

# A New Approach for the Estimation of Kinetic Parameters in Emulsion Polymerization Systems. I. Homopolymerization under Zero-One Conditions

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## Synopsis

A new method for the estimation of kinetic parameters in emulsion polymerization systems is presented. This method is based on studies of the evolution of monomer conversion in chemically initiated seeded emulsion polymerization systems. In this paper, homopolymerization under zero-one conditions is considered. The method is based on a fundamental model that includes 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. These parameters, as well as the propagation rate constant, are the estimable parameters. This method, which uses all available data simultaneously in order to estimate the parameters, is checked by using simulated experimental data generated with exact values of the parameters. The criteria for deciding the usefulness of the present approach are the closeness of the fit to the original data and the match of the estimated kinetic parameters to the exact values of the parameters. It was found that accurate values of the parameters are obtained with the present approach provided that a sufficient number of experiments with a minimum range of variation are available. A study of both the minimum number of experiments and the minimum range of variation of the experimental conditions needed to estimate reliable parameters is presented. Also, the effect of both random and systematic errors is included in this study. Finally, a comparison between the present approach and those previously published in the literature is presented.

## INTRODUCTION

The development of predictive mathematical models for emulsion polymerization is a primary goal in the investigation of industrial polymerization processes.<sup>1</sup> The critical point in the development of these mathematical models is the elucidation of the mechanisms involved in emulsion polymerization and the estimation of the corresponding parameters. Although most of the kinetic-oriented investigations in emulsion polymerization include mechanistic considerations, the validation of these mechanisms is usually based on the fitting of limited data by global modeling. However, this can lead to false conclusions. Considerable effort has therefore been devoted to develop strategies for kinetic investigation of the emulsion polymerization process and the

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group at the University of Sydney has been the most active in this field.<sup>2-13</sup> Two main approaches have been developed by this group. The first is based on the analysis of the time dependence of the conversion during Interval II or III of a seeded emulsion polymerization using both chemical and  $\gamma$ -radiolysis initiation.<sup>2,3,5-8,10-12</sup> The second approach is based on the analysis of the evolution of the particle size distribution during Interval II of a seeded emulsion polymerization.<sup>4</sup>

In order to generate conversion data using chemical initiation, a seed of monodisperse polymer particles is swollen with monomer, heated to the desired temperature, and then the water soluble chemical initiator is added. The evolution of the reaction is followed by dilatometry.<sup>2</sup> The final product is checked by electron microscopy for the occurrence of secondary particle nucleation and the results from any run exhibiting secondary nucleation discarded. When  $\gamma$ -radiation initiation is used, a dilatometer containing a similar monomer swollen seed is introduced into the radiation field whereupon polymerization commences. After some period of time (generally when steady state is reached), the dilatometer is removed from the radiation field and the rate of polymerization monitored.<sup>3</sup> In order to analyze experimental data from both chemical and  $\gamma$ -radiolytically initiated experiments, the Sydney group uses the monomer material balance coupled with the population balances for particles containing  $i$  radicals:

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

$$\begin{aligned} \frac{dN_i}{dt} = & \rho(N_{i-1} - N_i) + k_d[(i+1)N_{i+1} - iN_i] \\ & + c[(i+2)(i+1)N_{i+2} - i(i-1)N_i] \end{aligned} \quad (2)$$

where  $x$  is the conversion,  $t$  the time,  $k_p$  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 volume of water,  $\bar{n}$  the average number of radicals per particle,  $N_T$  the number of polymer particles per volume of water,  $N_i$  the number of particles containing  $i$  radicals per volume of water,  $k_d$  the desorption rate coefficient,  $c$  the pseudo-first-order termination rate coefficient ( $c = k_t/v_p N_A$ ),  $v_p$  the volume of one monomer swollen polymer particle, and  $k_t$  the second-order termination rate coefficient. The entry coefficient  $\rho$  is defined as follows<sup>7</sup>:

$$\rho = \rho_A + \alpha k_d \bar{n} \quad (3)$$

where  $\rho_A$  is the radical entry rate coefficient in the absence of exit and  $\alpha$  is a fate parameter accounting for reentry of desorbed radicals into the particles. According to Whang et al.,<sup>6</sup>  $\alpha$  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. It should be noted that both  $\rho_A$  and  $\alpha$  vary with the number of particles and the initiator concentration. An increase

in  $N_T$  results in an increase in  $\alpha$  and a decrease in  $\rho_A$ , while an increase in the initiator concentration serves to decrease  $\alpha$  and increase  $\rho_A$ .

The Sydney group<sup>6,7,12</sup> proposed different methods of data analysis for systems in which the average number of radicals per particle is less than 0.5, a zero-one system, and systems where  $\bar{n}$  is greater than 0.5. In this work, attention is focused on systems with experimental conditions which result in  $\bar{n} < 0.5$ . In general, such experimental conditions may be reached by lowering the initiator concentration, increasing the number of polymer particles and/or decreasing the particle diameter. For a zero-one system, eqs. (1) and (2) reduce to

$$\frac{dx}{dt} = \frac{k_p[M]_p N_1}{M_0 N_A} \quad (4)$$

$$\frac{dN_1}{dt} = \rho(N_T - 2N_1) - k_d N_1 \quad (5)$$

The propagation rate constant can be obtained from the literature or determined from independent experiments.<sup>9,14</sup> Equations (4) and (5) may be integrated analytically, given the initial conditions, to yield a solution for  $x(t)$  by assuming that the rate parameters are constant with time and that the monomer concentration is known, being constant in Interval II or changing in a predictable way in Interval III. The analytic solutions for both chemical initiation and initiation by  $\gamma$ -radiolysis are identical, differing only in the initial values of  $\bar{n}$ , i.e.,  $\bar{n}(t=0) = 0$  for the case of chemical initiation and  $\bar{n}(t=0) > 0$  for  $\gamma$ -radiolysis initiation. At long times, the solution for  $x(t)$  becomes

$$x = at + b \quad (6)$$

where  $a$  and  $b$ , the slope and intercept of the straight line portion of an  $x$  vs.  $t$  curve, are functions of the parameters  $\rho_A$ ,  $\alpha$ , and  $k_d$ . Thus, for an individual experiment,  $\rho_A$  and  $k_d$  can be obtained provided  $\alpha$  is known. The Sydney group used two criteria to estimate a single value of  $\alpha$  that would describe a seeded styrene emulsion polymerization system in the presence of any concentration of aqueous phase soluble initiator<sup>6</sup>: (1) the exit rate coefficient obtained from the slope and intercept analysis should be independent of initiator concentration and particle number and (2) the value of  $k_d$  should agree with the value deduced from relaxation studies where  $\alpha$  was assumed to equal +1.

The resulting value of  $\alpha$  was used to describe the kinetics of experiments that had an initiator concentration range over 3 orders of magnitude and a particle number concentration that ranged by a factor of 4. However, it seems more reasonable to expect that  $\alpha$  would vary from values close to +1 at low initiator concentrations and high numbers of particles, to lower values at high initiator concentrations and low numbers of particles. No approach for estimating  $\rho_A$  and  $k_d$  without assuming a constant value of  $\alpha$  for the system has been proposed, and it does not appear to be a simple task to apply the slope and intercept method when the variation of  $\alpha$  is considered.

An additional problem of the above analysis arises from the fact that  $\rho_A$  and  $\alpha$  are not fundamental parameters of a particular system but in fact

depend upon individual experimental conditions such as initiator concentration and particle number. The estimated parameters have, therefore, only a limited application for predictive mathematical modeling. It is intrinsically more desirable to obtain the values of more fundamental rate parameters, such as the second-order rate coefficient for entry, for use in mechanistic studies. Moreover, when the values of  $\rho_A$  and  $\alpha$  determined by the slope and intercept method are used in mechanistic studies, for example, to discriminate between the different mechanisms proposed for radical entry, a more fundamental equation, such as the balance of radicals in the aqueous phase, is required. One additional fitting is involved and the value of the termination rate coefficient in the aqueous phase has to be known (i.e., by assuming that it is equal to the one obtained from bulk polymerization at approximately zero weight fraction of polymer).<sup>11</sup> Thus the final results contain large uncertainties in the estimates of the rate parameters.

Lichti et al.<sup>4</sup> used the time evolution of the particle size distribution (PSD) to estimate the rate coefficients for entry, exit, and propagation of free radicals in seeded and *ab initio* styrene emulsion polymerizations. The method is laborious because it requires the measurement of at least 3000 particles of each sample to ensure reproducible results. In addition, the authors<sup>4</sup> found the PSD to be insensitive to the value of the radical desorption rate coefficient for two out of the three cases studied. The model proposed by Lichti et al.<sup>15</sup> has recently been used by Chen and Wu to determine kinetic parameters from particle size distributions.<sup>16</sup> These authors proposed the use of the first three moments of the PSD to estimate the kinetic parameters and applied their method to the experimental data obtained by Lichti et al.<sup>17</sup> Surprisingly, they found the desorption rate coefficient to be proportional to the particle surface area, i.e., the rate of desorption increases with increasing particle size. This result is the opposite of theories proposed by others workers<sup>18,19</sup> and Chen and Wu<sup>16</sup> did not draw any mechanistic conclusions from their findings. It is worth noting that, in order to estimate the parameters, Chen and Wu<sup>16</sup> used the second and third moments of the PSD while both of these, though particularly the third moment, are very sensitive to inaccuracies in the measurement of the larger particle size tail of the PSD. However, even when a large number of particles are measured, the accuracy of the tails of the PSD is limited (see, for example, Fig. 2 of Ref. 4). In addition, in order to obtain the basic equations in their approach, these authors<sup>16</sup> considered both  $\rho$  and  $k_d$  to be independent of the volume of the particle but then used the resulting equations to determine the dependency of  $\rho$  and  $k_d$  on the particle size.

