence the exact values of these parameters are irrelevant. When the termination in the aqueous phase is significant, $\bar{n}$ depends on the values of k_a and hence k_a can be estimated. In addition, the average number of radicals per particle can be slightly dependent on k_d as shown by the Ugelstad–Hansen plots for $Y > 0$.[16]

Effect of Extent of Aqueous Phase Termination

The algorithm presented in Appendix I was used to estimate k_p, k_t, and k_I from the simulated butyl acrylate emulsion polymerization data. Reparameterization was used to enhance the convergence of the algorithm by redefining the kinetic parameters in such a way that they all have similar values:

$$k'_p = k_p \times 10^{-3} = 0.17 \qquad (19)$$

Table II   Estimated Values of k_p, k_t, and k_I, for the Butyl Acrylate Emulsion Polymerization Data[a]

No. Experiments	k_p	k_t	k_I
18	170.8	3351	0.976×10^{-6}
12	171.2	3162	0.922×10^{-6}

[a] Aqueous phase termination negligible ($k_{tw} = 3400\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$).

Table III Estimation of k_p, k_t, k_I, and k_a for a System with Substantial Aqueous Phase Termination[a]

No. Experiments	k_p	k_t	k_I	k_a
18	173.7	3504	0.955×10^{-6}	4.011×10^6

[a] $k_{tw} = 7 \times 10^7$ dm^3 mol^{-1} s^{-1}.

$$k_t' = k_t \times 10^{-4} = 0.34 \qquad (20)$$

$$k_I' = k_I \times 10^5 = 0.1 \qquad (21)$$

Substantial computer time was saved when population balances for particles containing i radicals were written in terms of the fraction of particles (N_i/N_T) instead of the number of particles (N_i).

Table II shows the results obtained by using two different experimental designs: (i) 18 experiments including three different numbers of particles and six different initiator concentrations and (ii) 12 experiments including two different numbers of particles and six initiator concentrations. It can be seen that in both cases accurate values of the parameters were obtained. These values were independent of the initial guess used in the algorithm. In addition, Table II shows that the deviation of the estimated parameters increased when the number of experiments used in the estimation decreased. An attempt was made to estimate k_a in addition to k_p, k_t, and k_I. In this case, convergence was not always achieved and when the algorithm converged, the estimated value of k_a depended on the initial guess.

As discussed previously, k_a can only be estimated in systems in which termination in the aqueous phase is significant. Therefore, the algorithm was applied to estimate k_p, k_t, k_I, and k_a from the data simulated with $k_{tw} = 7 \times 10^7$ dm^3 mol^{-1} s^{-1}. In this estimation, k_a was reparameterized as follows:

$$k_a' = k_a \times 10^{-7} = 0.4 \qquad (22)$$

Table III presents the results obtained using an experimental design of 18 experiments. It can be seen that the four parameters were estimated accurately. The estimated values were independent of the initial guess.

When the termination in the aqueous phase is significant, $\bar{n}$ can be slightly dependent on k_d.[16] Therefore, there is some possibility of also estimating k_d and it was carried out an attempt at estimating k_p, k_t, k_I, k_a, and k_d for the system in which the aqueous phase termination was significant. The convergence of the algorithm was very slow and even after 150 iterations convergence was not achieved. Nevertheless, Table IV shows that the values of the parameters estimated after 150 iterations were close to the actual values.

Therefore, it can be concluded that in order to estimate k_a and k_d, these parameters should be kinetically significant. k_a has a distinct effect on the polymerization rate when there is substantial aqueous phase termination. On the other hand, k_d affects the kinetics when both the aqueous phase termination is important and $\bar{n}$ is not much greater than 0.5. Therefore, in most cases, under conditions in which $\bar{n} > 0.5$, only a rough estimation of the desorption rate coefficient can be achieved. Nevertheless, it has to be pointed out that k_d can be accurately estimated working under conditions where $\bar{n} < 0.5$.[1]

Effect of Experimental Noise

Under some circumstances, such as poor temperature control, the experimental noise may be more intense than that used to simulate the experimental data. Therefore, it would be worthwhile to check the behavior of the parameter estimation approach when the data are affected by "intense" experimental noise. In order to do this, new data were simulated for the butyl acrylate emulsion polymerization system (negligible aqueous phase termination) using a Gaussian random number generator with a standard deviation equal to 0.06. This results in a maximum experimental noise of 18%, which largely exceeds the usual magnitude of the experimental noise. The termination in the aqueous phase is negligible for

