Estimation of Copolymerization Kinetic Parameters by Maximum Likelihood Method

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DOI 10.1002/aic.10109

A kinetic study of free-radical solution copolymerization of isobutyl methacrylate and lauryl methacrylate in benzene, initiated with 2,2-azoisobutyronitrile (AIBN) was performed at different monomer feed compositions, at low conversion level. To avoid the complications of copolymerization kinetics, the compositional-averaged rate constant method was applied to dead-end polymerization in constant and variable volume polymerization systems. A conditional probability approach, with "maximum likelihood function" (MLF), was used for estimating the kinetic parameters from experimental data. This method provides point estimates as well as joint probability regions. The validity of this method was approved for the statistically justified and best estimation of the rate parameters in copolymerization systems. Statistical analysis indicated that, although copolymer composition is well described by the terminal unit model (TUM), the rate data are not. Like many other systems recently examined, the data were well represented by the implicit penultimate unit effect (IPUE) model of Fukuda and coworkers. It was found that the coupled rate parameter $\bar{k}_p/\bar{k}_t^{0.5}$ is greater than the TUM predictions, whereas most of the previous systems studied have coupled rate parameters lower than those predicted by the TUM. An interactive computer simulator for parameter estimation was developed, which is run in two modes of estimation and prediction and is capable of receiving input data from both keyboard and databank. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 1260–1272, 2004

Keywords: methacrylate, dead-end polymerization, kinetics, maximum likelihood estimation (MLE), implicit penultimate unit effect (IPUE)

Introduction

Kinetic studies are a powerful tool for better understanding of polymerization. As pointed out by Hutchinson et al. (1997) many investigators found that the copolymer composition and sequence distribution are well described by the terminal unit model (TUM), but the copolymerization rate is not (Davis et al., 1991; Fernandez-Garcia and Madruga, 1997; Fukuda et al., 1985). Jenkins and O'Driscoll (1995) attributed the rate abnormalities to termination reactions and represented them by introducing physically unrealistic cross-termination rate constants. However, there is convincing evidence that shows rate deviations are not the consequence of diffusion-controlled termination reactions but result from the failure of TUM to

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explain the propagation kinetics (Fukuda et al., 1992). The failure of TUM to describe propagation kinetics in free-radical copolymerization was originally reported by Fukuda et al. (1985). In an attempt to explain the experimental results, Fukuda and coworkers suggested a penultimate unit model based on a postulate that radical stabilization energies are influenced by the penultimate units. The experimental technique used in these studies was a conventional rotating-sector procedure (Ma et al., 1993, 1994). The failure of TUM to describe the propagation kinetics for styrene/methacrylate (Davis et al., 1990), styrene/acrylate (Schoonbrood et al., 1995), and acrylate/methacrylate (Buback et al., 2001) copolymerization systems have also been demonstrated by application of pulsed-laser methods. For most of these systems to date, except for *n*-butyl acrylate/methyl methacrylate (BA/MMA) studied by Madruga and Fernandez-Garcia (1996), and Hutchinson et al. (1997), experimental measures of the copolymerization rate are lower than those predicted by TUM. The data of Buback et al. (2001) also show $\bar{k}_p$ values that are greater than those predicted by the TUM.

Estimation of kinetic parameters is a critical part of developing a process model for industrial polymerization processes (Bonilla et al., 2002; Bosch et al., 1998; Fernandez-Garcia and Madruga, 1997; Hutchinson et al., 1997; Woo-Hyeon et al., 1998). The best estimates can be obtained when the model is perfect and correct estimates of normally distributed errors in all variables are known. Maximum likelihood estimation (*MLE*) provides a consistent approach to parameter estimation problems. The main advantage of the *MLE* method is that it accounts for all the errors in all variables, as well as numerical simplicity and stability. This method has many large sample properties that make it attractive for use. It is asymptotically consistent and is the minimum variance unbiased estimator as the sample size increases. By unbiased, we mean that if we take a very large number of random samples with replacement from a population, the average value of the parameter estimates will be theoretically exactly equal to the population value. By minimum variance, we mean that the estimator has the smallest variance, and thus the narrowest confidence interval, of all estimators of that type. It is asymptotically efficient, which means that for large samples it produces the most precise estimates. The distribution of the estimates themselves is normal, if the sample is large enough, and this is the basis for confidence bounds. The *MLE* method also has desirable mathematical and optimality properties and can handle suspensions and interval data (Vandal and Gentleman, 1998) better than rank regression, particularly when dealing with a heavily censored data set with few exact failure times, or when the censoring times are unevenly distributed. It also can provide estimates with one or no observed failures, which rank regression cannot do. This method has recently been applied for estimation of monomer reactivity ratios (Oracz and Kiam, 2001).

Recent studies show that the copolymer of isobutyl methacrylate and lauryl methacrylate (i-BMA/LMA) is an important base for oil additives with several functions such as viscosity-index improver, pour point depressant, and sludge dispersant (Habibi and Mahabadi, 1998). This copolymer is an example of a system that surprisingly has not been studied, at least to the authors' knowledge. The objective of this work is to acquire an experimental database for this new copolymer and to demonstrate the use of a proper experimental and statistical procedure to estimate kinetic parameters of the copolymerization. In addition, the validity of the *MLE* method for estimation of copolymerization kinetic parameters is tested against some existing data given in the literature. It is demonstrated that our formulation of *MLE* can be reliably and effectively used to determine the optimal parameter values, while simultaneously performing data reconciliation. The results of estimation method ensure the validity of the proposed reaction mechanism and predictions can be made to see whether the model is reasonable and consistent with experimental data.

Theoretical Background

Copolymerization rate

Modeling conversion against time is difficult because of the uncertainty of rate parameter values, which are usually both composition and conversion dependent. The average values of initiation, propagation, and termination rate parameters, which are functions of conversion because of compositional drift, are expressed as $\bar{k}_d$, $\bar{k}_p$, and $\bar{k}_t$, respectively. However, assuming a first-order rate equation with respect to monomer concentration $[M]$, the overall copolymerization rate R_p, either in the presence or the absence of solvent, may be in a general sense formally expressed in a way similar to homopolymerization (Madruga and Fernandez-Garcia, 1996; O'Driscoll and Huang, 1989; Tobita and Hamielec, 1991)

$$R_p = -\frac{d[M]}{dt} = (2f\bar{k}_d)^{0.5}\frac{\bar{k}_p}{\bar{k}_t^{0.5}}[I]^{0.5}[M] \tag{1}$$

where $[I]$ is the initiator concentration and f is the initiator efficiency, respectively.

Dead-End Polymerization. When the initiator concentration in the polymerization system decreases to a low value, the half-life of the propagating polymer chain approximates that of the initiator. Under such condition, a limiting conversion is observed. This condition refers to one in which the initiator concentration decreases to a low value that stops the polymerization short of completion. If this concentration can be determined accurately and if the polymerization does not exhibit autoacceleration effects, the corresponding limiting value of $[M]$ can be used to assess the kinetic parameters. This procedure guarantees the existence of the necessary conditions for the initial rate method, and conducts the experiments to remove autoacceleration, viscosity, and diffusional effects. Therefore, kinetic-controlled rate expressions can be used safely for reliable parameter estimation. Moreover, because of expanding the reaction time, the sampling procedure is easier and more reliable.