Recently, Nomura<sup>20</sup> has proposed an approach to determine kinetic parameters by using the steady state portion of the  $x$  vs. time curves of seeded polymerizations. This approach involves the use of  $\bar{n}$  vs.  $\alpha'$  relationships, first presented by Ugelstad and Hansen<sup>18</sup> [note that there is no relation between  $\alpha'$  in those plots and  $\alpha$  in eq. (3)]. In practice, this implies an assumption of the extent of the termination in the aqueous phase ( $Y$  in the Ugelstad-Hansen plots). Therefore, the method can only be safely applied if the termination in the aqueous phase is negligible ( $Y = 0$ ).

A novel approach for parameter estimation is presented in this paper. The approach is based on the study of the time evolution of the conversion in chemically initiated seeded emulsion polymerizations as first proposed by

Hawkett et al.<sup>2</sup> There are two main reasons for this choice. First, the time dependence of the conversion during the approach to steady-state values of  $\bar{n}$  is more sensitive to the values of the parameters than both the steady-state measurements<sup>20</sup> and PSD analysis.<sup>4,16</sup> Secondly, the experiments are carried out easily with standard laboratory equipment and neither laborious postexperiment manipulations (as in the case of using the PSD) nor sophisticated equipment other than electron microscopy is required (note that in the relaxation experiments a  $\gamma$ -ray source is necessary). The basic equations of the model include the radical balance in the aqueous phase and fundamental parameters such as the rate coefficient for radical entry, instead of the global parameters  $\rho$  and  $\alpha$  used by the Sydney group. An algorithm for parameter estimation in stiff differential equations has been developed. This algorithm does not require an analytic integration of eqs. (1) and (2) and uses all experimental points of each experiment, as well as all experiments carried out under different experimental conditions, at the same time in order to minimize the residual sum of squares. The algorithm allows the estimation of all of the parameters of the model, including the propagation rate coefficient.

In order to check the usefulness of the present approach, a classic methodology is used. Data are generated by simulation using arbitrary but reasonable values of the rate coefficients and then the present method is applied to the generated data in an attempt to estimate these rate coefficients. The fit of the data and a comparison of the values of the rate coefficients used in the data generation and the estimated ones give a measure of the usefulness of this method. This is also used to study the effect of both random and systematic errors on the estimated parameters as well as to determine how many experiments and which range of experimental conditions are needed for the estimation of reliable parameters. Finally, a comparison between the present approach and the one proposed by the Sydney group is presented.

In the present paper, attention is restricted to an emulsion homopolymerization system in which the zero-one assumption applies, i.e., where the steady state value of the average number of radicals per particle does not exceed 0.5. A wide variety of monomers will polymerize under zero-one conditions if a sufficiently low initiator concentration, small particle size, and/or high number of polymer particles are used.

## THEORETICAL FRAMEWORK

The mechanistic events involved in an emulsion polymerization reaction are as follows: (i) generation of free radicals by decomposition of the initiator in the aqueous phase (for water-soluble initiators); (ii) propagation of the free radicals in the aqueous phase; (iii) termination of free radicals in the aqueous phase; (iv) entry of free radicals into the latex particles; (v) desorption of the free radicals from the polymer particles; (vi) propagation within the polymer particles; and (vii) termination within the polymer particles.

In these events, free radicals with different characteristics are involved, namely, radicals of different chain length and different chemical composition, according to whether they arose from the initiator or from a desorbed monomeric radical. In principle, the rate of a particular event is different for each type of oligomer. A distinction being made between all these oligomers

would result in a model that contains so many parameters that they cannot be estimated from experimental data. Therefore, some kind of averaged parameters have to be used. By using averaged parameters, the material balance for free radicals in the aqueous phase can be written as follows:

$$\frac{d[\mathbf{R}]_w}{dt} = \frac{2k_1[\mathbf{I}_2]}{\phi_w} + \frac{k_a\bar{n}N_T}{N_A} - \frac{k_a[\mathbf{R}]_wN_T}{N_A} - \frac{2k_{tw}[\mathbf{R}]_w^2}{\phi_w} \quad (7)$$

where the left-hand side represents the accumulation of free radicals in the aqueous phase. 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 the latex particles, the third for the entry of radicals into the polymer particles, and the fourth for the consumption of radicals by bimolecular termination. Note that eq. (7) does not make any distinction between the different types of radicals. Therefore, the kinetic coefficients have to be clearly defined.

The rate coefficient for the generation of free radicals from initiator decomposition includes all effects usually taken into account by the efficiency factor. Therefore, this term represents the free radicals that undergo some polymerization. In this term,  $[\mathbf{I}_2]$  is the molar concentration of initiator in the aqueous phase and  $\phi_w$  the volume fraction of water in the aqueous phase.

The rate of desorption of radicals from the polymer particles is assumed to be proportional to the total number of radicals in the latex particles. Note that for a zero-one system  $\bar{n}N_T$  equals  $N_1$ . No additional assumption is made about the processes involved in radical desorption (for example, the existence of a previous transfer reaction) nor the type (length) of radical involved.

The radical absorption phenomenon has been previously treated as a collisional process,<sup>21</sup> as well as a diffusional process<sup>18</sup> and a colloidal process.<sup>11</sup> In all cases, the rate of radical absorption per polymer particle is expressed as an entry rate coefficient  $k_a$  multiplied by the concentration of radicals in the aqueous phase. The probability that a free radical enters a polymer particle increases with its length, although this effect is more pronounced for oligomers formed from initiator due to the presence of a charged hydrophilic end group than for uncharged oligomers arising from exited radicals. In addition, one would expect a continuous distribution of rates of entry for the different radicals rather than a step distribution where oligomers of length less than a critical value do not enter the polymer particles and oligomers greater than that critical length all enter the latex particles with the same rate. Therefore,  $k_a$  is an average entry rate coefficient that accounts for the effect of the distributions of probability of entry.

It is also doubtful that oligomers with different lengths and chemical composition terminate with the same rate, and once again a distribution of termination rates would be expected. Such a distribution would be affected by the two oligomers involved in each termination. A detailed accounting of these termination rates is obviously impractical and, hence, an average termination rate coefficient,  $k_{tw}$ , has to be used.

For most systems, the contribution of the aqueous phase polymerization to the overall conversion is negligible and, hence, the monomer material balance

for a zero-one system is

$$\frac{dx}{dt} = \frac{k_p[M]_p N_1}{M_0 N_A} \quad (8)$$

where  $N_1$  is the number of particles (per  $\text{dm}^3$  of water) containing one radical.

The population balance for  $N_1$  is as follows:

$$\frac{dN_1}{dt} = k_a[\text{R}]_w(N_T - N_1) - k_a[\text{R}]_w N_1 - k_d N_1 \quad (9)$$

For a chemically initiated system, the initial conditions for eqs. (7)–(9) are

$$t = 0, \quad x = 0, \quad [\text{R}]_w = 0, \quad N_1 = 0 \quad (10)$$

Equations (7)–(10) are a system of initial-value stiff differential equations containing four unknown parameters  $k_a$ ,  $k_d$ ,  $k_1$ , and  $k_{tw}$ . As a first approximation, it is assumed that  $k_p$  is known from the literature or been previously determined.<sup>14</sup>

Equations (7)–(9) can be written as follows:

$$\frac{d\mathbf{S}}{dt} = \mathbf{F}(t, \mathbf{S}, \mathbf{Y}, \mathbf{K}) \quad (11)$$

where  $\mathbf{S}$  is the vector of the state variables,  $\mathbf{Y}$  the vector of independent variables, and  $\mathbf{K}$  the vector of adjustable parameters, where

$$\mathbf{S} = \{x, N_1, [\text{R}]_w\} \quad (12)$$

$$\mathbf{K} = \{k_a, k_d, k_1, k_{tw}\} \quad (13)$$

In the present case, the conversion is the only observable variable.

Although algorithms for parameter estimation in ordinary differential equations have been well known for some time<sup>22</sup> and successfully applied in the polymer field,<sup>23,24</sup> it is only recently that the problem of parameter estimation in stiff differential equations has been treated in the literature.<sup>25,26</sup> Parameter estimation involves the choice of an objective function to be minimized. This objective function should incorporate the specific error structure for the experimental data. The likelihood function provides a general formulation for the objective function by which many types of error relationships can be represented. In this paper, the experimental errors are assumed to be distributed in such a way (see Ref. 27 for further details) that the likelihood function reduces to a residual sum of squares:

$$\text{Sum} = \sum_{j=1}^M \sum_{i=1}^{G_j} (\mathbf{X}_e - \mathbf{X}_c)_{i,j}^T \mathbf{Q}_{i,j} (\mathbf{X}_e - \mathbf{X}_c)_{i,j} \quad (14)$$

where  $M$  is the number of experiments,  $G_j$  the number of experimental points in experiment  $j$ , the superscript  $T$  stands for the transposed matrix, and  $\mathbf{Q}_{i,j}$

is a weighting matrix.  $(\mathbf{X}_e - \mathbf{X}_c)$  is the vector of residuals of the observable variables, where  $\mathbf{X}_e$  is the measured value and  $\mathbf{X}_c$  the model prediction. In the present case, there is only one observable variable, the conversion, and the weighting matrix is taken to be equal to 1.

