

Copolymerization Reactivity Ratios Analysis of Sequentially Sampled Data by Error in Variables Method

Ahmet Paril, Ahmet Giz, Huçeste Çatalgil-Giz

İTÜ Fen-Edebiyat Fakültesi, 34469 Maslak, Istanbul, Turkey

Received 22 December 2003; accepted 12 August 2004

DOI 10.1002/app.21376

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A new method for estimating copolymerization reactivity ratios, by sequentially sampling the reaction medium and analyzing the samples by ultraviolet spectroscopy and gravimetry, was developed. The data were analyzed by a new error-in-variables method. The method was applied to solution copolymerization of the styrene (Sty)-methyl methacrylate (MMA) system in butyl acetate at 65°C, for which reactivity ratios were $r_{\text{MMA}} = 0.660 \pm 0.050$ and

$r_{\text{Sty}} = 0.309 \pm 0.050$. The data were also analyzed by the Kelen-Tüdös and the Extended Kelen-Tüdös methods where the methods are applicable. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 393–399, 2005

Key words: copolymerization; radical polymerization; kinetics (polym.); reactivity ratios; sequential sampling

INTRODUCTION

A considerable number of studies on styrene (Sty)-methyl methacrylate (MMA) copolymerization reactivity ratios have been reported in the literature.¹ The effect of the reaction medium on the reactivity ratios was reported by many researchers. For bulk copolymerization some of the reactivities quoted in the literature are $r_{\text{MMA}} = 0.45$, $r_{\text{Sty}} = 0.47$ with benzoyl peroxide initiation² and $r_{\text{MMA}} = 0.23$, $r_{\text{Sty}} = 0.31$ for UV initiation with azobisisobutyronitrile (AIBN).³ Bonta et al.⁴ indicated the effect of dielectric constant of the medium on the reactivities of Sty and MMA. In dioxane, Sty is slightly more active: $r_{\text{Sty}} = 0.56$, $r_{\text{MMA}} = 0.53$.⁴ On the other hand, MMA is the more active monomer in cyclohexane, $r_{\text{MMA}} = 0.64$, $r_{\text{Sty}} = 0.37$.⁵ The reactivities in butyl acetate with AIBN were $r_{\text{MMA}} = 0.62$, $r_{\text{Sty}} = 0.23$.⁶

This dependency on the reaction conditions indicates that an all-purpose set of reactivity ratios does not exist. One should use reactivities obtained under conditions similar to the intended reaction conditions. For this reason experimental methods that can obtain the reactivity ratios from relatively few experiments are useful.

Methods for determining the reactivity ratios, with a few exceptions, call for a set of experiments with different initial monomer compositions, which are terminated at a certain moment; then the polymer is separated and its composition and overall conversion are obtained. In these methods each reaction yields a single data point.

Some methods make use of data obtained during the reaction. Samples are removed, either periodically as in sequential sampling methods,⁷ or continuously by an on-line technique such as the automatic, continuous on-line monitoring of polymerization (ACOMP),⁶ or the experiment is performed *in situ*.⁸ These methods allow multiple data points to be obtained from each experiment.

On-line and *in situ*, continuous monitoring methods yield hundreds, even thousands, of data points from each experiment; thus they enable the greatest possible amount of information to be extracted. However the advantages of continuous monitoring come at a cost. The setup is expensive and specialized. Few laboratories have access to the specific instruments, detectors, pumping facilities, and so forth required for these methods.

Sequential sampling methods (SSM), on the other hand, yield several data points from each experiment.⁷ Although they are not as powerful as the on-line methods they do not require specialized equipment and can be implemented in any laboratory. SSM can be the best choice for a chemist who wants to obtain the reactivity ratios of monomers under specific reaction conditions.

In data analysis, nonlinear fitting methods are gradually replacing the older, linearized techniques of

Correspondence to: H. Çatalgil-Giz (catalgil@itu.edu.tr).

Contract grant sponsor: İTÜ; contract grant numbers: 1653, 1673.

Contract grant sponsor: TÜBİTAK; contract grant number: TBAG 2174.

Contract grant sponsor: TÜBİTAK-BDP.

finding the reactivity ratios. Many investigators have shown that nonlinear methods, minimizing chi square (χ^2) and taking error propagation and individual errors on each of the measurements into account, are superior in error handling.^{9–17} They avoid much of the distortion of the error structure and have smaller and better defined regions for a given percentage probability. In particular the error-in-variables methods (EVMs), which take into consideration errors in all measurements, are becoming more popular. The computational power necessary for these methods is now readily available in almost every laboratory.