(1) *Dead-end polymerization without shrinkage.* Integration of R_p in Eq. 1 with respect to time yields

$$-\ln(1-X) = 2\bar{k}_p\left(\frac{2f[I]_0}{\bar{k}_t\cdot\bar{k}_d}\right)^{0.5}\left\{1-\exp\left(\frac{-\bar{k}_d t}{2}\right)\right\} \tag{2}$$

Power-series expansion of the exponential term and neglecting terms higher than first-order gives

$$F(X) = -\frac{\ln(1-X)}{t} = \left\{(2\overline{fk}_d)^{0.5}\left(\frac{\bar{k}_p}{\bar{k}_t^{0.5}}\right)[I]_0^{0.5}\right\}\left(1+\frac{\bar{k}_d t}{4}\right) \tag{3}$$

(2) *Dead-end polymerization with shrinkage.* Because of the difference in densities between polymer and monomer, the reaction volume shrinks as polymerization proceeds. Considering shrinkage, the rate of polymerization is given by (Dube et al., 1990)

$$\frac{dX}{dt} = \left(\frac{\bar{k}_p^2}{\bar{k}_t} 2\overline{fk_d}[I]_0\right)^{0.5} \frac{1 - X}{(1 + \varepsilon X)^{0.5}} \exp\left(-\frac{\bar{k}_d t}{2}\right) \tag{4}$$

where the shrinkage factor ε is defined by the following relation

$$\varepsilon = \frac{V|_{X=1} - V|_{X=0}}{V|_{X=0}} = \frac{V|_{X=1}}{V|_{X=0}} - 1 = \frac{\rho|_{X=0}}{\rho|_{X=1}} - 1 \tag{5}$$

where V is the reaction volume, and $\rho|_{X=0}$ and $\rho|_{X=1}$ are the density of the reaction mixture at zero and full conversion, respectively. Integration of Eq. 4 and power-series expansion of the exponential term yields

$$\int_0^X \frac{(1 + \varepsilon X)^{0.5}}{1 - X} dX = \left\{(2\overline{fk_d})^{0.5}\left(\frac{\bar{k}_p}{\bar{k}_t^{0.5}}\right)[I]_0^{0.5}\right\} \times \left[1 - \frac{1}{2!}\left(\frac{\bar{k}_d}{2}\right)t + \frac{1}{3!}\left(\frac{\bar{k}_d}{2}\right)^2 t^2 + \cdots\right] t \tag{6}$$

Neglecting terms higher than first order gives

$$G(X) = \frac{\int_0^X \frac{(1 + \varepsilon X)^{0.5}}{1 - X} dX}{t} = \left\{(2\overline{fk_d})^{0.5}\left(\frac{\bar{k}_p}{\bar{k}_t^{0.5}}\right)[I]_0^{0.5}\right\}\left(1 - \frac{\bar{k}_d t}{4}\right) \tag{7}$$

To determine the compositional variation of $\bar{W} = \bar{k}_p/\bar{k}_t^{0.5}$, it is assumed that $2\overline{fk_d}$ varies linearly with monomer feed composition according to the following empirical relationship (Madruga and Fernandez-Garcia, 1996)

$$2\overline{fk_d} = f_1(2fk_d)_1 + f_2(2fk_d)_2 \tag{8}$$

Fukuda et al. (1992) coined the phrase "explicit penultimate unit effect" (EPUE) to describe the systems that require all eight rate parameters in the penultimate model to describe the copolymer composition and rate. Following the treatment of Fukuda and coworkers, assuming that termination in copolymerization can be expressed by the Walling chemical factor equal to unity (Fukuda et al., 1985), the penultimate model expression yields

$$\bar{W} = \frac{\bar{r}_1 f_1^2 + 2f_1 f_2 + \bar{r}_2 f_2^2}{\left(\frac{\bar{r}_1 f_1}{\bar{W}_1}\right) + \left(\frac{\bar{r}_2 f_2}{\bar{W}_2}\right)} \tag{9a}$$

in which

$$\bar{W}_i = \frac{w_i(r_{ii} f_i + f_j)}{r_{ii} f_i + f_j s_i^{-1}} \qquad (i \neq j) \tag{9b}$$

$$\bar{r}_i = \frac{r_{ji}(f_i r_{ii} + f_j)}{f_i r_{ji} + f_j} \tag{9c}$$

$$w_i = \frac{k_{iii}}{k_{ti}^{0.5}} \qquad (i = 1, 2) \tag{9d}$$

$$r_{ii} = \frac{k_{iii}}{k_{iij}} \tag{9e}$$

$$r_{ji} = \frac{k_{jii}}{k_{jij}} \tag{9f}$$

$$s_i = \frac{k_{jii}}{k_{iii}} \tag{9g}$$

The rate parameters in the above equations refer to the following kinetic scheme for propagation

$$M_i M_j^* + M_k \xrightarrow{k_{ijk}} M_i M_j M_k^* \qquad i, j, k = 1, 2 \tag{10}$$

A comprehensive survey of the mechanism of the propagation step in free-radical copolymerization was recently provided by Coote and Davis (1999).

The implicit penultimate unit model assumes that the monomer reactivity ratios r_{11} and r_{22} are not affected by penultimate units, but that the ratios $s_i = k_{jii}/k_{iii}$ differ from unity because of penultimate effects. For the majority of the copolymerization systems, the copolymer composition is well described by TUM, but $\bar{k}_p/\bar{k}_t^{0.5}$ is not. These systems are well represented by setting $r_{11} = r_{21} = \bar{r}_1$ and $r_{22} = r_{12} = \bar{r}_2$ and are said to have an "implicit penultimate unit effect" (IPUE). For IPUE systems, composition data can be used to fit $\bar{r}_1$ and $\bar{r}_2$ according to TUM, with the resulting values then used to determine the s_i values from the rate or $\bar{W} = \bar{k}_p/\bar{k}_t^{0.5}$ data. Based on stabilization energy arguments, Fukuda et al. (1985) suggested that $\bar{r}_1\bar{r}_2 = s_1 s_2$. Because it is often difficult to obtain accurate estimates of both radical reactivities from experimental data, Fukuda et al. (1985) also suggested the simplification that $s_1 = s_2$. This approximation may do a reasonable job of correlating the available experimental data.

Maximum likelihood estimation

Many good statistical procedures use values for the population parameters that best explain the observed data. One meaning of the *best* is to select the parameter values that maximize the joint density evaluated at the observations. To make the procedure rigorous, a particular model is used and the method of "maximum likelihood estimation" (*MLE*) is developed around the model. The *likelihood L* of a sample of N observations, $X_1, X_2, \ldots, X_N$, is the joint probability function $p(X_1, X_2, \ldots, X_N)$ when $X_1, X_2, \ldots, X_N$ are discrete random variables (Johnson and Wichern, 1998; Neter et al., 1989). Simply speaking, the likelihood of a set of data is the probability of obtaining that particular set of data given the chosen probability model. This expression contains the unknown parameters. Those values of the parameter that maximize the sample likelihood are known as the *maximum likelihood estimates*. Another procedure is to maximize the log-likelihood function or to minimize the negative log-likelihood function. Using the properties of these estimators, it is possible to make inferences regarding the parameters in the underlying model. If e_i is considered to be the error of estimation, a statistically sound method like *MLE* must also be satisfied in the following error model conditions.

Error Model Conditions

(1) e_i possesses mean 0; $E(e_i) = 0$.

(2) e_i have a constant variance; $\mathrm{var}(e_i) = I\sigma^2$.

(3) e_i constitutes an independent collection of random variables; $\mathrm{cov}(e_i, e_j) = 0$.

(4) e_i are normally distributed; $e_i \sim N(0, I\sigma^2)$.

The normality condition is serious for estimation problems by the *MLE* method. Therefore the *Box–Cox* transformation was applied to the values of $F(X)$ and $G(X)$ in Eqs. 3 and 7 to bring them near to normality (Duever et al., 1988; Massart and Vandeginste, 1997). By selecting the *Box–Cox* transformation, we can produce a plot of the *residual sum of squares* as a function of the value of λ, where λ is used to define a transformation of $F(X)$ or $G(X)$. The value of λ, for which the residual sum of squares is a global minimum, is the maximum likelihood estimate for λ. Typically, the *Box–Cox* transformation of $F(X)$ can be written as follows

$$\psi = \begin{cases} \dfrac{\{F(X)\}^{\lambda} - 1}{\lambda g^{\lambda-1}} & \lambda \neq 0 \\ g \ln\{F(X)\} & \lambda = 0 \end{cases} \tag{11}$$

in which g is the geometric mean of $F(X)$. After considering normal distribution, the likelihood function for copolymerization rate data can be written as

$$L(\psi^m, \psi, t^m, t) = \frac{1}{\sqrt{2(\pi)^{2N}} \prod_{i=1}^{N} [\sigma(\psi_i)\sigma(t_i)]} \exp\left(-0.5 \sum_{i=1}^{N} \left\{ \left[\frac{\psi_i^m - \psi_i}{\sigma(\psi_i)}\right]^2 + \left[\frac{t_i^m - t_i}{\sigma(t_i)}\right]^2 \right\}\right) \tag{12}$$

where t is the polymerization time and ψ is the normal transform of $F(X)$ or $G(X)$. ψ^m, ψ, t^m, and t denote corresponding vectors for measured (superscript m) and expected (no superscript) values; N stands for the number of data points. The likelihood function is maximized by minimizing the following objective function

$$H = \sum_{i=1}^{N} \left\{ \left[\frac{\psi_i^m - \psi_i}{\sigma(\psi_i)}\right]^2 + \left[\frac{t_i^m - t_i}{\sigma(t_i)}\right]^2 \right\} \tag{13}$$