Equation (14) can be modified as follows:

$$\text{Sum} = \sum_{j=1}^M \sum_{i=1}^{G_j} [(x_e - x_c^h) - (x_c - x_c^h)]^2 \quad (15)$$

where  $x_c^h$  is the value of the conversion predicted by the model with a particular set of parameters,  $h$ .

In order to linearize Sum,  $x_c$  is expanded in a Taylor series around  $x_c^h$  and substituted into eq. (15), giving

$$\text{Sum} = \sum_{j=1}^M \sum_{i=1}^{G_j} \left[ (x_e - x_c^h) - \left( \frac{\partial [x_c]}{\partial [\mathbf{S}]} \right)^h \left( \frac{\partial [\mathbf{S}]}{\partial [\mathbf{K}]} \right)^h \Delta \mathbf{K}^{h+1} \right]^2 \quad (16)$$

Equation (16) is linear in  $\Delta \mathbf{K}^{h+1}$  and minimization of Sum with respect to  $\Delta \mathbf{K}^{h+1}$  gives

$$\Delta \mathbf{K}^{h+1} = [\mathbf{H}^h]^{-1} \sum_{j=1}^M \sum_{i=1}^{G_j} [\mathbf{J}^h]_{i,j}^T (x_e - x_c^h)_{i,j} \quad (17)$$

where

$$\mathbf{H}^h = \sum_{j=1}^M \sum_{i=1}^{G_j} [\mathbf{J}^h]_{i,j}^T [\mathbf{J}^h]_{i,j} \quad (18)$$

and

$$\mathbf{J}_{i,j} = \left( \frac{\partial [x_c]}{\partial [\mathbf{S}]} \right)_{i,j}^h \left( \frac{\partial [\mathbf{S}]}{\partial [\mathbf{K}]} \right)_{i,j}^h \quad (19)$$

In order to calculate  $\partial[\mathbf{S}]/\partial[\mathbf{K}]$ , both sides of eq. (11) are differentiated with respect to  $\mathbf{K}$  giving

$$\frac{\partial [d\mathbf{S}/dt]}{\partial [\mathbf{K}]} = \frac{\partial [\mathbf{F}]}{\partial [\mathbf{K}]} + \frac{\partial [\mathbf{F}]}{\partial [\mathbf{S}]} \frac{\partial [\mathbf{S}]}{\partial [\mathbf{K}]} \quad (20)$$

Interchanging the order of differentiation yields

$$\frac{d(\partial[\mathbf{S}]/\partial[\mathbf{K}])}{dt} = \frac{\partial [\mathbf{F}]}{\partial [\mathbf{K}]} + \frac{\partial [\mathbf{F}]}{\partial [\mathbf{S}]} \frac{\partial [\mathbf{S}]}{\partial [\mathbf{K}]} \quad (21)$$

At  $t = 0$ , all of the state variables have a constant value and hence, the initial conditions for eq. (21) are  $\partial[\mathbf{S}]/\partial[\mathbf{K}] = 0$ .



The Levenberg–Marquardt method proposes a nonnegative addition to  $\mathbf{H}$  in order to enhance convergence:

$$\Delta \mathbf{K}^{h+1} = [\mathbf{H} + \lambda \mathbf{I}]^{-1} \sum_{j=1}^M \sum_{i=1}^{G_j} [\mathbf{J}^h]_{i,j}^T (x_e - x_c^h)_{i,j} \quad (22)$$

where  $\mathbf{I}$  is the identity matrix and  $\lambda$  is a scalar.

Based on these equations, an algorithm for parameter estimation in stiff differential equations has been developed. The algorithm can be applied to a set of  $M$  experiments carried out under different experimental conditions.  $G_j$  experimental points are measured in experiment  $j$ . The algorithm can be summarized as follows:

1. Guess some initial value of  $\mathbf{K}$ .
2. For the conditions of experiment 1:
  - a. Integrate eqs. (7)–(9) and (21) using a numerical integration technique such as the Gear algorithm.<sup>28</sup>
  - b. Calculate  $\mathbf{J}_{i1}$  [eq. (19)] and  $(x_e - x_c^h)_{i1}$  at each time for which an experimental value of conversion is available.
  - c. Calculate

$$\sum_{i=1}^{G_1} [\mathbf{J}^h]_{i,1}^T (x_e - x_c^h)_{i,1} \quad (23)$$

$$\sum_{i=1}^{G_1} [\mathbf{J}^h]_{i,1}^T \mathbf{J}_{i,1}^h \quad (24)$$

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

$$\sum_{j=1}^M \sum_{i=1}^{G_j} [\mathbf{J}^h]_{i,j}^T (x_e - x_c^h)_{i,j} \quad (25)$$

$$\mathbf{H}^h = \sum_{j=1}^M \sum_{i=1}^{G_j} [\mathbf{J}^h]_{i,j}^T \mathbf{J}_{i,j}^h \quad (26)$$

4. Calculate  $\Delta \mathbf{K}^{h+1}$  using eq. (22).
5. Calculate the new values of the parameters

$$\mathbf{K}^{h+1} = \mathbf{K}^h + \Delta \mathbf{K}^{h+1} \quad (27)$$

6. Repeat steps 2–5 until convergence is reached.

### CHECK OF THE PRESENT APPROACH

Data were generated by integration of eqs. (7)–(9) using a given set of parameters that will be referred to as the “exact” parameters. The methodology was checked by estimation of the parameters from the generated data, and comparison of the results with the exact parameters was used to establish the accuracy of the method.

### Data Simulation

The conversion vs. time profiles of chemically initiated seeded emulsion polymerizations of styrene during Interval II were simulated by integrating eqs. (7)–(9) by a Gear algorithm. Table I lists the values of the rate constants used for data simulation. A constant monomer concentration of  $5.8 \text{ mol dm}^{-3}$  was used throughout the calculations (i.e., Interval II). Initiator concentration and total number of particles were varied. The range of these varying experimental conditions was chosen as follows. 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  $[I_2]$ , is controlled by the colloidal stability of the system. As a first approximation, constancy of the rate parameters was assumed over the whole range of experimental conditions.

As real experimental data never result in a perfectly smooth curve, some estimate of the error is required in order to produce data closer in character to real experiments. For experiments monitored dilatometrically, the main source of random errors are the measurement of the meniscus height and the temperature fluctuations. Using a cathetometer that reads to 0.001 cm, one can estimate that the maximum error in the reading is  $\pm 0.002 \text{ cm}$ . Temperature fluctuations will affect the reading through both density fluctuations and the reaction rate by changing the value of the rate parameters. For a dilatometer that contains a reaction bulb of 50 ml and a total capillary volume of 3 mL, a variation of  $\pm 0.02 \text{ K}$  at 323 K (a less accurate temperature controller will result in excessive experimental noise) will give a height error of 0.014 cm. This error, together with the one related to the measurement of the meniscus height, results in an absolute error of less than  $\pm 0.1$  in the percentage conversion. The effect of temperature fluctuations on the kinetic parameters is more difficult to evaluate because the temperature dependences of the rate constants are needed. In this paper, a random error of  $\pm 0.1$  in the percentage conversion has been assigned to this effect. Therefore, a maximum error of  $\pm 0.2$  was added to the perfect data in order to generate real data. The error assigned to each experimental point was varied by using a random number generator that varied between 0 and 1. Each particular value was calculated by

$$\text{error} = \frac{(\text{random number} - 0.5)0.2}{0.5} \quad (28)$$

This error was used for conversions greater than 0.2%; otherwise, smaller errors were used in order to avoid negative conversions.

TABLE I  
Values of the Parameters Used for Data Generation

$k_p$	258	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$k_a$	$4 \times 10^6$	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$k_d$	$1 \times 10^{-3}$	$\text{s}^{-1}$
$k_I$	$1 \times 10^{-6}$	$\text{s}^{-1}$
$k_{tw}$	$7 \times 10^7$	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Another source of experimental error is the run-to-run irreproducibility. In order to include this effect in our data, every point in a particular experimental conversion curve was shifted by a given fraction of the value of the percentage conversion. A Gaussian random number generator was used to assign the error to each experimental curve. Errors as large as  $\pm 8\%$  were included in the data. In our experience, these errors exceed those expected in carefully carried out seeded emulsion polymerization reactions.

In addition to the random errors, some systematic errors are related to dilatometric experiments. These experiments are typically started with some oxygen in the reaction mixture that results in an induction period. The starting point for the reaction is subjective. Hence a systematic error is easily included into the measurement. This error was introduced in the simulated data by decreasing the process times by one minute.