Table IV Estimation of k_p, k_t, k_I, and k_d for a System with Substantial Aqueous Phase Termination[a]

No. Experiments	k_p	k_t	k_I	k_a	k_d
18	184.9	3803	0.883×10^{-6}	3.985×10^6	0.327×10^{-2}

[a] $k_{tw} = 7 \times 10^7$ dm^3 mol^{-1} s^{-1}. Initial guess: $k_p = 500$; $k_t = 5000$; $k_I = 3 \times 10^{-6}$; $k_a = 6 \times 10^6$; $k_d = 0.1 \times 10^{-2}$.

**Table V Effect of Experimental Noise on the Estimated Parameters**

	Perfect Experiments	$\sigma = 0.02$	$\sigma = 0.06$
k_p	170	170.8	172.8
k_t	3400	3351	3270
k_I	0.999×10^{-6}	0.976×10^{-6}	0.930×10^{-6}

this system, so only k_p, k_t, and k_I were estimated. Table V presents the effect of the experimental noise on the values of the estimated parameters. It can be seen that in all cases a good agreement between the estimated values and the actual ones was achieved. This means that the estimation approach is not significantly affected by random experimental noise.

Effect of Irreproducibility between Runs

When replicate experiments are carried out, the conversion versus time curves usually do not generally superimpose exactly, but instead the conversions obtained in one experiment are systematically either higher or lower than those obtained in another experiment. This effect is referred to as irreproducibility between runs. In order to include this effect in our data, a Gaussian random number generator was used to assign a random error to each conversion curve. Errors as large as 12% were included and two different sets of data were considered. In the first, the error was added to perfect data (without experimental noise). Figure 4 presents an example of conversion versus time curves generated by this method. In this figure, the solid lines correspond to perfect data and the dashed lines to the data in which the run-to-run irreproducibility was included. All of these data were used to estimate the parameters presented in the top half of Table VI. It can be seen that a reasonable agreement between the estimated values and the actual ones was obtained. Table VI does not show any improvement in the accuracy of the estimation when the number of experiments was increased from 12 to 18. This result is an artifact
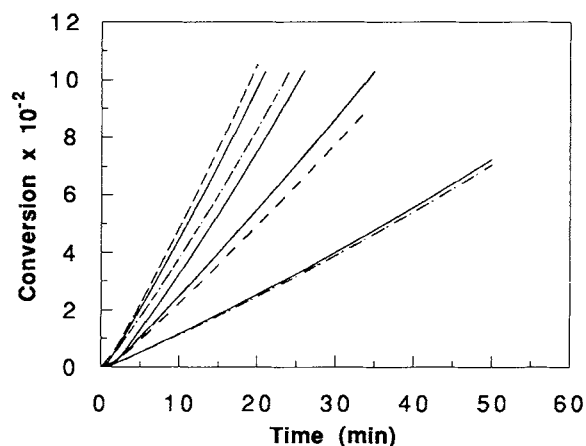
Figure 4 Comparison between perfect data (solid lines) and the first set of data used to study the effect of the irreproducibility between runs for some experiments (dashed lines).

produced by the Gaussian random number generator. This random number generator was used to assign different errors to each conversion curve. In the particular sequence of errors obtained, the errors assigned to experiments 13–18 were greater (as an average) than those assigned to experiments 1–12. Therefore, the values of the parameters estimated with 18 experiments deviated from the exact values more than those estimated using 12 experiments.

In the second set of data, the error was added to data containing experimental noise. The values of the parameters estimated with these data are given in the bottom half of Table VI. It can be seen that these values are similar to those obtained without experimental noise.

Effect of Error in Setting the Starting Time of the Polymerization

Detection of the exact time at which the polymerization begins is critical to obtaining good estimates of the kinetic parameters. It was previously demonstrated[1] for $\bar{n} < 0.5$ systems that the estimated values were sensitive to errors in setting this

Table VI Effect of the Irreproducibility between Runs on the Values of the Estimated Parameters

	No. Experiments	k_p	k_t	k_I
Without experimental noise	18	156.7	2896	1.028×10^{-6}
	12	189.5	3360	0.775×10^{-6}
With experimental noise	18	158.1	2850	0.994×10^{-6}
	12	191.8	3170	0.716×10^{-6}

starting point. It was found that variations greater than 100% were obtained for some of the parameters when the starting time was shifted by as little as 60 s.