The objective function H should be minimized for all variables and parameters as follows

$$\frac{\partial H}{\partial t_i} = 0 \qquad \text{for} \qquad i = 1, \ldots, N \tag{14a}$$

$$\frac{\partial H}{\partial \bar{k}_d} = 0 \tag{14b}$$

$$\frac{\partial H}{\partial \bar{W}} = 0 \tag{14c}$$

It is clear to see that having $2N$ data (t_i^m, ψ_i^m) and $2N + 2$ unknowns (t_i, ψ_i, $\bar{k}_d$, $\bar{W}$) the minimization problem cannot be solved. However, the problem can be solved in terms of so-called independent and dependent variables. Normal transforms of Eqs. 3 and 7 offer a usable constraint for expressing the expected value of ψ in terms of polymerization time and rate parameters. In other words, ψ is selected as a dependent variable and then the objective function H depends on the polymerization time, rate parameters, and estimated variances of t and ψ. The estimated variance of ψ is calculated by the following error propagation method

$$\sigma(\psi_i) = \left[\left(\frac{\partial \psi_i}{\partial t_i}\right)^2 \sigma_{t_i}^2 + \left(\frac{\partial \psi_i}{\partial X_i}\right)^2 \sigma_{X_i}^2 \right]^{0.5} \tag{15}$$

where σ_{t_i} and σ_{X_i} are the uncertainties in the measurement variables t_i and X_i. The partial derivatives $\partial\psi_i/\partial t_i$ and $\partial\psi_i/\partial X_i$ are calculated at the sample mean of the measured variables and the necessary derivatives $\partial t_i/\partial \bar{k}_d$ or $\partial t_i/\partial \bar{W}$ are calculated by the following Maxwell relation

$$\frac{\partial t_i}{\partial \bar{k}_d} = -\frac{(\partial\psi_i/\partial\bar{k}_d)_{t_i}}{(\partial\psi_i/\partial t_i)_{\bar{k}_d}} \qquad \frac{\partial t_i}{\partial \bar{W}} = -\frac{(\partial\psi_i/\partial\bar{W})_{t_i}}{(\partial\psi_i/\partial t_i)_{\bar{W}}} \tag{16}$$

Substitution of Eq. 11 into Eq. 13 and performing differentiation according to Eqs. 14a–14c, a set of $N + 2$ equations with $N + 2$ unknown is obtained. One way to simplify these computations is to construct the design matrix so that its columns

Table 1. Chemical Formula of Monomers in the Copolymerization System

$H_2C{=}C(CH_3)CO_2C(CH_3)HCH_2CH_3$ Monomer 1: Isobutyl methacrylate (i-BMA)	$H_2C{=}C(CH_3)CO_2(CH_2)11CH_3$ Monomer 2: Lauryl methacrylate (LMA)

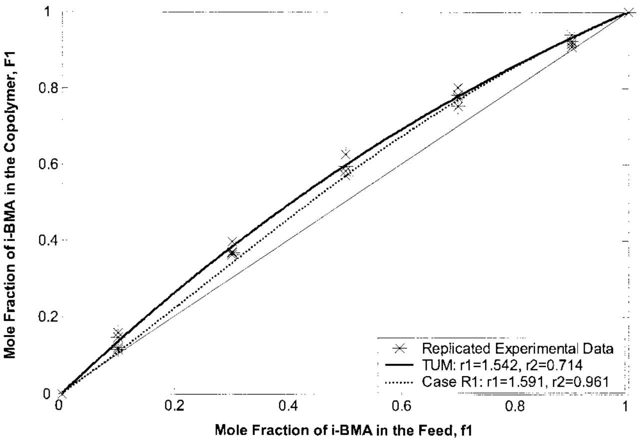


Figure 1. Copolymer composition vs. monomer feed composition in four replicated polymerization experiments at low conversion.

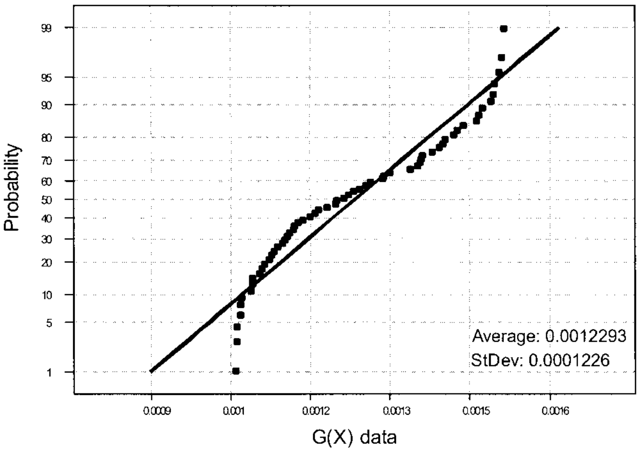


Figure 3. Normal probability plot of *G*(*X*) before *Box–Cox* transformation.

are orthogonal, which simply means that the dot product of any two distinct columns of design matrix is zero. For such a case, the product of design matrix with its transposes will be a diagonal matrix and therefore possess a trivially obtainable inverse. A modified Gram–Schmidt method is applied for orthogonalization and solving the estimation equations. This method also provides the expected variance–covariance matrix of parameter estimates as a by-product of its computations. In this problem solving, the results provide not only an estimate of the parameters but also an estimate of the "true" values of dependent and independent variables that can be obtained. Thus, there is an advantage that both parameter estimation and data reconciliation problems are being solved simultaneously.

Gram–Schmidt Method. The basic method for construction of orthogonal and orthonormal bases was first discovered by Laplace in the eighteenth century. The most basic is Gram–Schmidt orthogonalization (Arfken, 1985), in which the new basis functions are built up sequentially. The Gram–Schmidt process can be reinterpreted as a new kind of matrix factorization, in which a nonsingular matrix **A** = **QR** is written as the product of an orthogonal matrix **Q**, meaning a matrix whose columns form an orthonormal system, and an upper triangular matrix **R**. There are several different variations of the Gram–Schmidt method including classical Gram–Schmidt (CGS), modified Gram–Schmidt (MGS), and modified Gram–Schmidt with pivoting (MGSP). Rice (1966) provided analysis of serial versions of CGS, MGS, and MGSP as well as error analysis for each. Zapata et al. (1991) described an algorithm for MGS-QR factorization.

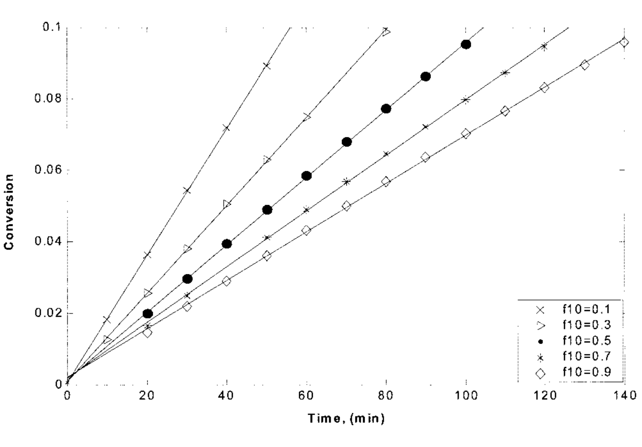


Figure 2. Conversion vs. time for different initial monomer feed compositions in benzene (f_{10}: initial mole fraction of i-BMA in the feed mixture).

We have chosen to implement MGS because it economizes storage and is generally more stable than CGS (Golub and van Loan, 1996) and also because MGSP shows only a small improvement while increasing the amount of work to be done (Rice, 1966). The modified Gram–Schmidt process takes a set of m linearly independent vectors of size n, $\{W_1, W_2, \ldots, W_m\}$, where $m \leq n$, and calculates a set of m orthonormal vectors of size n, $\{V_1, V_2, \ldots, V_m\}$. This method is a recursive procedure and can be implemented through the following recurrence relation

$$V_k = W_k - \sum_{j=1}^{k-1} \frac{(W \cdot V)}{\|V_j\|} V_j \qquad k = 1, \ldots, n \tag{17}$$

For this study, we consider the Euclidean inner product, represented by $(W \cdot V) = \sum_{i=1}^{n} W_i V_i$, and the Euclidean length or norm of a vector V, as $\| V \| = (V \cdot V)^{0.5}$.