### Parameter Estimation

#### *Effect of the Steady-State Assumption for the Aqueous Phase Radical Concentration*

One important feature of any method of parameter estimation is the amount of computer time required to implement the method. The computer time is considerably reduced if the pseudo-steady-state assumption for the radical concentration in the aqueous phase is applied, i.e., if eq. (7) can be converted to an algebraic equation by making the left-hand side, the accumulation term, equal to zero. In order to check the validity of this assumption, integration of eqs. (7) and (9) under pseudo-steady-state and non-steady-state conditions were carried out. The results, presented in Table II, show that there is no significant difference between the integrations and, hence, the pseudo-steady-state assumption can be safely used.

#### *Effect of the Initial Guess*

The parameter estimation was first carried out under the least demanding conditions, i.e., by using a large number of experiments. Tables III-V present these data which represent experiments carried out at several different con-

TABLE II  
Check of the Pseudo-Steady-State Assumption

Time (s)	Non-steady state		Pseudo-steady state	
	$x$ (%)	$N_1 \times 10^{-16}$	$x$ (%)	$N_1 \times 10^{-16}$
0	0	0	0	0
5	0.00	2.22	0.00	1.73
10	0.01	4.19	0.01	3.75
20	0.03	7.46	0.03	7.13
40	0.10	12.04	0.10	11.83
60	0.20	14.83	0.20	14.70
80	0.32	16.53	0.31	16.46
100	0.45	17.57	0.44	17.53
120	0.58	18.21	0.57	18.18

TABLE III  
 "Experimental" Percentage Conversion Data<sup>a</sup>

Time (s)	$[I_2] = 10^{-5}$	$[I_2] = 5 \times 10^{-5}$	$[I_2] = 10^{-4}$	$[I_2] = 3 \times 10^{-4}$	$[I_2] = 7 \times 10^{-4}$	$[I_2] = 10^{-3}$
60.0	0.0033	0.0395	0.0224	0.0512	0.0984	0.1025
120.0	0.0340	0.0970	0.1186	0.2221	0.2836	0.2926
180.0	0.0397	0.1921	0.2806	0.4006	0.5138	0.5248
240.0	0.1102	0.3115	0.4539	0.6245	0.7250	0.7251
300.0	0.1556	0.4239	0.6182	0.8358	0.9382	0.8990
360.0	0.2312	0.6151	0.7788	1.0226	0.9412	0.9981
420.0	0.2765	0.7493	0.9070	1.2937	1.5101	1.2561
480.0	0.3440	0.8937	0.9652	1.3433	1.6767	1.6811
540.0	0.4871	1.0995	1.1554	1.7846	1.7613	1.7277
600.0	0.5045	1.1499	1.6897	1.7364	1.9091	1.8128
660.0	0.6450	1.2283	1.6580	2.0099	2.2614	2.2785
720.0	0.7523	1.4873	1.9048	2.1953	2.3249	2.3086
780.0	0.8356	1.6100	2.2712	2.3493	2.5941	2.7085
840.0	0.9503	2.0170	2.3173	2.4457	2.9419	2.8261
900.0	1.1128	1.9639	2.3438	2.8318	3.1256	2.9420
960.0	1.2235	2.3860	2.5834	2.9822	3.3919	3.1561
1020.0	1.4464	2.6305	2.9781	3.1340	3.4747	3.6929
1080.0	1.4249	2.7311	3.0066	3.3936	3.6263	3.5233
1140.0	1.4572	2.8974	3.3819	3.5710	4.0377	4.1141
1200.0	1.7461	3.1886	3.5373	3.8691	3.9163	4.3082
1260.0	1.7232	3.1351	3.7992	3.9544	4.3910	4.1946

<sup>a</sup>  $N_T = 2 \times 10^{16}$  particles  $\text{dm}^{-3}$ .

TABLE IV  
 "Experimental" Percentage Conversion Data<sup>a</sup>

Time (s)	$[I_2] = 10^{-5}$	$[I_2] = 5 \times 10^{-5}$	$[I_2] = 10^{-4}$	$[I_2] = 3 \times 10^{-4}$	$[I_2] = 7 \times 10^{-4}$	$[I_2] = 10^{-3}$	$[I_2] = 3 \times 10^{-3}$
60.0	0.0114	0.0184	0.0608	0.1146	0.1739	0.2206	0.3040
120.0	0.0126	0.1335	0.1833	0.3844	0.4765	0.5836	0.6848
180.0	0.0654	0.2498	0.4310	0.6732	0.8877	1.0282	0.9802
240.0	0.1232	0.4678	0.6316	1.2455	1.1480	1.2962	1.7014
300.0	0.1820	0.6257	0.9162	1.4017	1.7230	2.0318	1.9616
360.0	0.2454	0.8997	1.2267	1.7102	2.1063	2.3177	2.3933
420.0	0.3470	1.2849	1.5091	2.2874	2.6402	2.7015	2.9143
480.0	0.3911	1.4761	2.0654	2.5106	3.1645	3.0142	3.4045
540.0	0.5820	1.5754	2.1307	3.1969	3.5434	3.5176	3.6722
600.0	0.6935	2.1349	2.5392	3.3340	4.0447	3.8280	4.2696
660.0	0.8044	2.1683	3.0428	3.7188	4.0906	4.4660	4.5893
720.0	0.9573	2.7072	3.2996	4.4196	4.7557	4.9396	5.2207
780.0	1.1271	2.7310	3.6704	4.5619	5.2690	5.3788	5.5579
840.0	1.2166	3.4090	4.1736	5.0907	5.4800	5.8072	6.0085
900.0	1.3618	3.6750	4.4166	5.6959	5.9991	5.9386	6.5378
960.0	1.3891	3.9023	4.7630	5.8877	6.4102	6.4190	6.7843
1020.0	1.7754	4.2784	5.2472	6.3706	6.9421	7.0462	7.2740
1080.0	1.6759	4.4466	5.4933	6.5444	7.2416	7.3095	7.6957
1140.0	1.8524	5.0228	6.0888	7.2058	7.6590	7.8127	8.0607
1200.0	2.1533	5.1661	6.3652	7.4085	8.1088	8.2769	8.5021
1260.0	2.4683	5.5139	6.6082	7.8283	8.4077	8.4669	9.0504

<sup>a</sup>  $N_T = 4 \times 10^{16}$  particles  $\text{dm}^{-3}$ .

TABLE V  
 "Experimental" Percentage Conversion Data<sup>a</sup>

Time (s)	$[I_2] = 10^{-5}$	$[I_2] = 5 \times 10^{-5}$	$[I_2] = 10^{-4}$	$[I_2] = 3 \times 10^{-4}$	$[I_2] = 7 \times 10^{-4}$	$[I_2] = 10^{-3}$	$[I_2] = 3 \times 10^{-3}$
60.0	0.0249	0.0363	0.0580	0.1487	0.2363	0.2687	0.4113
120.0	0.0357	0.1276	0.2390	0.5075	0.7247	0.7955	1.0820
180.0	0.0580	0.2874	0.4952	1.0045	1.2081	1.5275	1.5467
240.0	0.1338	0.5172	0.8235	1.3706	1.9523	2.1723	2.3518
300.0	0.1726	0.7738	1.0882	1.9627	2.4578	2.6377	2.8750
360.0	0.2756	1.1295	1.7496	2.5739	3.3540	3.3663	3.7870
420.0	0.3606	1.2427	1.9594	3.1340	3.8727	3.8967	4.3601
480.0	0.4351	1.8526	2.4710	3.8712	4.3346	4.7598	4.7680
540.0	0.5690	2.1305	3.0134	4.4207	5.1593	5.1659	5.7606
600.0	0.7570	2.3934	3.6440	4.8108	5.8282	5.9107	6.0517
660.0	0.8619	2.7248	4.0953	5.4156	6.2450	6.5543	6.8995
720.0	0.9668	3.3901	4.6270	6.2345	6.8273	7.1150	7.4008
780.0	1.3386	3.8583	4.9152	6.6919	7.6625	7.7947	8.1079
840.0	1.2506	3.9338	5.6070	7.4856	8.0446	8.4077	8.8075
900.0	1.3643	4.5277	6.2964	7.9988	8.9217	8.9141	9.5864
960.0	1.4873	4.8513	6.6024	8.5745	9.4812	9.5756	10.2884
1020.0	2.0357	5.5173	7.3354	9.0031	10.1293	10.2804	10.8530
1080.0	2.1849	5.7032	7.8208	9.7262	10.5711	10.8832	11.6355
1140.0	2.2541	6.2484	8.3146	10.3619	11.2640	11.5145	12.2367
1200.0	2.4307	6.9578	8.5967	11.1800	12.0376	12.1615	12.6258
1260.0	2.7067	7.2979	9.2441	11.3888	12.4208	13.0278	13.2930

<sup>a</sup>  $N_T = 6 \times 10^{16}$  particles  $\text{dm}^{-3}$ .