In this work we describe an SSM, based on a gravimetric and a spectroscopic measurement per sample to determine its monomer concentrations, and an EVM method especially developed to treat this type of data. The SSM described here is based on the on-line method in Sünbül et al.¹⁸ Unlike the method of German and Heikens,⁷ which fits the data to the analytical Skeist solution, it fits the data to a numerical solution of the copolymerization equation. The method is applied to MMA/Sty copolymerization in butyl acetate and the reactivities obtained by the new calculation technique are $r_{\text{MMA}} = 0.660 \pm 0.05$ and $r_{\text{Sty}} = 0.309 \pm 0.05$. Results are also consistent with those obtained by two traditional methods, the Kelen–Tüdös (KT)¹⁹ and the Extended Kelen–Tüdös (EKT)²⁰ methods, using data at up to 15 and 60% conversion, respectively.

EXPERIMENTAL

Materials

Methyl methacrylate (Aldrich, Milwaukee, WI) and styrene (Aldrich) were freed from inhibitor by washing with 5% sodium hydroxide. The monomers were dried over calcium sulfate and fractionally distilled and stored at low temperature. The initiator, 2,2'-azobisisobutyronitrile (AIBN, Aldrich), and solvent, butyl acetate (BuAc, Aldrich), were used as received.

Polymerization

The MMA/Sty monomer mixture was polymerized with AIBN in BuAc in a nitrogen atmosphere at 65°C. Samples were withdrawn every 15 min after the addition of initiator. To immediately stop the reaction in the aliquot, the sample was withdrawn into an injector

TABLE I
Reaction Parameters at Different Reactions

Experiment	MMA (g)	Sty (g)	AIBN (g)	BuAc (g)
80/20	18.8	4.55	2.5	22
50/50	11.75	11.375	2.5	22
20/80	4.70	18.20	2.5	22

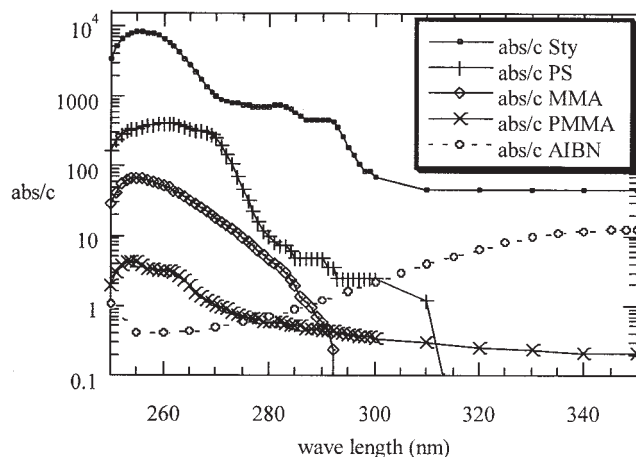


Figure 1 Values of abs/c in the 250–400 nm range for the monomers, their homopolymers, and the initiator.

containing chilled solvent. The diluted sample was quenched in liquid nitrogen. A portion of each sample was precipitated and dried in a vacuum oven until the weight was constant. The remainder was further diluted for UV measurements, which were performed at 260 nm, where the absorption was dominated by the styrene monomer. The UV absorbance coefficients were determined immediately before the measurements to avoid instrument drifts. The monomer and initiator amounts of the experiments are given in Table I. The reactions were performed at the nominal initial weight compositions of 80% MMA/20% Sty (80/20), 50% MMA/50% Sty (50/50), and 20% MMA/80% Sty (20/80). The experiment using the 50/50 composition was repeated three times to obtain error bars.

Measurements were performed in a Shimadzu 150-02 double-beam UV spectrophotometer (Shimadzu, Kyoto, Japan) with a 1-cm cell against BuAc solvent.

Monomer detection

UV absorption spectra of MMA, Sty, their homopolymers (PMMA, PS), and AIBN are given in Figure 1. The absorption at 260 nm is dominated by monomeric Sty. This wavelength was therefore used to determine the monomer concentrations. For convenience the differential UV absorption coefficients in the measurement cell at 260 nm were denoted U_{MMA} , U_{PMMA} , U_{Sty} , U_{PS} , and U_{AIBN} for MMA, PMMA, Sty, PS, and AIBN, respectively. U -values are given in Table II. Because both Sty and MMA are vinyl monomers, they have a C=C bond per monomer molecule. During copolymerization, this double bond disappears. The decrease of the UV absorption during the reaction and the increase of the overall conversion are shown in Figures 2 and 3, respectively.