Experimental

Materials

AIBN (Fluka Chemica, >98%) as an initiator was crystallized three times from a mixture of chloroform and methanol below 40°C in subdued light, dried under vacuum at room temperature over P_2O_5, and stored in the dark below −10°C until used. The melting point, measured by Perkin–Elmer DSC at a heating rate of 5°C/min, was 104.2°C.

The monomers, isobutyl methacrylate (Aldrich 99%) and lauryl methacrylate (Fluka, 98%), with 15 ppm methylethyl hydroquinon (MEHQ), were washed three times with a 10% NaOH, and then three times with freshly distilled water; dried over $CaCl_2$; and distilled under vacuum. Copper stearate was

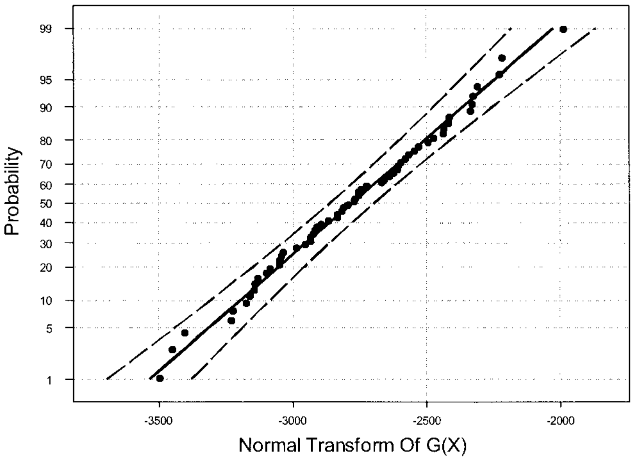


Figure 4. Normal probability plot of *G*(*X*) after *Box–Cox* transformation.

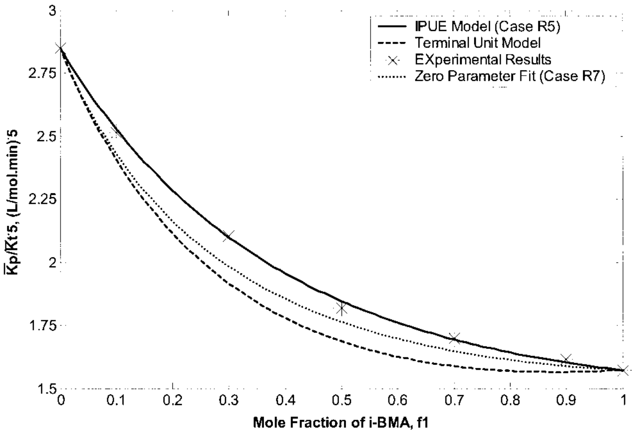


Figure 6. Variation of coupled rate parameter $\bar{k}_p/\bar{k}_t^{0.5}$ with monomer feed composition.

used for peroxide breaking in a distillation chamber and the middle fraction of distillate was collected and dried under vacuum at room temperature over $CaCl_2$ and stored at −10°C. The chemical formula of these monomers is shown in Table 1. Benzene was used as a solvent for solution copolymerization of these monomers. All other solvents and other reagents used over the course of experiments and characterization were used as received without further purification.

Polymerization

Borosilicate glass ampoules of length 7.5 cm and ID 15 mm were prepared. The initiator concentrations were 2.0×10^{-4} molar and the volume ratio of monomers to solvent (benzene) was 50%. The feed mixture, containing accurately known weights of monomers, solvent, and initiator, was placed in ampoules and flushed with oxygen-free nitrogen for 10 min for removing dissolved gases before sealing. The reaction mixture was then subdued to three freeze–pump–thaw cycles to remove residual oxygen. The sealed ampoules were vigorously shaken on the vortex mixer and immersed in a water bath regulated at the polymerization temperature. All copolymerization reactions were carried out at 70°C for 10 h to satisfy the dead-end polymerization condition. The limiting conversion in all cases was below 50%. Only the data up to 10% conversion were taken for the estimation of kinetic parameters. The complete data are not shown here for the sake of brevity, but are available from the authors.

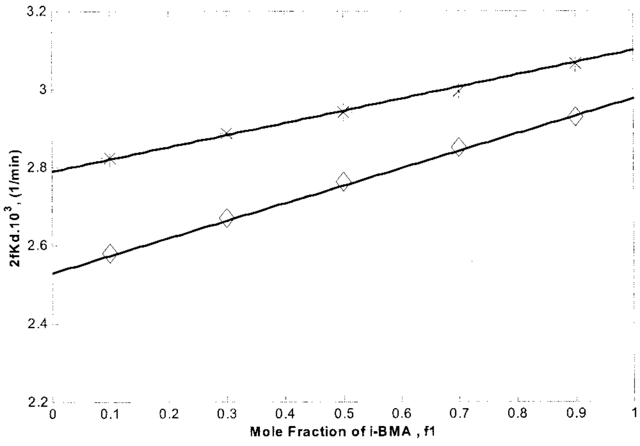


Figure 5. Variation of $2f\bar{k}_d$ with monomer feed composition.

The experiments were performed in seven different monomer feed compositions. At least four polymerization runs at each monomer feed composition were performed. After a prescribed period, the reaction mixture was quenched and precipitated in 10- to 20-fold excess by volume of isopropyl alcohol (IPA) containing a small amount (0.02 wt. %) of hydroquinone (99% Aldrich) solution to prevent further polymerization. The precipitate was allowed to stand for about 10 min, and the contents of the flasks were swirled to coagulate the polymers and collect the solids. Residual monomer was removed by three cycles of redissolving and reprecipitation in THF (Merck) and IPA, respectively. The copolymer was dried in a vacuum oven at 40°C for several days to reach constant weight. The conversion of monomer to polymer was measured by gravimetry and confirmed by dilatometry. The CHO content of copolymer, overall mass conversion, and global copolymer composition at different monomer feed compositions were determined.

Polymer characterization

Elemental Analysis. A Heraeuse apparatus model CHN-O-Rapid was used for elemental analysis. The apparatus was first calibrated and checked for gas leaking.

Densitometry. The density of monomer mixture was calculated by a simple mixing rule without considering the interaction between constituents. Density of polymerization samples was measured by an Anton Par digital densitometer. A small volume of sample (about 0.7 mL) was introduced into an oscillating sample tube and the change in the oscillating frequency, caused by the change in the mass of the tube, was used in conjunction with calibration data to determine the density of the sample. The samples must be homogeneous and free of even the smallest bubbles. After the instrument displayed a steady reading to four significant figures, indicating that a temperature equilibrium has been reached, the reading for

Table 2. Estimation of Kinetic Rate Parameters for $f_{10} = 0.9$ by Maximum Likelihood Function

	Without Shrinkage		With Shrinkage	
Parameter*	$\bar{k}_d$ (1/min)	$\bar{k}_p/\bar{k}_t^{0.5}$ (L/mol · min)$^{0.5}$	$\bar{k}_d$ (1/min)	$\bar{k}_p/\bar{k}_t^{0.5}$ (L/mol · min)$^{0.5}$
Mean Value	0.002354	1.6355	0.002456	1.5673
Asymptotic std. error	1.222E-09	1.061E-07	1.249E-07	1.454E-09
LCL(0.05)	0.002353	1.6302	0.002455	1.5614
UCL(0.05)	0.002355	1.6376	0.002457	1.5732
Covariance of rate parameters	3.141E-014		2.888E-014	

*LCL, lower confidence limit; UCL, upper confidence limit.

density change was recorded. The shrinkage factor was determined by Eq. 5.

Results and Discussion

Determination of experimental rate parameters

The efficiency factor of initiator *f*, which was determined from the "mean kinetic chain length" approach (Odian, 1998), was nearly 0.62, in the range of values that were reported by other investigators. The average shrinkage factor ε, calculated from Eq. 5, was nearly 9%.

The theoretical copolymer composition was calculated using the reactivity ratios that were obtained from the Mao–Lewis copolymerization model by applying nonlinear least-square methods (Habibi et al., 2004). The theoretical diagram, which is represented by the solid line in Figure 1, adequately fits the four replicates of experimental composition data. Throughout the entire composition range, the fraction of i-BMA polymerized $F_{i\text{-}BMA}$ exceeds the i-BMA mole fraction in the feed $f_{i\text{-}BMA}$. This preference is most likely attributable to the higher stability of the radical formed upon the addition of an i-BMA monomer.