TABLE VI  
Effect of the Initial Guess on the Estimated Parameters

$k'_a$	Initial guess				Estimated parameters				Sum $\times 10^4$
	$k'_d$	$k'_i$	$k'_{tw}$	$k'_a$	$k'_d$	$k'_i$	$k'_{tw}$	$k'_a$	
0.4	0.1	0.1	0.7	—	—	—	—	—	4.019
0.4	0.1	0.1	0.7	0.3959	0.0992	0.0999	0.7012	0.0999	4.016
0.9	0.5	0.5	0.3	0.3995	0.0992	0.0999	0.7140	0.0999	4.016
0.1	0.7	0.2	0.6	0.3532	0.0992	0.0999	0.5580	0.0999	4.016
1.0	0.1	0.3	1.0	0.5275	0.0992	0.0999	1.2450	0.0999	4.016
0.1	0.05	0.9	0.1	0.1353	0.0992	0.0999	0.0818	0.0999	4.016

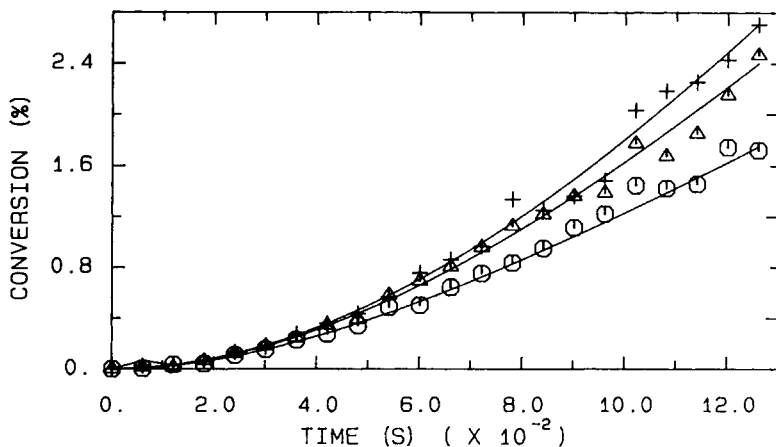


Fig. 1. Comparison between calculated (solid lines) and "experimental" conversions;  $[I_2] = 10^{-5} \text{ mol dm}^{-3}$ : ( $\odot$ )  $N_T = 2 \times 10^{16} \text{ particles dm}^{-3}$ ; ( $\Delta$ )  $N_T = 4 \times 10^{16} \text{ particles dm}^{-3}$ ; (+)  $N_T = 6 \times 10^{16} \text{ particles dm}^{-3}$ .

centrations of initiator and three values of the total number of particles. A random error of  $\pm 0.2$  in the percent conversion was included in these data. Reparametrization was used to enhance the convergence of the algorithm by redefining the kinetic parameters in such a way that they all have similar values:

$$k'_a = k_a/10^7 = 0.4 \quad (29)$$

$$k'_d = k_d/10^{-2} = 0.1 \quad (30)$$

$$k'_I = k_I/10^{-5} = 0.1 \quad (31)$$

$$k'_{tw} = k_{tw}/10^8 = 0.7 \quad (32)$$

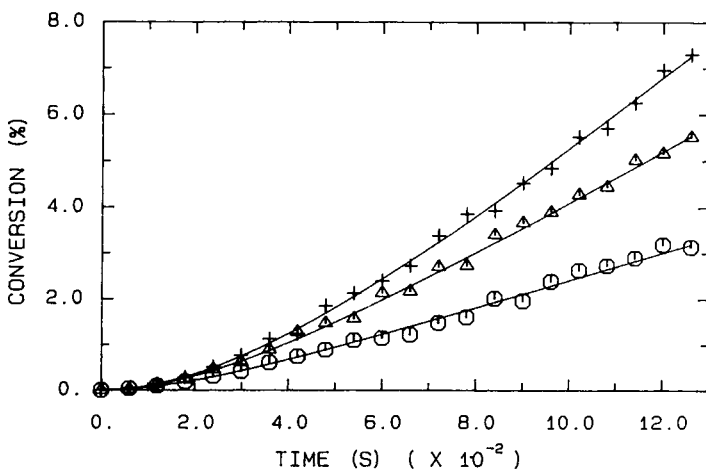


Fig. 2. Comparison between calculated (solid lines) and "experimental" conversions;  $[I_2] = 5 \times 10^{-5} \text{ mol dm}^{-3}$ : ( $\odot$ )  $N_T = 2 \times 10^{16} \text{ particles dm}^{-3}$ ; ( $\Delta$ )  $N_T = 4 \times 10^{16} \text{ particles dm}^{-3}$ ; (+)  $N_T = 6 \times 10^{16} \text{ particles dm}^{-3}$ .



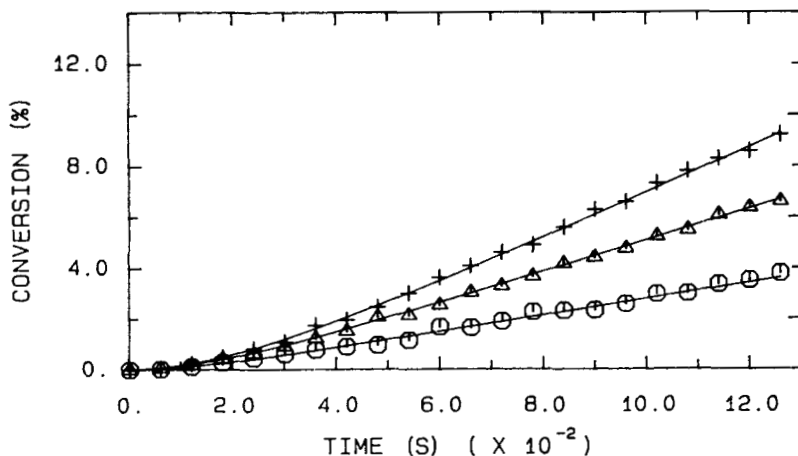


Fig. 3. Comparison between calculated (solid lines) and "experimental" conversions;  $[I_2] = 10^{-4} \text{ mol dm}^{-3}$ : ( $\odot$ )  $N_T = 2 \times 10^{16} \text{ particles dm}^{-3}$ ; ( $\Delta$ )  $N_T = 4 \times 10^{16} \text{ particles dm}^{-3}$ ; (+)  $N_T = 6 \times 10^{16} \text{ particles dm}^{-3}$ .

Table VI summarizes the results obtained for different initial guesses. It was found that a good fit of the data was achieved with all the initial guesses, which all resulted in the same residual sum of squares. The residual sum of squares, which is based on the fractional, not percentage, conversion, obtained with the exact parameters is included in the table for reference. Figures 1-7 show the results obtained with the first set of parameters, and the same results were reached with the other sets of parameters. It can be seen from Table VI that good estimates of the radical desorption coefficient ( $k_d$ ) and the initiator decomposition constant ( $k_i$ ) were obtained irrespective of the initial guess. However, different values of  $k_a$  and  $k_{tw}$  resulted in fits of the data that were indistinguishable from each other with respect to both the residual sum

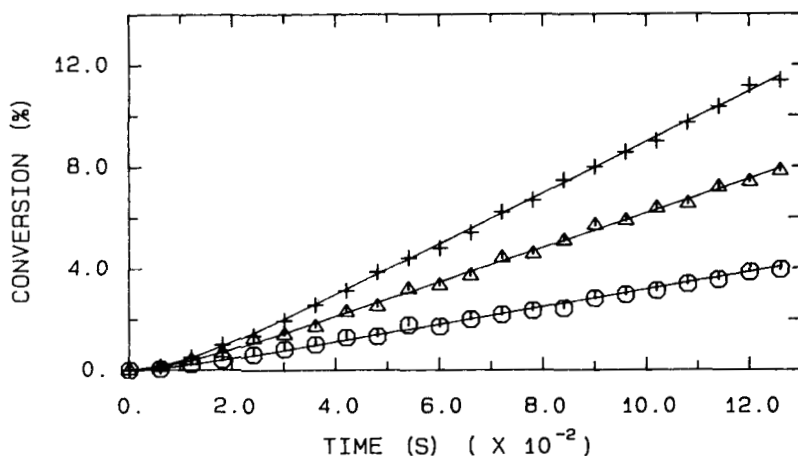


Fig. 4. Comparison between calculated (solid lines) and "experimental" conversions;  $[I_2] = 3 \times 10^{-4} \text{ mol dm}^{-3}$ : ( $\odot$ )  $N_T = 2 \times 10^{16} \text{ particles dm}^{-3}$ ; ( $\Delta$ )  $N_T = 4 \times 10^{16} \text{ particles dm}^{-3}$ ; (+)  $N_T = 6 \times 10^{16} \text{ particles dm}^{-3}$ .

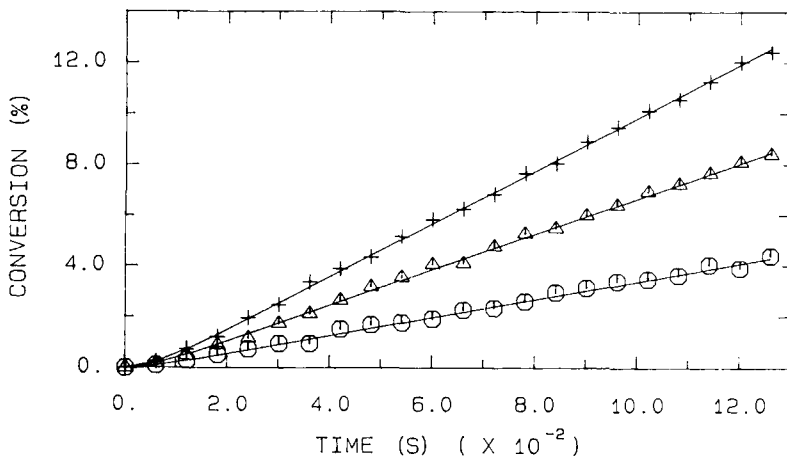


Fig. 5. Comparison between calculated (solid lines) and "experimental" conversions;  $[I_2] = 7 \times 10^{-4} \text{ mol dm}^{-3}$ ; (O)  $N_T = 2 \times 10^{16} \text{ particles dm}^{-3}$ ; ( $\Delta$ )  $N_T = 4 \times 10^{16} \text{ particles dm}^{-3}$ ; (+)  $N_T = 6 \times 10^{16} \text{ particles dm}^{-3}$ .

of squares and the conversion, suggesting either the presence of multiple minima in the objective function or a correlation between  $k_a$  and  $k_{tw}$ .