Experimental procedures have been designed to circumvent this problem[2] by deliberately allowing the presence of dissolved oxygen in the reaction mixture so as to create a significant inhibition period. This allows for thermal equilibration of the system and precludes any perturbations caused by addition of the initiator solution. However, establishing the precise starting time from dilatometric or other data is limited by the sensitivity of the device and the realization that the polymerization can be initially quite slow particularly for experiments employing low initiator concentrations. Therefore, the true starting point of the polymerization will not be detected.

In order to investigate the effect of the poor determination of the starting time on the values of the parameters for the case in which $\bar{n} > 0.5$, the experimental data should be modified to include these errors. To do this, let us consider the dilemma facing the experimentalist after conducting an experiment using a 12-bit data acquisition board, with ± 1-V bipolar input range and 1.3/1 monomer/polymer relationship in which the minimum detectable conversion is 0.00027. From the data, the experimentalist initially sets a time zero when the conversion is 0.00027 but is aware that the polymerization had already started before this time. Therefore, a decision should be made to increase the measured time by a given amount that is unknown to the experimentalist. In order to illustrate the effect of this choice on the values of the estimated parameters, three cases were considered for the simulated butyl acrylate emulsion polymerization system. In the first case, the initial time of each polymerization was set at the moment when the reaction would be detected, namely, when $x = 0.00027$. In the second case, the time of the first case (measured time) was increased by 60 s for all of the experiments, and in the third,

Table VII Effect of the Error in Setting the Initial Time on the Estimated Parameters (18 Experiments)

Added Time (s) Δt_0^*	k_p	k_t	k_I
0	152.3	4597	0.173×10^{-6}
60	242.7	3080	0.394×10^{-6}
120	338.5	3282	0.181×10^{-6}

Table VIII Results Obtained Using the Iterative Procedure when the Initial Time is Unknown (18 Experiments)

Δt_0^* (s)	Iteration	k_p	k_t	k_I
60	1	242.7	3080	0.394×10^{-6}
	2	175.5	3176	0.870×10^{-6}
	3	170.6	3358	0.980×10^{-6}
120	1	338.5	3282	0.181×10^{-6}
	2	181.3	2999	0.763×10^{-6}
	3	171.1	3326	0.956×10^{-6}

the measured times of the experiments were increased by 120 s. The "actual" times elapsed before a conversion of 0.00027 was reached varied for the different experiments and ranged from 11 to 32 s. Table VII presents the values of the estimated parameters for the three cases. It can be seen that the poor determination of the initial time results in significant errors in the values of the estimated parameters.

In order to circumvent this problem the following iterative procedure was adopted:

1. Estimate the parameters of the model using an arbitrary added time (i.e., $\Delta t^* = 60$ s).
2. Using the estimated parameters, simulate the data and estimate Δt_1^* for each experiment as the time when the simulated conversion was 0.00027.
3. Estimate the parameters of the model using the new added time, Δt_1^*.
4. Repeat steps 2 and 3 until convergence is reached.

Table VIII summarizes the results obtained using this method. It can be seen that irrespective of the added time initially chosen, the method converged rapidly to accurate values of the estimated parameters.

CONCLUSIONS

An approach for the estimation of kinetic parameters in emulsion polymerization systems in which the average number of radicals per particle exceeds 0.5 has been presented. The approach uses the time evolution of the conversion in chemically initiated systems and is based on a model that includes the radical balance in the aqueous phase and fundamental parameters such as the propagation rate

constant, the termination rate constant in the polymer particles, the rate coefficient for initiator decomposition, and the entry and exit rate coefficients. It was found that when the termination in the aqueous phase is significant, k_p, k_t, k_I, and k_a were accurately estimated. In addition, when the system is not completely insensitive to k_d, a rough estimation of the exit rate coefficient is possible. In the cases in which the termination in the aqueous phase is negligible, the polymerization rate is not sensitive to k_a or k_d and hence only the values of k_p, k_t, and k_I can be estimated. Notice that under these circumstances the values of k_a and k_d are kinetically insignificant. It was found that the accuracy of the estimates is almost independent of the experimental noise level. On the other hand, the irreproducibility between runs can have a deleterious effect on the accuracy of the estimated parameters when a low number of experiments is used. More serious inaccuracies result from the poor determination of the initial polymerization time. An iterative procedure to circumvent this problem is proposed. This procedure allows the accurate estimation of the parameters irrespective of the errors made in setting the initial time.