As can be observed in Figure 2 that plots of conversion vs. time for different initial monomer feed compositions afforded a good linearity. From the data of this figure it is possible to determine the compositional variations of $\bar{k}_d$ and $\bar{k}_p/\bar{k}_t^{0.5}$ using the kinetic expressions in Eqs. 3 and 7. In this way we have assumed that the estimated values for initiator efficiency and shrinkage factor do not change appreciably over the course of polymerization.

The normal probability plots was used to assess the normality of the distribution of a variable, that is, whether and to what extent the distribution of the variable follows the normal distribution. This plot was constructed as follows. First, the deviations from the mean (residuals) were rank ordered. From these ranks *z*-values were computed (that is, standardized values of the normal distribution) based on the assumption that the data come from a normal distribution. The normal probability value Z_j for the *j*th value (rank) in a variable with *N* observations was computed as $Z_j = \Phi^{-1}[(3j - 1)/(3N + 1)]$, where Φ^{-1} is the inverse normal cumulative distribution function. These *z*-values were plotted on the *y*-axis and the observed residuals on the *x*-axis. In this manner the normal probability plot of *G*(*X*) before *Box–Cox* transformation is presented in Figure 3. The results in this figure reveal that the outliers may also become important in this plot. Outliers have a profound influence on estimation and consequently on the value of correlation coefficient. Because of the lack of fit, and the clear pattern of data around the fitted line, the predicted variable *G*(*X*) must be transformed in some way (e.g., *Box–Cox* transformation). The

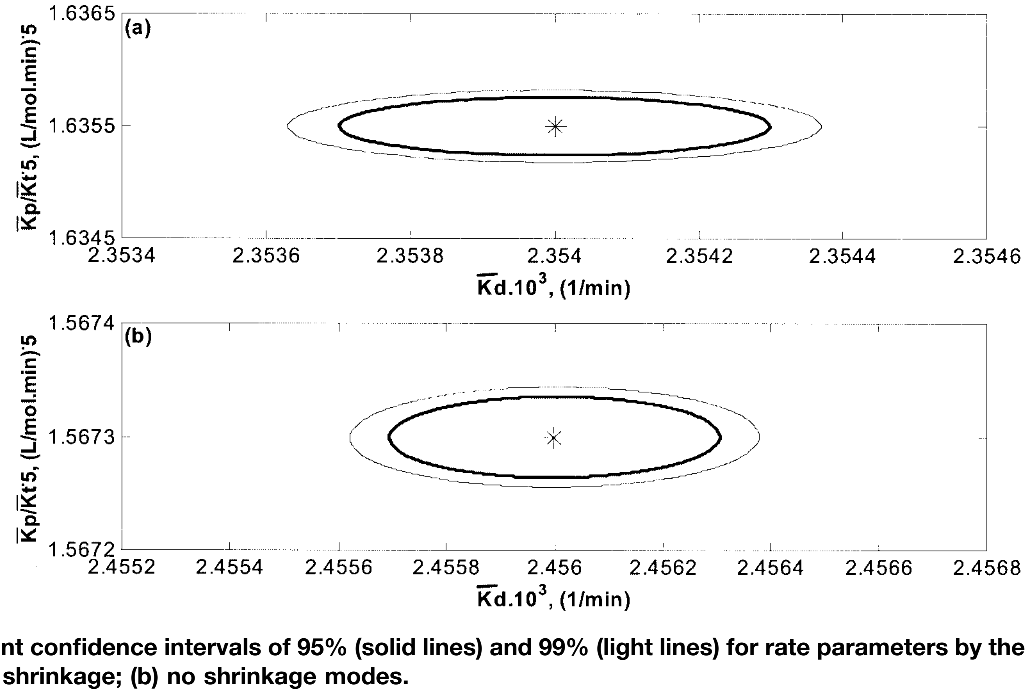


Figure 7. Joint confidence intervals of 95% (solid lines) and 99% (light lines) for rate parameters by the *MLE* method: (a) shrinkage; (b) no shrinkage modes.

Table 3. ANOVA Table for Parameter Estimation in No-Shrinkage Mode by *MLE* (f_{10} = 0.9)

Parameter	Degree of Freedom	Sum of Squares	Mean Square
Regression	1	208350.2243	208350.2243
Residuals	12	2.2500	0.5635
Total	13	208352.4743	—
F-statistics	370428.108	Significant $F(0.05)$ = 0.032	P-value = 0.000
Multiple r	0.9247		

normal probability plots of $G(X)$ after *Box–Cox* transformation is also presented in Figure 4. It is evident that, after applying transformation, the outliers are removed and the data come close to normality.

Observations that are outside the range of ±3 standard deviations around the mean were excluded. The rest of the data were then used for estimation of rate parameters by the *MLE* method. The estimated values of $2f\bar{k}_d$ at different monomer feed compositions, determined by the *MLE* method, are shown in Figure 5. By assuming f nearly equal to 0.62 the values of $\bar{k}_d$ vary from 2.04×10^{-3} to 2.51×10^{-3} min^{-1}, which are in the range of values reported in the literature (Brandrup et al., 1999). Also the estimated values of the coupled rate parameter $\bar{k}_p/\bar{k}_t^{0.5}$, at different monomer feed compositions, are shown in Figure 6.

Typically the results of estimation for $f_{10} = 0.9$, which are presented in Table 2, indicate that the standard errors for estimated parameters become acceptable. Therefore the model is grossly specified. Also the results of Table 2 indicate that the shrinkage phenomenon has changed the estimated values of initiator decomposition and coupled propagation–termination rate parameters by about 5%. Joint confidence intervals (JCIs), which are contours of constant density, are ellipsoids defined by Y with probability α, such that $(Y - \mu)'\Sigma^{-1}(Y - \mu) \leq \chi_p^2(1 - \alpha)$. These ellipsoids are centered at $\mu = [\bar{k}_d, \bar{k}_p/\bar{k}_t^{0.5}]$ and have axes $\pm\sqrt{\chi_p^2\lambda_i}\ell_i$, where λ_i and ℓ_i are eigenvalues and eigenvectors of the variance–covariance matrix $\mathbf{\Sigma}$ of parameter estimates, respectively. Joint confidence intervals of $\bar{k}_d$ and $\bar{k}_p/\bar{k}_t^{0.5}$ for $f_{10} = 0.9$ were calculated and the results of calculation for 95 and 99% certainty levels are shown in Figure 7. These results show the smallest area of the JCIs and confirm the precision of the estimation process.

Table 4. ANOVA Table for Parameter Estimation in Shrinkage Mode by *MLE* (f_{10} = 0.9)

Parameter	Degree of Freedom	Sum of Squares	Mean Square
Regression	1	160189.6788	160189.6788
Residuals	12	2.2500	0.5628
Total	13	160191.9288	—
F-statistics	4708	Significant $F(0.05)$ = 0.032	P-value = 0.000
Multiple r	0.999		

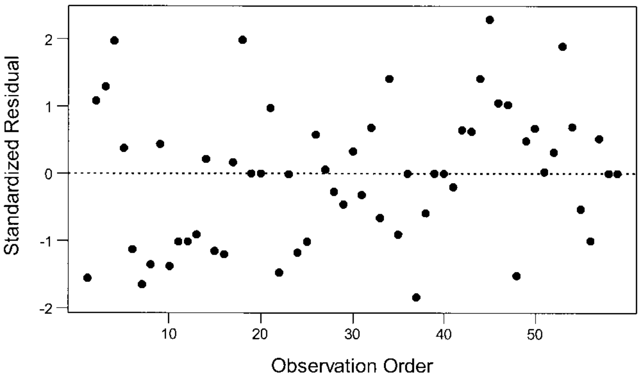


Figure 8. Standard residual vs. observational order of predictor variable in estimation of kinetic parameters by the *MLE* method.