TABLE II
U-Values of Monomers, Their Corresponding Homopolymers, and the Initiator (in Volts per cm³/g) at 260 nm in the Measurement Cell

	Sty	PS	MMA	PMMA	AIBN
<i>U</i>	6439.8	409.82	53.339	2.2019	0.4353

UV measurements were performed to determine the copolymer composition. Total absorption is given by

$$U_{\text{MMA}}C_{\text{MMA}} + U_{\text{PMMA}}C_{\text{PMMA}} + U_{\text{Sty}}C_{\text{Sty}} + U_{\text{PS}}C_{\text{PS}} + U_{\text{AIBN}}C_{\text{AIBN}} = UV_{\text{aliquot}} \quad (1)$$

Here C_{Sty} , C_{MMA} , and C_{AIBN} are the concentrations of Sty, MMA, and AIBN in the aliquot. C_{PS} and C_{PMMA} are the concentrations of Sty and MMA units in the copolymer in the aliquot and UV_{aliquot} is the measured absorbance of the aliquot.

Because the UV absorbance of AIBN at 260 nm is less than 10^{-4} times that of Sty, its contribution was neglected. Absorptions of all other species were taken into account in the calculations.

If the decreases in UV absorption on conversion of both monomers are nearly equal, eqs. (1) and (2) are not effective. For this reason it is important to have one monomer dominate the UV absorption. Because of conjugation, Sty is the much stronger UV absorber at 260 nm. All other species—MMA, PS, PMMA, BuAc, and AIBN—are dominated by Sty, which ensures that the equations are effective. Note that, because the measurements are made against the solvent, its absorption does not enter the equation.

The benzene ring in the copolymer is attached to a backbone carbon atom whose nearest neighbors are $-\text{CH}_2-$ groups. For this reason the UV absorption coefficient of a styrene unit is relatively independent

of whether the next unit is MMA or Sty. Furthermore, at 260 nm, the absorption is dominated by monomeric Sty and the contribution of the polymeric units is minor, as seen from Table I. For this reason the error caused by using the absorption coefficient of homopolystyrene, instead of styrene units, in the copolymer is negligible.

Gravimetry gives the total copolymer concentration C_{copolyr}

$$C_{\text{PMMA}} + C_{\text{PS}} = C_{\text{copolyr}} \quad (2)$$

The conservation laws give two additional equations:

$$C_{\text{MMA}} + C_{\text{PMMA}} = C_{0,\text{MMA}} \quad (3)$$

$$C_{\text{Sty}} + C_{\text{PS}} = C_{0,\text{Sty}} \quad (4)$$

where $C_{0,\text{MMA}}$ and $C_{0,\text{Sty}}$ denote the initial concentrations of the monomers. The experiments were performed at low concentrations so that the density increase of the medium resulting from volume contraction during polymerization could be neglected in eqs. (3) and (4).

Equations (1)–(4) are solved to obtain the conversion of each monomer and composition of the copolymer at the time of aliquot removal. The polymer and monomer concentrations were calculated at each point during the reactions by eqs. (1)–(4) and the results are given in Figures 4–6.

CALCULATION

Nonlinear fit procedure

For a given pair of reactivity ratios r_a and r_b , and initial concentrations $[a]_0$ and $[b]_0$, a theoretical $[a]_{\text{the}}$ is ob-

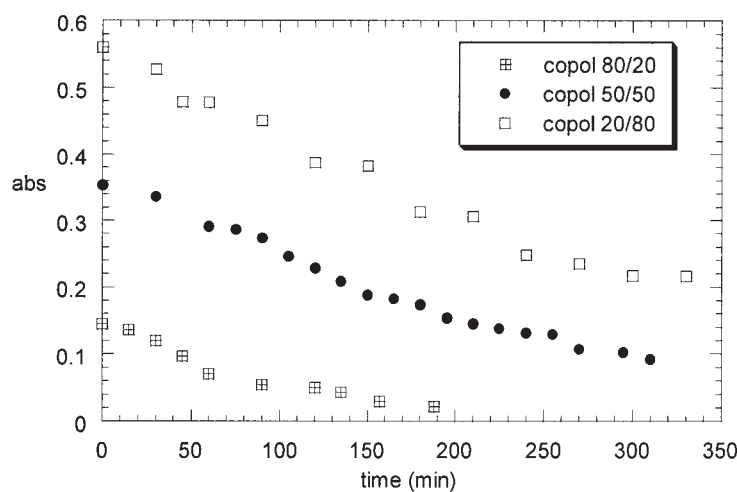


Figure 2 Decrease of absorptions of aliquots in different copolymer compositions during the reactions.