A close fit of the data was obtained for all of the experimental conditions, i.e., for all initiator concentrations and particle numbers, as illustrated by Figures 1-7. This implies that the value of  $N_1$  at all times is close to the exact value. If  $N_1$  and  $k_d$  have the correct values then, from eq. (9), the product  $k_a[R]_w$  must also have the correct value. Therefore, the four sets of parameters in Table VI result in the same value of  $k_a[R]_w$  at any given process time and experimental condition. The same is true for the first two terms on the right-hand side of eq. (7). Taking into account that the pseudo-steady-state

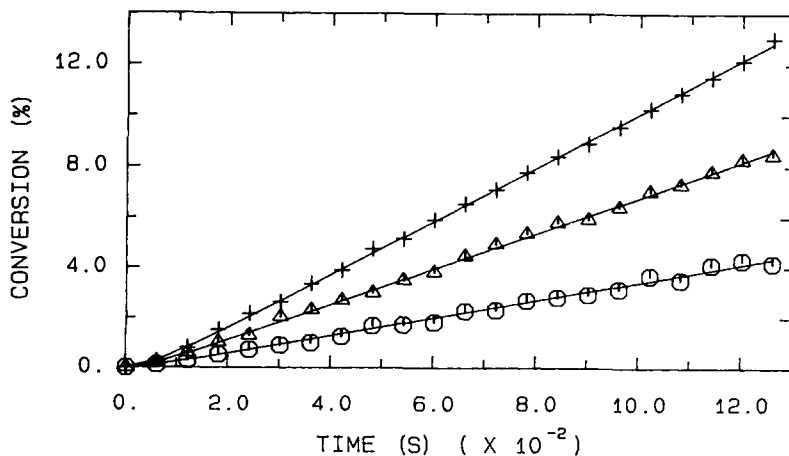


Fig. 6. Comparison between calculated (solid lines) and "experimental" conversions;  $[I_2] = 10^{-3} \text{ mol dm}^{-3}$ ; (O)  $N_T = 2 \times 10^{16} \text{ particles dm}^{-3}$ ; ( $\Delta$ )  $N_T = 4 \times 10^{16} \text{ particles dm}^{-3}$ ; (+)  $N_T = 6 \times 10^{16} \text{ particles dm}^{-3}$ .

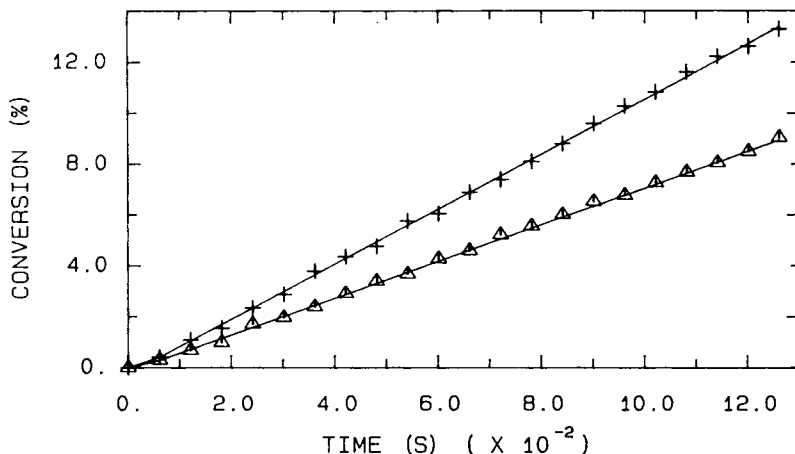


Fig. 7. Comparison between calculated (solid lines) and "experimental" conversions;  $[I_2] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ ; ( $\Delta$ )  $N_T = 4 \times 10^{16} \text{ particles dm}^{-3}$ ; (+)  $N_T = 6 \times 10^{16} \text{ particles dm}^{-3}$ .

condition holds for eq. (7), the previous arguments lead to

$$\frac{2k_{tw}[\text{R}]_w^2}{\phi_w} + \frac{k_a[\text{R}]_w N_T}{N_A} + \text{const}_1 = 0 \quad (33)$$

$$k_a[\text{R}]_w = \text{const}_2 \quad (34)$$

Combination of eqs. (33) and (34) and solving for  $[\text{R}]_w$  results in

$$[\text{R}]_w = \text{const}_3/k_{tw}^{1/2} \quad (35)$$

Substitution of eq. (35) into eq. (34) gives

$$k_a = \text{const}_4 k_{tw}^{1/2} \quad (36)$$

Figure 8 shows that the estimated values of  $k_a$  and  $k_{tw}$  presented in Table VI satisfy eq. (36). This equation states that  $k_{tw}$  and  $k_a$  cannot be unambiguously determined unless some independent measurement of the concentration of radicals in the aqueous phase is available. In the derivation of eq. (36), the only assumptions made were that the experimental conversion vs. time curves are well fitted and that the other parameters are well determined. Therefore, this conclusion is not restricted to the zero-one system or to this particular type of experiment, but holds for any experimental design based on the evolution of a property related to the polymer particles (conversion, molecular weight distribution or PSD).

It is worth examining the effect of the correlation between  $k_a$  and  $k_{tw}$  on both fundamental studies and on the use of these parameters in predictive mathematical models. The main goal in determining  $k_a$  is to elucidate the mechanism of entry of free radicals into latex particles by establishing the dependence of the entry rate coefficient on such characteristics of emulsion

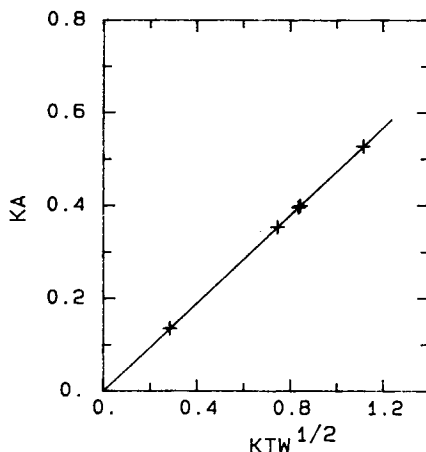


Fig. 8. Correlation between  $k_a$  and  $k_{tw}$ .

polymerization systems as seed latex particle size. The correlation between  $k_a$  and  $k_{tw}$  does not create a difficulty for these types of studies because the dependence of  $k_a$  on a given characteristic of the system can be readily analyzed by setting  $k_{tw}$  equal to a constant value. Although the actual value of  $k_a$  is not known (the estimated value of  $k_a$  is its actual value divided by the square root of the error in  $k_{tw}$ ), it is not the actual value but the dependence with respect to the characteristics of the system that is important in these types of studies. The actual value could have some effect in the predictions of mathematical models. However, each set of estimated  $k_a$  and  $k_{tw}$  together will accurately predict the behavior of the system because, as shown previously, they fit the simulated data obtained over a wide range of experimental conditions.

Due to the correlation between  $k_a$  and  $k_{tw}$ ,  $k_{tw}$  will be equal to  $7 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in all subsequent calculations.

#### *Effect of the Reparametrization*

The use of reparametrization implies some estimation of the order of magnitude of the kinetic parameters. Although it seems reasonable to assume that this estimation will be within 2 orders of magnitude of the actual value of a given parameter, in general, one will expect a reparametrization less favorable than the one given by eqs. (29)–(32), i.e., that the reparametrized rate constants, instead of having similar values, will have values that may differ by 2 orders of magnitude. Therefore, the influence of the reparametrization factor was investigated by using 12 simulated experiments in which the initiator concentration ranged from  $2 \times 10^{-4}$  to  $3.9 \times 10^{-4} \text{ mol dm}^{-3}$  and the number of particles varied between  $2 \times 10^{16}$  and  $4 \times 10^{16} \text{ dm}^{-3}$ . The results are presented in Table VII. From this table it can be seen that accurate values of the parameters were obtained for all of the reparametrization factors. However, the larger the differences between the reparametrized rate constants, the larger the computer time required for the estimation.