The results of ANOVA tests for $f_{10} = 0.9$ are collectively presented in Tables 3 and 4, which confirm the goodness of fit and model adequacy of the estimation method. The P-value in these tables represents a decreasing index of the reliability of a result. In this work, the P-value of 0.05 is customarily treated as a “border-line acceptable” error level. Often the validation of a model seems to consist of nothing more than quoting the r^2-statistic from the fit. Unfortunately, a high r^2 value does not guarantee that the model fits the data well. There are many statistical tools for model validation, but the primary tool for most process modeling applications is graphical *residual analysis*. Different types of plots of the residuals from a fitted model provide information on the adequacy of different aspects of the model. Scatter plots of the residuals vs. the explanatory variables and the predicted values from the model allow comparison of the amount of random variation in different parts of the data. The plot in Figure 8 shows residuals from a straight-line fit to the $G(X)$–time data. In this plot the range of the residuals looks essentially constant across the observational order of the predictor variable, which suggests that the standard deviation of the random errors is the same for the responses observed at each time. Observed residual fluctuations are normally distributed about zero central value with known standard deviation S. This fluctuating behavior, presented in Figure 9, shows that most of the residuals are in control. Unacceptable results could very well be detected by the measurements falling outside some pair of limits. LCL $= -3S/\sqrt{N}$ and UCL $= 3S/\sqrt{N}$, in Figure 9, are the lower and upper control limits, respectively. Rather than using the residual standard deviation S, it is common to use the moving residual range $\bar{R}$, in Figure 9. If the differences for two neighboring points have the op-

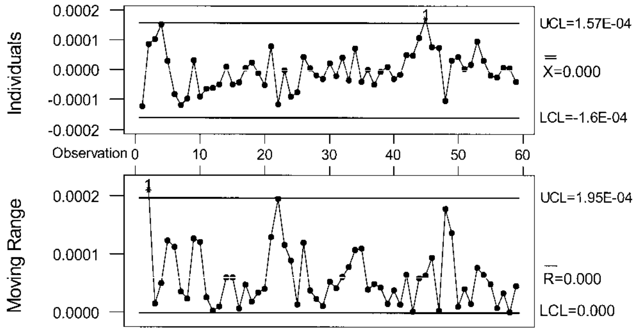


Figure 9. Variance stabilization between individual and moving control limits (*S*, standard deviation; $\bar{\bar{X}}$, mean; $\bar{R}$, moving average mean).

Table 5. Results of Parameter Estimation for Terminal (TUM) and Implicit Penultimate Unit Effect (IPUE) Models*

Model	N_p	r_1	r_2	s_1	s_2	$\sigma(r_1)$	$\sigma(r_2)$	$\sigma(s_1)$	$\sigma(s_2)$	*MSE*	*F*-statistics ($\times 10^7$)
TUM											
R1	2 r_1, r_2	1.591	0.961	1.000	1.000	0.011	0.058	—	—	0.8491	0.00000562
IPUE Model											
R2	4 $\bar{r}_1, \bar{r}_2, s_1, s_2$	1.551	0.684	2.835	0.456	1.303	0.143	133.50	9.9600	9.067E-06	1.10698136
R3	3 $s_1 = s_2$	1.608	0.670	1.229	1.229	0.0310	0.0390	0.0240	0.0240	8.990E-06	1.48865406
R4	3 $s_2 = \bar{r}_1\bar{r}_2/s_1$	1.538	0.709	1.763	0.618	0.2780	0.0490	5.7660	—	6.020E-06	2.22308970
R5	2 s_1, s_2	1.542	0.714	1.553	0.714	0.0054	0.0021	0.0690	0.0390	8.958E-06	2.24098012
R6	1 $s_1 = s_2$	1.542	0.714	1.177	1.177	0.0054	0.0021	0.0006	0.0006	1.344E-05	2.98729910
R7	0 $s_1 = s_2 = (\bar{r}_1\bar{r}_2)^{0.5}$	1.542	0.714	1.049	1.049	0.0054	0.0021	—	—	—	—

*N_p, number of independent parameters; σ, standard deviation; *MSE,* mean square of error.

posite sign, one speaks of a sign change. The measure of the randomness is the number of sign changes, which should be roughly equal to $N/2 \pm (N/2)^{0.5}$. The sign changes in Figure 9 are 31 in number, which is a statistically justified value within acceptable limits.

Determination of radical reactivity ratios

The values of homopolymerization rate constants, together with the experimental coupled rate parameters $\bar{k}_p/\bar{k}_t^{0.5}$, allow us to determine radical reactivity ratios s_1 and s_2 using the Levenberg–Marquardt optimization method. Table 5 contains a summary of the parameter estimates with standard deviations for the various cases discussed below. The arrangement of this table is similar to that presented by Hutchinson et al. (1997) and was sorted by the values of *F*-statistics.

(1) *Fit with terminal unit model.* The dotted line in Figure 6 shows the fit of the terminal unit model rate equation (Eq. 9 with $s_1 = s_2 = 1$) to the experimental $\bar{k}_p/\bar{k}_t^{0.5}$ data. It is clear that for this case (**R1** in Table 5) the data are not well represented by the TUM rate equation. It is also evident that the mean square of error (*MSE*) from the fit to experimental rate data is significantly higher than that of the model fit to other cases in Table 5.

(2) *Fit with the penultimate unit model.* Unfortunately, the EPUE model requires six reactivity ratio parameters (compared to four such parameters from the IPUE model and to two reactivity ratios with the TUM). Attempts to derive this considerable number of EPUE parameters from experimental data mostly yield indeterminate values. It is clear that, like the majority of copolymerization systems, i-BMA/LMA can be well modeled by the IPUE; that is, composition data are well represented by the terminal unit model, but rate data are not. The first case (**R2** in Table 5) to be considered is the four-parameter IPUE model with $w_{i\text{-}BMA}$ and w_{LMA} fixed at 1.684 and 2.833 (L/mol·min), respectively. The model gives a better fit to the rate data than TUM, and the mean square of error (*MSE*) from the fit to the rate data is significantly lower than that from case **R1**. Using the *F*-test, one can also statistically show this conclusion, but the standard deviation of radical reactivity ratios in this case is very high and statistically unacceptable. The next cases that must be examined are the three-parameter implicit penultimate unit models ($\bar{r}_1$, $\bar{r}_2$, and s_1). Two approaches can be taken, as follows:

(1) Simultaneously fit all three parameters, with $s_2 = s_1$ (**R3** in Table 5). This approximation was suggested by Fukuda et al. (1985) to deal with data for which it is not possible to estimate both s_i values. In this case the *MSE* and *F*-statistics of regression were improved with respect to the previous cases discussed above and the standard errors of parameter estimates are acceptable, indicating that the model simplification is justified.

(2) Fit all three parameters, using the suggestion of Fukuda et al. (1985). That is $s_2 = (\bar{r}_1\bar{r}_2)/s_1$ (**R4** in Table 5). In this case the *MSE* and *F*-statistics of regression were again improved with respect to the previous cases discussed above but the standard error of s_1 is very high and unacceptable.

(3) The monomer reactivity ratios for this copolymerization system were determined from composition data by nonlinear least-square methods and the detailed descriptions were presented in another article (Habibi et al., 2004). Therefore, the next cases to be considered are two-step parameter estimations. Three approaches can be taken, as follows:

(a) Use $\bar{r}_1$ and $\bar{r}_2$ estimates from the fit to the copolymer composition for estimation of the radical reactivity ratios, a two-step parameter fit (**R5** in Table 5). The resulting kinetic curve is shown in Figure 6 as a solid line. It is evident that not only do the estimates for monomer reactivity ratios converge to the same values obtained by the four-parameter IPUE model, but also the standard deviations for the radical reactivity ratios are greatly reduced, which supports the validity of the decou-