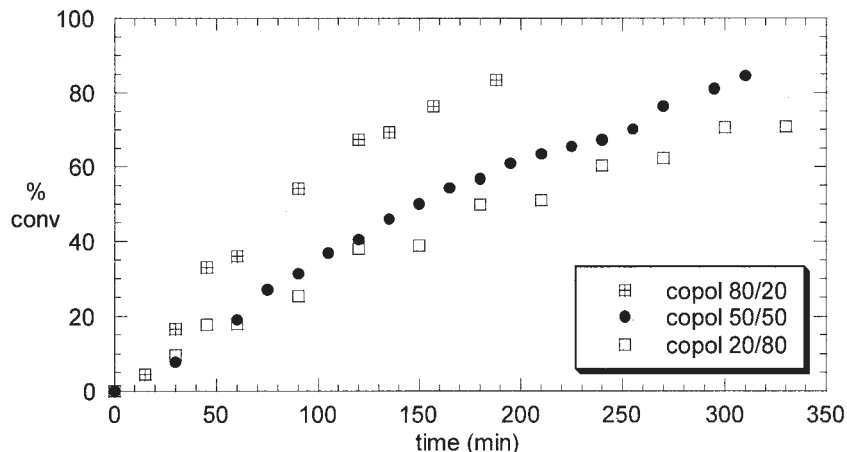


Figure 3 Evolution of conversion during the reactions.

tained by numerically solving the copolymerization equation

$$\frac{d[a]}{d[b]} = \frac{[a]}{[b]} \left(\frac{r_a[a] + [b]}{[a] + r_b[b]} \right) \quad (5)$$

by the fourth-order Runge–Kutta method with variable step size. This is then compared with the experimental $[a]_{\text{exp}}$ obtained from the same aliquot. The procedure produces a $\chi^2(r_a, r_b)$ value by

$$Q = [a]_{\text{exp}} - [a]_{\text{the}}([b]_{\text{exp}}, [a]_0, [b]_0, r_a, r_b) \quad (6a)$$

$$\chi^2 = \sum_{j=1}^{n(\text{exp})} \sum_{i=1}^{n(\text{data})} Q_{ij}^2 / \text{Var}(Q_{ij}) \quad (6b)$$

Here the index “ j ” denotes the experiment number and the index “ i ” represents the data point on that experiment. The sum involves all data points in all of the experiments.

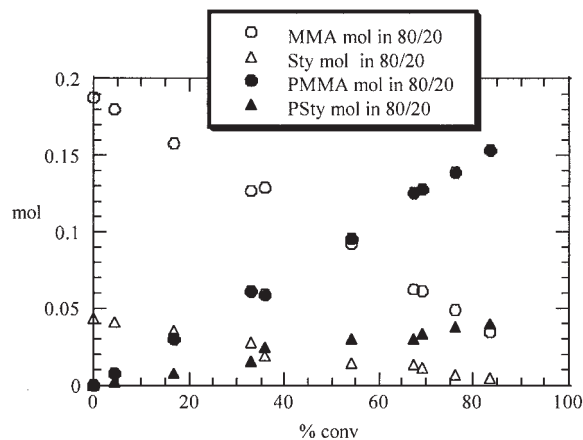


Figure 4 Evolution of composition during the 80/20 experiment.