TABLE VII  
Effect of the Reparametrization Factor

Reparametrization factor		Estimated parameters					
$f(k_a)$	$f(k_d)$	$f(k_1)$	$f(k_{tw})$	$k_a$	$k_d$	$k_1$	$k_{tw}$
$10^7$	$10^{-2}$	$10^{-5}$	$10^8$	$0.4086 \times 10^6$	$0.1055 \times 10^{-2}$	$0.1018 \times 10^{-5}$	$0.7 \times 10^8$
$10^9$	$10^{-2}$	$10^{-5}$	$10^8$	$0.4086 \times 10^6$	$0.1055 \times 10^{-2}$	$0.1018 \times 10^{-5}$	$0.7 \times 10^8$
$10^7$	$10^{-2}$	$10^{-6}$	$10^8$	$0.4086 \times 10^6$	$0.1055 \times 10^{-2}$	$0.1018 \times 10^{-5}$	$0.7 \times 10^8$

*Influence of the Number of Experiments and Range  
of Experimental Conditions*

Although constancy of the rate parameters was assumed in order to generate the data, there is some doubt as to whether these parameters remain constant when the concentration of initiator varies by 2 orders of magnitude or the total number of polymer particles changes by a factor of 2 or 3. Therefore, it is important to determine the minimum number of experiments needed to accurately estimate the kinetic parameters, as well as the minimum range of variation of the experimental conditions. Table VIII summarizes the results of the analysis, with the results obtained using 20 experiments included as a reference. Both initiator concentration and total number of particles were varied. Due to the correlation between  $k_a$  and  $k_{tw}$ ,  $k_{tw}$  was held constant and the other three parameters were estimated. As a different number of simulated experiments were used in each case, the residual sum of squares per experiment is used as a measure of the accuracy of the fit. However, it should be pointed out that this is an approximate criterion because the absolute values of the conversion change with experimental conditions and, for equivalent fittings, the value of the residual sum of squares increases with the value of the conversion, namely with  $[I_2]$  and  $N_T$ . The values of the residual sum of squares presented in Table VIII indicate that, under all conditions, the data are well fitted and the degree of fitting is similar for all cases. However, in some cases the values of the estimated parameters are quite different from those in Table I. A good fit of the data and values of the estimated parameters far from the exact ones indicate too many degrees of freedom in the system, i.e., too few experimental results to estimate so many parameters. From Table VIII, it can be seen that, in general, the accuracy of the estimated parameters increases when either the number of experiments or the range of experimental conditions increases. Nevertheless, Table VIII shows that when only the initiator concentration is varied, the accuracy of the estimated parameters is limited, even if a wide range of initiator concentrations and seven experiments are considered. On the other hand, Table VIII shows that when both the initiator concentration and the number of particles are varied and a minimum of 9–12 experiments are available, the kinetic parameters can be accurately estimated even if a narrow range of initiator concentrations is used. From Table VIII, one can infer that in order to carry out a reliable parameter estimation, a minimum of 9–12 experiments are needed. In addition, the experimental design should include variation of both initiator concentration and number of polymer particles. The same particle size has to be used in all of the runs.

*Effect of the Experimental Noise*

As explained previously, the experimental noise expected in well-controlled experiments can be estimated to be less than  $\pm 0.2$  in the percentage conversion. However, under some circumstances, such as poor temperature control, the experimental noise may be more intense. The effect of different degrees of experimental noise is presented in Table IX. The noise is assumed to be random. It can be seen that accurate values of the estimated parameters were obtained even with experimental noise as large as  $\pm 0.4$  in the percentage

TABLE VIII  
Influence of the Number of Experiments and Range of Experimental Conditions on the Accuracy of the Estimated Parameters

Range [ $I_2$ ]	No. levels	Range $N_T$	No. levels	Expts	$k'_a$	$k'_d$	$k'_i$	$k'_{iw}$	(Sum/expts)
$10^{-5}$ - $3 \times 10^{-3}$	7	$2 \times 10^{16}$ - $4 \times 10^{16}$	3	20	0.3958	0.0992	0.0999	0.700	$2.008 \times 10^{-5}$
$2 \times 10^{-4}$ - $3.2 \times 10^{-4}$	3	$4 \times 10^{16}$	1	3	0.2719	0.1019	0.1462	0.700	$2.196 \times 10^{-5}$
$2 \times 10^{-4}$ - $3.9 \times 10^{-4}$	4	$4 \times 10^{16}$	1	4	0.2597	0.1021	0.1545	0.700	$2.307 \times 10^{-5}$
$10^{-4}$ - $10^{-3}$	3	$4 \times 10^{16}$	1	3	0.3917	0.0837	0.0896	0.700	$3.450 \times 10^{-5}$
$10^{-4}$ - $10^{-3}$	4	$4 \times 10^{16}$	1	4	0.3891	0.0765	0.0872	0.700	$3.563 \times 10^{-5}$
$10^{-5}$ - $3 \times 10^{-3}$	7	$4 \times 10^{16}$	1	7	0.3685	0.0895	0.0993	0.700	$3.677 \times 10^{-5}$
$2 \times 10^{-4}$ - $3.2 \times 10^{-4}$	3	$2 \times 10^{16}$ - $4 \times 10^{16}$	2	6	0.4737	0.1052	0.0901	0.700	$1.870 \times 10^{-5}$
$2 \times 10^{-4}$ - $3.9 \times 10^{-4}$	4	$2 \times 10^{16}$ - $4 \times 10^{16}$	2	8	0.4726	0.1048	0.0891	0.700	$1.998 \times 10^{-5}$
$2 \times 10^{-4}$ - $3.2 \times 10^{-4}$	3	$2 \times 10^{16}$ - $6 \times 10^{16}$	3	9	0.4090	0.1045	0.1009	0.700	$2.066 \times 10^{-5}$
$2 \times 10^{-4}$ - $3.9 \times 10^{-4}$	4	$2 \times 10^{16}$ - $6 \times 10^{16}$	3	12	0.4086	0.1055	0.1018	0.700	$2.166 \times 10^{-5}$

TABLE IX  
Effect of the Experimental Noise on the Estimated Parameters

	Perfect experiments	$(x \pm 0.2)\%$	$(x \pm 0.4)\%$
$k'_a$	0.4	0.3962	0.3949
$k'_d$	0.1	0.0992	0.0969
$k'_1$	0.1	0.0999	0.1016
$k'_{tw}$	0.7	0.7000	0.7000
Sum	$4.6 \times 10^{-11}$	$4.02 \times 10^{-4}$	$1.25 \times 10^{-3}$

conversion. This value largely exceeds the usual magnitude of the experimental noise.

### *Effect of the Systematic Errors*

The effect of the systematic error due to a poor determination of the initial time is presented in Table X. Parameter estimation was carried out using the 12 experiments of the last case in Table VIII, with the initial times of all or some of the experiments shifted by 1 min. Although it is doubtful that the distribution of errors allows the reduction of the likelihood function to the residual sum of squares, eq. (14) was used as the objective function to estimate the parameters. Comparison between estimated and exact values of the parameters gives an estimation of the errors introduced by both incorrect determination of the initial time and use of eq. (14) as the objective function. Table X shows that, although the estimated values of the parameters are in the same range as the exact ones, variations greater than 100% were obtained for some parameters in all cases.

Other sources of systematic errors are the inaccuracy of the determination of the number of particles and the uncertainty related to the value of  $k_p$ . Table XI shows that an error of 10% in either  $N_T$  or  $k_p$  results in variations of

TABLE X  
Effect of the Error in Setting the Initial Time on the Estimated Parameters

Fraction of erroneous expts	$k'_a$	$k'_d$	$k'_1$	$k'_{tw}$
3/12	0.7623	0.1317	0.0953	0.700
4/12	1.2110	0.1234	0.0804	0.700
12/12	1.9020	0.3896	0.2412	0.700

TABLE XI  
Effect of the Errors in  $k_p$  and  $N_T$  upon the Estimated Parameters

	$k_p \times 1.1$	$N_T \times 1.1$
$k'_a$	0.2084	0.2180
$k'_d$	0.1971	0.1772
$k'_1$	0.1306	0.1352
$k'_{tw}$	0.7000	0.7000
Sum	$1.96 \times 10^{-3}$	$1.45 \times 10^{-3}$



TABLE XII  
 Estimation of All of the Parameters of the Model

Experiments	Initial guess				Estimated parameters				
	$k'_a$	$k'_d$	$k'_i$	$k'_p$	$k'_a$	$k'_d$	$k'_i$	$k'_{iw}$	$k'_p$
20	0.9	0.5	0.5	0.3	0.3869	0.1010	0.1004	0.7000	0.2587
12	0.9	0.5	0.5	0.3	0.4273	0.0967	0.1004	0.7000	0.2557
12	0.9	0.5	0.5	0.03	0.4273	0.0967	0.1004	0.7000	0.2557
12	0.9	0.5	0.5	1.00	0.4273	0.0967	0.1004	0.7000	0.2557

100% in the values of the estimated parameters. The only method of reducing the error in  $N_T$  is to have a more accurate measure before the beginning of the experiments. However,  $k_p$  can be included as an estimable parameter and determined simultaneously with the rest of the kinetic parameters. In this way, the uncertainty in the rate parameters arising from any error in  $k_p$  is removed.

#### *Estimation of all of the Parameters of the Model*

Table XII shows the results obtained by using different numbers of experiments and different initial guesses when  $k_p$  is included as a parameter. Two different experimental designs were considered: (1) 20 experiments including three different numbers of particles and seven different initiator concentrations ranging from  $1 \times 10^{-5}$  mol dm<sup>-3</sup> to  $3 \times 10^{-3}$  mol dm<sup>-3</sup> (data given in Tables III–V) and (2) 12 experiments including three different numbers of particles and four initiator concentrations ranging from  $2 \times 10^{-4}$  mol dm<sup>-3</sup> to  $3.9 \times 10^{-4}$  mol dm<sup>-3</sup> (last case in Table VIII). In these calculations the propagation rate constant was reparametrized as follows:

$$k'_p = k_p/10^3 = 0.258 \quad (37)$$

It can be seen that, in all cases, accurate values of all of the parameters were obtained. This demonstrates that the approach presented in this paper allows the accurate determination of all of the parameters of the model, including the propagation rate constant, by using data obtained from a simple experimental design.