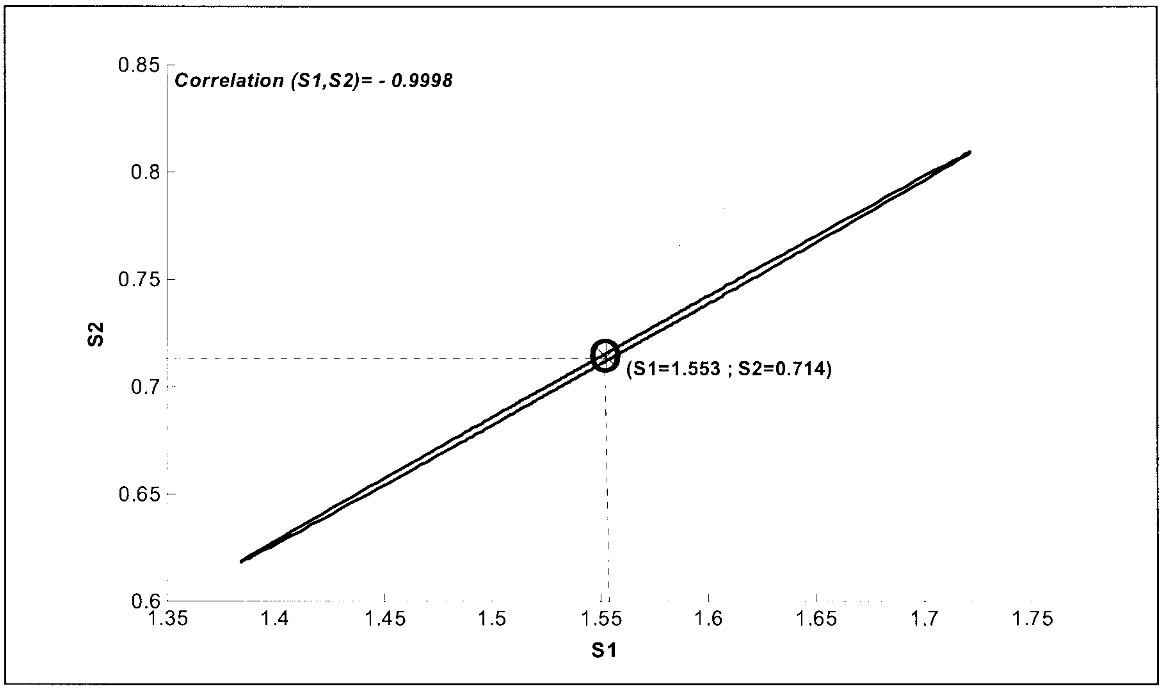


Figure 10. Joint confidence intervals of 95% for s_1 and s_2 according to the IPUE model: case R5 in Table 5.

pling approach in fitting of monomer reactivity ratios from radical reactivity ratios.

(b) Set $\bar{r}_1$ and $\bar{r}_2$ to TUM values and fit the data with $s_2 = s_1$, a one-parameter fit (**R6** in Table 5). All the results including *MSE*, *F*-statistics, and standard deviation of radical reactivity ratios are better than those of other cases, indicating that the model simplification is justified.

(c) Combine **R4** and **R6**, which leads to $s_2 = s_1 = (\bar{r}_1\bar{r}_2)^{1/2}$, with no parameter estimate (**R7** in Table 5). The dotted curve in Figure 6 shows that the zero-parameter IPUE model is not sufficient to represent the experimental data and the sum of square of error (SSE) for this case is equal to 0.0321.

The 95% JCI of s_1 and s_2 for case **R5**, in Figure 10, shows that a significant penultimate effect is operating in this copolymerization system. This stretched long confidence interval indicates the existence of a high correlation between the two radical reactivity ratios. Because $\bar{r}_1\bar{r}_2$ for this copolymerization is close to unity, the correlation between radical reactivity ratios is high. The sufficiency of reactivity ratios, estimated from rate data, in well representing the copolymer composition is also deduced. The result of Case **R1** is shown as a dotted line in Figure 1 and the adequacy of other cases (**R2–R5**) is presented as a sum of square of errors (SSE) in Table 6.

Table 6. SSE Results for Cases R1–R5, Obtained from Copolymer Composition Equation

Case in Table 5	r_1	r_2	$\sigma(r_1)$	$\sigma(r_2)$	*SSE**
R1	1.591	0.961	0.011	0.058	0.0161
R2	1.551	0.684	1.303	0.143	0.0073
R3	1.608	0.670	0.0310	0.0390	0.0096
R4	1.538	0.709	0.2780	0.0490	0.0063
R5	1.542	0.714	0.0054	0.0021	0.0062

**SSE*, sum of square of error.

Model validation

Model validation is the most important step in the model building sequence. For this purpose, some copolymerization data from literature were taken and the efficiency and suitability of the *MLE* method for reproduction of rate parameters from real, simulated, and perturbed data were deduced.

Example 1. Low conversion kinetics of styrene with methyl methacrylate (STY/MMA), which was studied by O'Driscoll and Huang (1989), is reconsidered in this work. The purpose of these investigators was to extend the kinetic knowl-

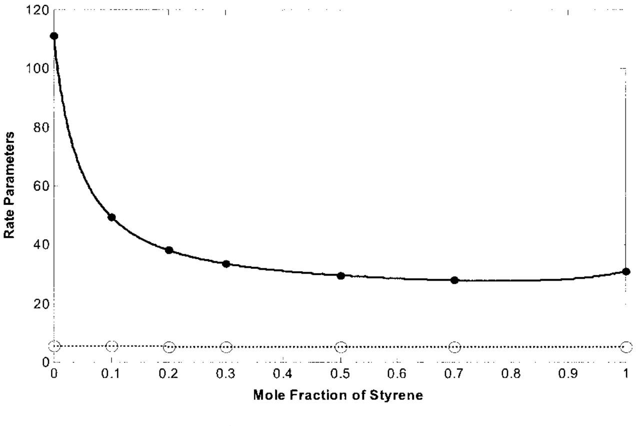
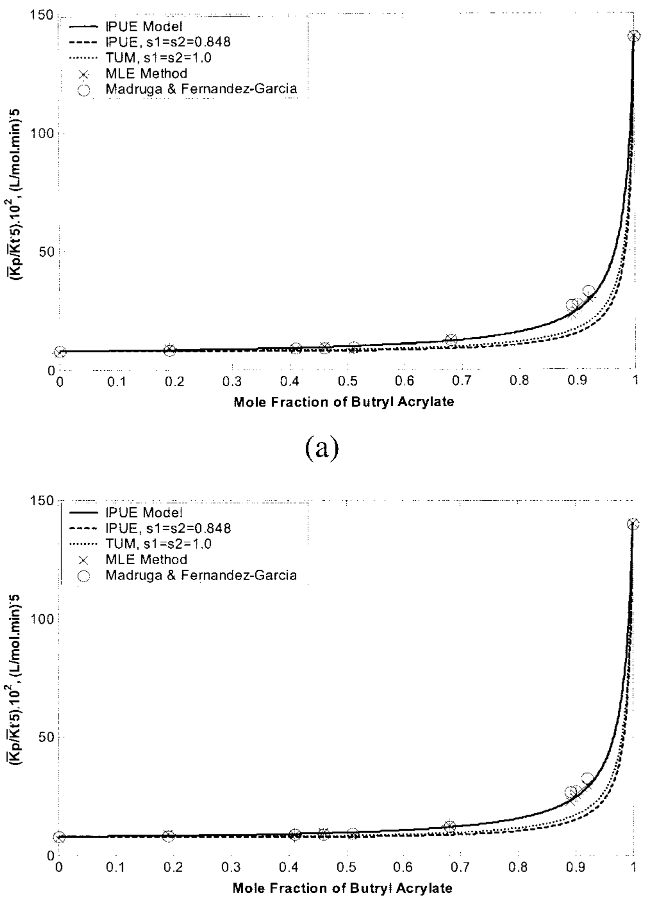


Figure 11. Effect of STY mole fraction on kinetic parameters in STY/MMA copolymerization at 60°C. $(2f\bar{k}_d\bar{k}_p^2/\bar{k}_t)^{0.5} \times (3 \times 10^5)$: (●) estimated values by the *MLE* method; (—) combined IPUE model and Eq. 8; $2f\bar{k}_d \times 10^6$: (○) estimated values by the *MLE* method; (· · ·) based on Eq. 8.

[Data were obtained, with permission, from O'Driscoll and Huang (1989).]



(a)

(b)

Figure 12. Variation of $\bar{k}_p/\bar{k}_t^{0.5}$ vs. f_{BA} for the system BA–MMA in (a) 3 mol/L benzene solution at 50°C; (b) 5 mol/L benzene solution at 50°C.

Data for both (a) and (b) were obtained, with permission, from Madruga and Fernandez-Garcia (1996).

edge of this copolymerization at low and high conversion. They determined the compositional variation of kinetic parameters by applying a composition-averaged rate constant method for copolymerization. The results of their studies are collectively presented in Figure 11. From these data the monomer and radical reactivity ratios were determined by a nonlinear least-square analysis ($r_1 = 0.472$, $r_2 = 0.454$, $s_1 = 0.412$, and $s_2 = 0.153$). They also showed that the IPUE model is adequate to describe the low conversion kinetic results.

For model validation, we have extracted the values of rate parameters for different monomer feed compositions and generated the low conversion data by Eq. 3. These simulated conversion–time data were used for determination of initiator decomposition and coupled propagation–termination rate parameters by the *MLE* method. The results presented in Figure 11 show 0.89% maximum absolute deviation in $\bar{k}_d$ and 1.02% in $\bar{k}_p/\bar{k}_t^{0.5}$ with respect to the corresponding values reported by these authors.