The error terms arise from the measurements and the calibration constants. In practice the dominant errors are those in the measurements of the samples. Only the drift of the instrument, between the calibration and the measurement, contributes to the calibration errors. Performing the calibration and the measurements at the same time minimized these errors. The initial concentrations, found by careful weighing, are also likely to have fewer errors than measurements of the aliquots. When the errors in the initial composition and the calibration errors are neglected the variations are given by the following:

$$\text{Var}(Q) = \text{Var}([a]_{\text{exp}}) + \text{Var}([a]_{\text{the}}) - 2 \text{Covar}([a]_{\text{exp}}, [a]_{\text{the}}) \quad (7a)$$

$$\text{Var}([a]_{\text{the}}) = \left(\frac{\partial [a]_{\text{the}}}{\partial [b]} \right)^2 \text{Var}([b]) \quad (7b)$$

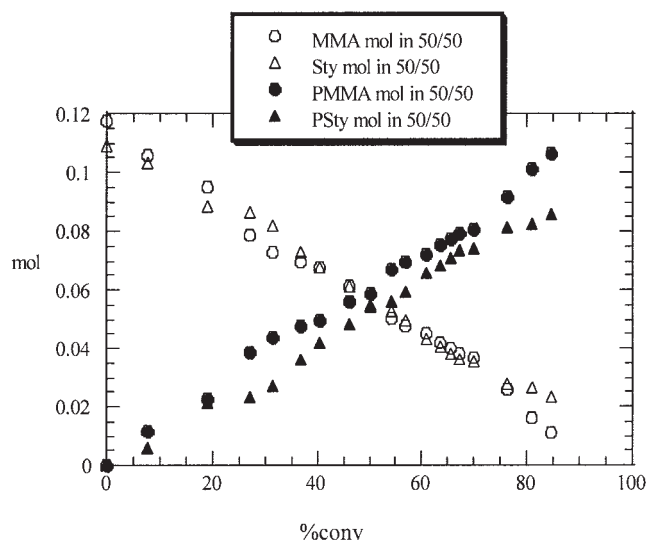


Figure 5 Evolution of composition during the 50/50 experiment.

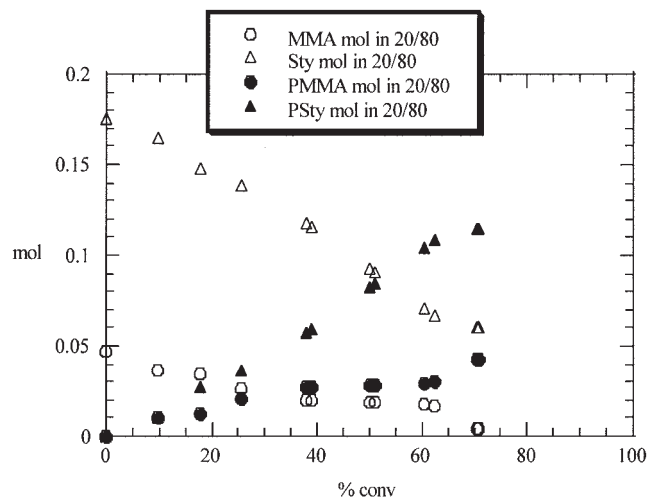


Figure 6 Evolution of composition during the 20/80 experiment.

$$\text{Covar}([a]_{\text{exp}}, [a]_{\text{the}}) = \left(\frac{\partial [a]_{\text{the}}}{\partial [b]} \right) \text{Covar}([a]_{\text{exp}}, [b]) \quad (7c)$$

$$\text{Var}([a]) = \{(\delta UV)^2 + (\Delta U_b)^2 (\delta M)^2\} / (\Delta U_a - \Delta U_b)^2 \quad (7d)$$

$$\text{Var}([b]) = \{(\delta UV)^2 + (\Delta U_a)^2 (\delta M)^2\} / (\Delta U_a - \Delta U_b)^2 \quad (7e)$$

$$\text{Covar}([a], [b]) = - \{(\delta UV)^2 + \Delta U_b \Delta U_a (\delta M)^2\} / (\Delta U_a - \Delta U_b)^2 \quad (7f)$$

where $(\delta UV)^2$ represents the variations in the UV signal and $(\delta M)^2$ is the error in the measurement of the polymer amount in the aliquot. Here ΔU_a and ΔU_b are the differences of UV absorption coefficient between monomer and its polymeric form.

The variations are found by repeating the 50/50 experiment three times and finding the standard deviation of the concentrations.

Sweeping through the $r_{\text{MMA}}, r_{\text{Sty}}$ parameter space a χ^2 map is obtained. For a reliable set of reactivity ratios three experiments, with widely differing initial compositions, were used.

Determination of the reactivity ratios from sequential data by KT and EKT methods

Because the KT method does not compensate for the composition drift, data, obtained at less than 15% conversion, were analyzed by this technique and are plotted in Figure 7. The data fall on a line, indicating no deviation from the terminal model. The reactivity ratios are $r_{\text{MMA}} = 0.634 \pm 0.090$ and $r_{\text{Sty}} = 0.275 \pm 0.090$.