#### *Effect of the Irreproducibility between Runs*

The effect of the run-to-run irreproducibility on the values of the estimated parameters is presented in Table XIII. The error assigned to each conversion curve was determined using a Gaussian random number generator. Errors as large as  $\pm 8\%$  were included and two different sets of experiments were considered. In the first, the 12 experiments of the last case of Table VIII were used to carry out the parameter estimation. Table XIII shows that, although the estimated values of the parameters are in the same range as the exact ones, significant deviations were obtained for some parameters. The experiments were duplicated by assigning a new error to each of the 12 experiments and the parameter estimation carried out again using all 24 experiments. Table XIII shows that the estimated values of the parameters become much closer to the exact ones when the duplicated experiments are considered in the estimation.

TABLE XIII  
Effect of the Irreproducibility between Runs on the Values of the Estimated Parameters

Number of experiments	$k'_a$	$k'_d$	$k'_i$	$k'_p$
12	0.3274	0.3878	0.0751	0.2749
24	0.3478	0.1605	0.1034	0.2737

*Comparison with the Sydney Approach*

The majority of the work done by the Sydney group on parameter estimation involves the use of the fate parameter  $\alpha$ . It is usually assumed that  $\alpha$  is a constant for a particular system, irrespective of the initiator concentration and particle number. This is probably only true under limited conditions, i.e., a narrow range of initiator concentration and a single particle number. This paper has focused on estimating more fundamental parameters without the need for such assumptions as a constant value of  $\alpha$  for a given system. Indeed, the Sydney group has already presented a model for aqueous phase events in order to estimate  $k_a$ , but their approach still requires a knowledge of  $\alpha$ , as well as the termination rate coefficient in the aqueous phase plus some additional fitting.<sup>11</sup>

In order to compare the approach of the Sydney group with the present method, the data generated for the parameter estimation by eqs. (7)–(9) were analyzed using the slope/intercept method developed by the Sydney group in terms of eqs. (3)–(5), to obtain both  $\rho_A$  and  $k_d$ . Each experimental curve must be analyzed separately and the value of  $\alpha$  must be assumed. This analysis was carried out for four different values of  $\alpha$ . The results are presented in Table XIV. At the higher initiator concentrations, the value of  $\alpha$  only marginally

TABLE XIV  
Sydney Analysis of the Simulated Data

$[I_2]$	$\alpha$	$\rho_A \times 10^2$	$k_d \times 10^4$
$10^{-3}$	-1	1.215	0.0978
	0	1.189	0.0998
	0.5	1.118	0.1020
	1	1.166	0.1020
$7 \times 10^{-4}$	-1	0.972	0.0970
	0	0.950	0.0995
	0.5	0.938	0.1008
	1	0.927	0.1022
$3 \times 10^{-4}$	-1	0.561	0.0940
	0	0.541	0.0982
	0.5	0.530	0.1005
	1	0.519	0.1029
$10^{-4}$	-1	0.257	0.0862
	0	0.242	0.0943
	0.5	0.233	0.0990
	1	0.224	0.1044
$5 \times 10^{-5}$	-1	0.151	0.0776
	0	0.139	0.0891
	0.5	0.132	0.0964
	1	0.125	0.1053
$10^{-5}$	-1	0.038	0.0491
	0	0.035	0.0668
	0.5	0.032	0.0819
	1	0.028	0.1067
$5 \times 10^{-6}$	-1	0.020	0.0374
	0	0.019	0.0551
	0.5	0.017	0.0725
	1	0.014	0.1074

affected the resulting values of  $\rho_A$  and  $k_d$ . However, at the lower initiator concentrations, the choice of  $\alpha$  is very important in determining  $k_d$ , and to a lesser extent  $\rho_A$ . This is to be expected as in this range the exited free radicals contribute significantly to the aqueous phase radical concentration, whereas at higher concentrations of initiator they only contribute a very small fraction of the radical population. As  $k_d$  should be independent of initiator concentration, it is possible to draw two conclusions from Table XIV: (1)  $\alpha$  is equal to 1 over the entire range of initiator concentration; or (2)  $\alpha$  varies from a value close to 1 at lower initiator concentrations to something less than 1 (but not easily quantified) at higher initiator concentrations.

In order to obtain some reference values,  $\alpha$  can be calculated from eqs. (7)–(9) by comparing the rate of entry of radicals into the particles in the presence and absence of radical desorption and using the exact values of the parameters given in Table I. The values of  $\alpha$  calculated ranged from 0.94 for  $[I_2] = 5 \times 10^{-6}$  to 0.24 for  $[I_2] = 10^3$  mol dm<sup>-3</sup>. These simple calculations invalidate the first possible conclusion, i.e., that  $\alpha = 1$  over the entire range of  $[I_2]$ . Therefore, no definitive value of  $\alpha$  could be obtained from the Sydney approach because no quantifications followed the second conclusion. Further mechanistic studies to estimate  $k_a$  required the knowledge of  $\alpha$ ,  $k_{tw}$ , and some additional fitting.<sup>11</sup> This resulted in large uncertainties in the estimation of the rate parameters. It was also required that  $k_p$  be known.

## CONCLUSIONS

A novel approach for the estimation of kinetic parameters in emulsion polymerization systems has been presented. The approach, which uses the time evolution of the conversion in chemically initiated seeded emulsion polymerization, is based on a model that includes the radical balance in the aqueous phase and fundamental parameters such as entry and exit rate coefficients, the termination rate constant in the aqueous phase and the rate coefficient for initiator decomposition. These parameters, together with the propagation rate constant, are estimated by using all of the available experimental data at the same time. Therefore, the method does not depend on any parameter value taken from the literature. It has been found that accurate values of all the parameters can be obtained through the present approach, provided that a minimum number of experiments are available. This minimum ranges between 9 and 12 and the use of three different values of the number of particles is advised. However, only chemically initiated emulsion polymerization experiments are needed. An important conclusion of this study is that the entry rate coefficient and the termination rate constant in the aqueous phase are correlated, with the result that these parameters cannot be unambiguously determined. It has been found that the values of the estimated parameters are not affected by the experimental noise due to random errors such as temperature oscillations and operator-related errors in the measurement of the height of the meniscus in the dilatometer. However, when the experiments contain systematic errors, the estimated parameters are greatly affected.

The present methodology offers more advantages than the previous approaches 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, including the propagation rate constant, by using data obtained from a simple experimental design.

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### APPENDIX: NOMENCLATURE

$c$	termination rate coefficient ( $s^{-1}$ )
$\mathbf{F}$	vector of functions [eq. (11)]
$G_j$	number of experimental points in experiment $j$
$\mathbf{H}$	matrix defined by eq. (18)
$[I_2]$	initiator concentration ( $\text{mol dm}^{-3}$ )
$\mathbf{J}$	vector defined by eq. (19)
$\mathbf{K}$	vector of adjustable parameters [eq. (13)]
$\Delta\mathbf{K}$	vector of increments of adjustable parameters
$k_a$	rate coefficient for radical entry ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )
$k'_a$	reparametrized rate coefficient for radical entry
$k_d$	radical desorption rate coefficient ( $s^{-1}$ )
$k'_d$	reparametrized radical desorption coefficient
$k_I$	rate constant for generation of polymerizing free radicals from initiator decomposition ( $s^{-1}$ )
$k'_I$	reparametrized rate constant for generation of polymerizing free radicals from initiator decomposition
$k_p$	propagation rate constant ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )
$k_t$	termination rate constant ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )
$k_{tw}$	termination rate constant in the aqueous phase ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )
$k'_{tw}$	reparametrized termination rate constant in the aqueous phase
$M$	number of experiments
$[M]_p$	monomer concentration in the polymer particles ( $\text{mol dm}^{-3}$ )
$M_0$	initial number of moles of monomer per $\text{dm}^3$ of water
$\bar{n}$	average number of radicals per particle
$N_A$	Avogadro's constant
$N_i$	number of particles containing $i$ radicals per $\text{dm}^3$ of water
$N_T$	number of polymer particles per $\text{dm}^3$ of water
$\mathbf{Q}$	weighting matrix
$[R]_w$	concentration of radicals in the aqueous phase ( $\text{mol dm}^{-3}$ )
$\mathbf{S}$	vector of state variables [eq. (12)]
Sum	residual sum of squares
$t$	time
$v_p$	volume of one polymer particle ( $\text{dm}^3$ )
$x$	conversion

$x_c$	conversion predicted by the model
$x_e$	"measured" conversion
$\mathbf{Y}$	vector of independent variables
$(\mathbf{X}_e - \mathbf{X}_c)$	vector of residuals of observable variables

### Superscripts

$h$  values calculated using a particular set of parameters

### Greek Symbols

$\alpha$	fate parameter
$\phi_w$	volume fraction of water in the aqueous phase
$\rho$	global radical entry rate coefficient defined by eq. (3)
$\rho_A$	global radical entry rate coefficient in absence of radical desorption ( $\text{s}^{-1}$ )

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