APPENDIX I

The algorithm can be summarized as follows:

1. Guess some initial value of **K**.
2. For the conditions of experiment 1:
   a. Determine the maximum number of radicals per particle in steady-state conditions using the Ballard et al.[17] algorithm.
   b. Integrate Eqs. (1), (3)–(7), and (18) using a numerical integration technique for stiff differential equations such as the Gear algorithm.[14]
   c. Calculate $J_{i,1}$ [Eq. (17)] and $(x_e - x_c^h)_{i,1}$ at each time for which an experimental value of conversion is available.
   d. Calculate

$$\sum_{i=1}^{G_1} [\mathbf{J}^h]_{i,1}^T (x_e - x_c^h)_{i,1} \qquad \text{(I-1)}$$

$$\sum_{i=1}^{G_1} [\mathbf{J}^h]_{i,1}^T \mathbf{J}_{i,1}^h \qquad \text{(I-2)}$$

3. Repeat step 2 for experiments 2, 3, ..., M and calculate

$$\sum_{j=1}^{M} \sum_{i=1}^{G_j} [\mathbf{J}^h]_{i,j}^T (x_e - x_c^h)_{i,j} \qquad \text{(I-3)}$$

$$\mathbf{H}^h = \sum_{j=1}^{M} \sum_{i=1}^{G_j} [\mathbf{J}^h]_{i,j}^T \mathbf{J}_{i,j}^h \qquad \text{(I-4)}$$

4. Calculate $\Delta\mathbf{K}^{h+1}$ using Eq. (15).
5. Calculate the new values of the parameters by Eq. (14).
6. Repeat steps 2 to 5 until convergence is reached.

NOMENCLATURE

F	vector of functions [Eq. (9)]
G_j	number of experimental points in experiment j
H	matrix defined by Eq. (16)
$[I_2]$	initiator concentration (mol dm^{-3})
J	vector defined by Eq. (17)
K	vector of adjustable parameters [Eq. (11)]
$\Delta\mathbf{K}$	vector of increments of adjustable parameters
k_a	rate coefficient for radical entry (dm^3 mol^{-1} s^{-1})
k_a'	reparameterized rate coefficient for radical entry (dm^3 mol^{-1} s^{-1})
k_d	radical desorption rate coefficient (s^{-1})
k_d'	reparameterized radical desorption coefficient (s^{-1})
k_I	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	propagation rate constant (dm^3 mol^{-1} s^{-1})
k_p'	reparameterized propagation rate constant (dm^3 mol^{-1} s^{-1})
k_t	termination rate constant (dm^3 mol^{-1} s^{-1})
k_t'	reparameterized termination rate constant (dm^3 mol^{-1} s^{-1})
k_{tw}	termination rate constant in the aqueous phase (dm^3 mol^{-1} s^{-1})
M	number of experiments
$[M]_p$	monomer concentration in the polymer particles (mol dm^{-3})
M_0	initial number of moles of monomer per dm^3 of water
$\bar{n}$	average number of radicals per particle
N_A	Avogadro's constant
N_i	number of particles containing i radicals per dm^3 of water

N_T number of polymer particles per dm^3 of water

$[R]_w$ concentration of radicals in the aqueous phase (mol dm^{-3})

S   vector of state variables [Eq. (10)]

Sum   residual sum of squares

t time (s)

v_p volume of one monomer swollen polymer particle (dm^3)

x conversion

X   vector of observable variables [Eq. (12)]

x_c conversion predicted by the model

x_e "measured" conversion

Superscripts

h values calculated using a particular set of parameters

T transposed matrix

Greek Symbols

ϕ_w volume fraction of water in the aqueous phase

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