The EKT method takes the composition drift into account. For this reason it is valid for moderate conversion. Data, where the overall conversion was less

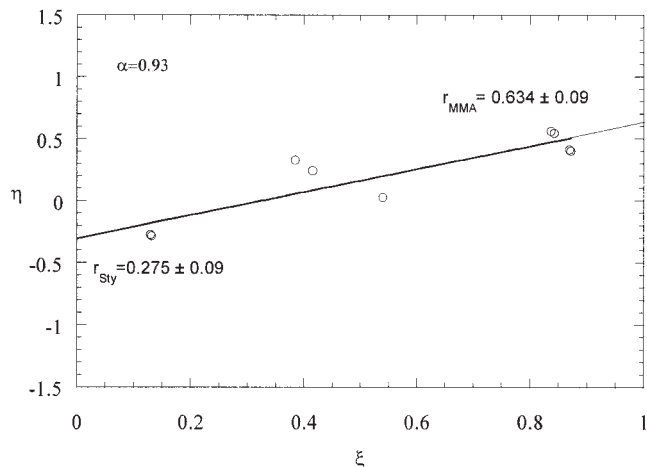


Figure 7 Reactivity ratios found by Kelen-Tüdös method.

than 60%, were analyzed with this method and the EKT plot is shown in Figure 8. The results are consistent with the above analysis in that no deviation from the terminal model is indicated and the reactivities are $r_{\text{MMA}} = 0.626 \pm 0.05$ and $r_{\text{Sty}} = 0.260 \pm 0.05$.

Determination of the reactivity ratios from all data by EVM

Data are fitted to solutions of the copolymerization equation with r_{MMA} and r_{Sty} both scanned between 0.0 and 1.0, with step size 0.02, generating a χ^2 value for each set of r_{MMA} and r_{Sty} . The relevant part of the contour map is given in Figure 9. The 1σ contour gives $r_{\text{MMA}} = 0.660 \pm 0.050$ and $r_{\text{Sty}} = 0.309 \pm 0.050$. This result is consistent with the above results in that large portions of the acceptable part of the parameter space, given by the three methods, overlap. The EVM, addi-

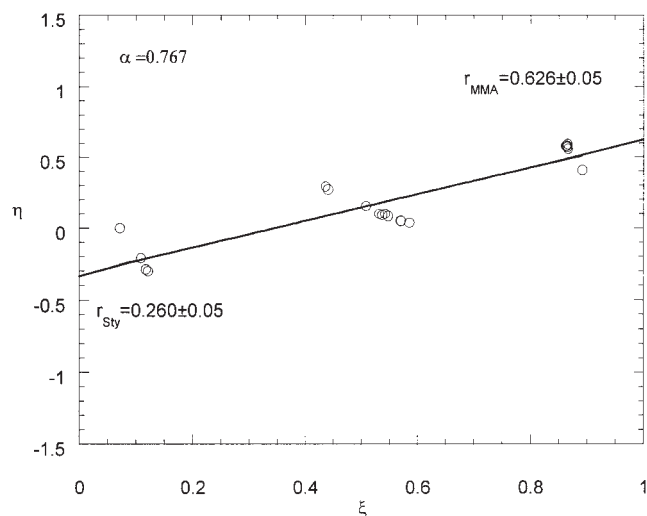


Figure 8 Reactivity ratios found by Extended Kelen-Tüdös method.

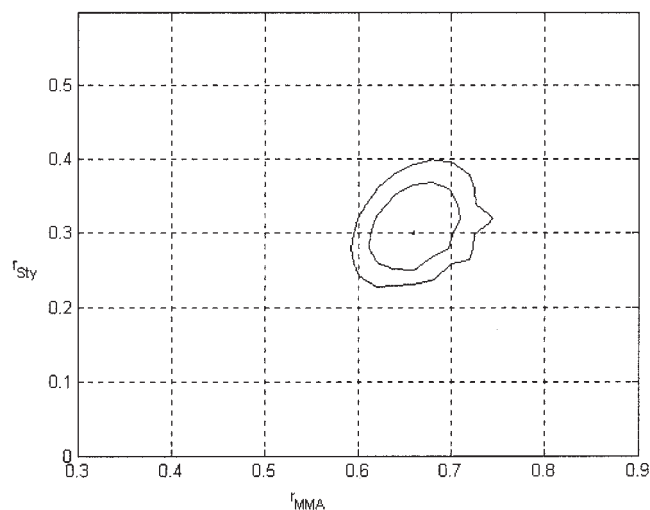


Figure 9 The χ^2 contours corresponding to 1 and 2 σ confidence levels obtained by EVM analysis of sequentially sampled data.

tionally, gives the region of the parameter space within each contour level. Data taken during the whole reaction were used for the EVM.