Example 2. Free-radical copolymerization of butyl acrylate (BA) with methyl methacrylate (MMA) was studied by Madruga and Fernandez-Garcia (1996) at 50°C in benzene solution using 3 and 5 mol/L as the overall monomer concentration. The purpose of these investigators was to study the solvent effect on both reactivity ratios and rate parameters. They determined the compositional variation of kinetic parameters from low conversion data. The results of their studies are presented in Figure 12a and 12b. From these data the monomer and radical reactivity ratios were determined by a nonlinear least-square analysis and the results are presented in Table 7. They showed that the IPUE model is adequate to describe the low conversion kinetic results.

This copolymerization system is reconsidered again in this work. For model validation, we have extracted the values of rate parameters for different monomer feed compositions and generated the low conversion-time data according to Eq. 3 for this copolymerization system. These simulated conversion data were used for determination of initiator decomposition and coupled propagation–termination rate parameters by the *MLE* method. The results of estimation for overall monomer concentrations of 3 and 5 mol/L are also presented in Figure 12(a) and (b), respectively. The results show a satisfactory maximum absolute deviation of 0.93% for $\bar{k}_d$ and 1.37% for $\bar{k}_p/\bar{k}_t^{0.5}$, with respect to the corresponding values reported by these investigators.

Example 3. Propagation rate parameters of dodecyl methacrylate (DMA) and methyl acrylate (MA) copolymerization system were determined by Buback et al. (2001) at 40°C and 1000 bars by pulsed-laser polymerization (PLP)–size-exclusion chromatography (SEC) technique. The experimental results of these authors are presented in Table 7. The monomer reactivity ratios were reported as: $r_1 = 2.37$, $r_2 = 0.21$. To evaluate the efficiency and suitability of the *MLE* method in kinetic parameter estimation, we conducted an exhaustive simulation study. In this study the homotermination rate constant of DMA was considered to be 2.5119e+006 L/mol·s and for MA, 1.2589e+008 L/mol·s; the termination rate parameter of copolymer at different copolymer compositions was then generated by the following relation (Buback and Kowollik, 1999)

$$\bar{k}_t = F_1 k_{t11} + F_2 k_{t22} \tag{18}$$

These data were perturbed by a uniform random number generator with the ramp change of expected variances and simu-

Table 7. Monomer, Radical Reactivity Ratios, and Homopolymerization Coupled Rate Parameters of Butyl Acrylate (BA) with Methyl Methacrylate (MMA) Copolymerization System*

Monomer	$[M]$ (mol/L)	r_{BA}	r_{MMA}	s_{BA}	s_{MMA}	w_{BA} ($\times 10^2$) (L/mol · s)$^{0.5}$	w_{MMA} ($\times 10^2$) (L/mol · s)$^{0.5}$
BA/MMA	3	0.349	2.63	0.404	1.782	140.3	8.1
	5	0.323	1.97	0.209	3.040	154.4	8.1

*Data were obtained from Madruga and Fernandez-Garcia (1996).

Table 8. Comparison between Experimental and Estimated Values of $\bar{k}_p/\bar{k}_t^{0.5}$ for Dodecyl Methacrylate (DMA) with Methyl Methacrylate (MA) Copolymerization System

f_1	F_1	Experimental $\bar{k}_p$ (L/mol · s)	Simulated $\bar{k}_t$ ($\times 10^{-8}$) (L/mol · s)	Regenerated $\bar{k}_p/\bar{k}_t^{0.5}$ by *MLE* Method	Absolute Percentage Difference between Experimental and *MLE* Method
1.000	1.0000	1607	0.0251	1.0366	2.2309
0.799	0.9082	1040	0.1383	0.2816	0.7215
0.645	0.8263	1074	0.2395	0.2184	0.4719
0.645	0.8263	1109	0.2395	0.2290	1.0325
0.496	0.7331	1159	0.3544	0.1956	0.4778
0.348	0.6191	1185	0.4951	0.1678	0.3722
0.348	0.6191	1242	0.4951	0.1792	1.5225
0.201	0.4652	1300	0.6849	0.1579	0.5291
0.201	0.4652	1422	0.6849	0.1751	1.8929
0.101	0.3062	1455	0.8811	0.1587	2.3732
0.101	0.3062	1529	0.8811	0.1625	0.2167
0.000	0.0000	28,567	1.2589	2.6017	2.1853

*$\bar{k}_p$ results were obtained from Buback et al. (2001). 1: dodecyl methacrylate (DMA); 2: methyl acrylate (MA).

lated low conversion–time data were computed from Eq. 3 by these perturbed rate parameters. Then the coupled rate parameter $\bar{k}_p/\bar{k}_t^{0.5}$ was estimated from these noisy data by the *MLE* method. The results of this estimation method are collectively presented in Table 7, which show a maximum 2.37% error with respect to the original rate parameters, produced from experimental data. This example shows the accuracy of the *MLE* method in regenerating the original rate parameters by an acceptable error.

All of the above-mentioned results confirm the accuracy, precision, reliability, and robustness of the *MLE* method for kinetic parameter estimation in copolymerization systems, and the values of estimated kinetic parameters are in the permissible range of methacrylates in free-radical polymerization (Bywater, 1999; Hutchinson et al., 1997). For all cases discussed above, convergence is stable and rapid. This method can be used as a new and reliable approach in future studies for kinetic parameter estimation.

Conclusions

The initiator decomposition $\bar{k}_d$ and coupled propagation–termination $\bar{k}_p/\bar{k}_t^{0.5}$ rate parameters were estimated for copolymerization of isobutyl methacrylate and lauryl methacrylate as a new copolymerization system. The method of "maximum likelihood function" was applied for estimation of rate parameters in shrinkage and no-shrinkage modes by satisfaction of "error model" conditions. It was found that considering shrinkage causes about 5% change in the estimated values of decomposition and coupled propagation–termination rate parameters.

Analysis of variance showed that the estimation procedure is strongly valid. The validity of the *MLE* method was also confirmed by testing it against existing rate parameters data reported for different copolymerization systems in the literature.

From a statistical point of view the method of *MLE*, with some exceptions, can be considered as the most robust parameter estimation technique. The main advantage of this formulation of the *MLE* method is that it accounts for all the errors in all variables, as well as numerical simplicity and stability. It can also yield information on model validation, assuming that the correct estimates of errors in all variables are known.

Redefinition of kinetic parameters by the implicit penultimate unit model yielded good predictions of rate data for this new copolymer. The results from this copolymerization study are consistent with previous works: although the TUM is able to predict either composition or rate data, it is unable to adequately represent both types of data simultaneously. This copolymerization, however, has proven to be a very interesting system to study for two particular reasons. First, although it is close to an ideal copolymerization system, it clearly does not obey terminal kinetics. Second, the TUM underestimates $\bar{k}_p/\bar{k}_t^{0.5}$ for the i-BMA/LMA system, although for most of the systems studied to date, $\bar{k}_p/\bar{k}_t^{0.5}$ is overestimated by TUM. The mechanistic interpretation of these observations is left for further investigations.

Notation

Cov = covariance
e_i = elements of erro vector
$E(e_i)$ = expected value of error, e_i
f = initiator efficiency
f_i = mole fraction of monomer i in the feed mixture
F_i = mole fraction of monomer i in the copolymer
[I] = initiator concentration, mol/L
$\bar{k}_d$ = decomposition rate parameter of initiator, min^{-1}
$\bar{k}_p$ = propagation rate parameter, L/mol·min
$\bar{k}_t$ = termination rate parameter, L/mol·min
[M] = overall monomer concentration, mol/L
SSE = sum of square of error
MSE = mean square of error
$p(X_1, X_2, \ldots, X_N)$ = joint probability of $X_1, X_2, \ldots, X_N$
R_p = polymerization rate, mol/L·min
r_i = reactivity ratio of monomer i
s_i = reactivity ratio of radical i
t = polymerization time, min
V = polymerization volume
var(e_i) = variance of error
X = overall conversion

Greek letters

ε = shrinkage factor
ρ = density of polymerization system
λ = parameter of *Box–Cox* transformation
ψ = normal transform of $F(X)$ or $G(X)$
σ^2 = variance of estimation
Φ = value of cumulative normal distribution

α = probability level

$\mathbf{\Sigma}$ = variance–covariance matrix of parameter estimates

λ_i = eigenvalue of variance–covariance matrix of parameter estimates

ℓ_i = eigenvector of variance–covariance matrix of parameter estimates

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Manuscript received Feb. 16, 2003, and revision received July 14, 2003.