RESULTS AND DISCUSSION

Because there are different reactivity ratios in different solvents and under different reaction conditions a method that can give the reactivities in a few experiments can be useful in finding these reactivities in a wide variety of reaction conditions. The results given here should be compared with results obtained in BuAc at 65°C.

The *in situ* method of Puskas constitutes an experimental cell connected with a fiber-optical interface to an FTIR spectrometer. The two monomer concentrations are obtained by integrating the areas of the various peaks of the spectral scans. The monomer concentration data are plotted with $[A]$ as a function of $[B]$ and fitted by a curve: the slope of this curve is the $d[A]/d[B]$ term of the Mayo differential copolymerization equation. Each point on the fitted line is treated as an infinitesimal reaction, to find the best fit parameters and the semimajor and semiminor axes of the elliptical region, denoting the acceptable part of the parameter space.

In the on-line method of Reed, the monomer concentrations are obtained, by UV detection and a refractometric detection, that give two linearly independent combinations of the concentrations. The concentration data are then compared with a numerical solution of the Mayo equation. No minimization procedure is applied; instead the relevant part of the parameter space is scanned by solving the differential equation for each set of (r_{a_scan}, r_{b_scan}) values in the scanning

range. As Van Herk and Dröge^{14,15} noted, such a scan has the advantage that, when the nonlinear terms are significant and the acceptable region is nonelliptical, the scanning technique gives the correct shape of the acceptable region.

Here the UV measurement is coupled with gravimetry. Gravimetric determination of the total polymer concentration is more direct and less subject to equipment calibration errors than the techniques available for continuous monitoring experiments. On the other hand several points, provided by each experiment, give larger fluctuations compared to the several thousand points obtained from each experiment with the on-line and *in situ* techniques. No minimization is performed; instead the parameter space is scanned and the χ^2 contour map is obtained.

The results were also analyzed by the KT method, valid at low conversion, and the EKT, valid at moderate conversion. These linear methods are simple and unsophisticated but very reliable. Although their error boxes are larger than the probable regions given by more advanced methods, their results are never far off. The fact that the results of the three analyses are consistent indicates that they are all sound.

Compared to the methods where only a single data point is obtained from each reaction, the sequential sampling method has the advantage of obtaining a greater amount of information from an experiment because several data points, instead of a single datum, are obtained from it.

Unlike the on-line and *in situ* methods, his method does not require any sophisticated equipment and can be implemented in almost any laboratory.

The financial supports of İTÜ research fund under projects 1653 and 1673 and TÜBİTAK under project TBAG 2174 are acknowledged. A. Paril acknowledges support from TÜBİTAK-BDP.

References

1. Greenly, R. Z. In: Copolymer Reactivity Ratios; Bandrup, J.; Immergut, E. H., Eds.; Polymer Handbook, 3rd ed.; Wiley: New York, 1989; pp. II/153ff.
2. O'Driscoll, K. F.; Kale, L. T.; Rubio, L. H. G.; Reilly, P. M. J Polym Sci 1984, 22, 2777T.
3. Ramelow, Ü. S.; Qiu, Q. H. J Appl Polym Sci 1995, 57, 911.
4. Bonta, G.; Gallo, B. M.; Russo, S. Polymer 1975, 25, 429.
5. Talpur, M. M. A.; Kaim, A.; Guttman, T. K.; Pirzada, T. Arab J Sci Eng 1999, 24, 133.
6. Çatalgil-Giz, H.; Giz, A.; Alb, A. M.; Öncül Koç, A.; Reed, W. F. Macromolecules 2002, 35, 6557.
7. German, A. L.; Heikens, D.; J Polym Sci Part A-1 1971, 9, 2225.
8. Paulo, C.; Puskas, J. E.; Angepat, S. Macromolecules 2000, 33, 4634.
9. Tidwell, P. W.; Mortimer, G. A. J Polym Sci Part A 1965, 3, 369.

10. Meyer, V. E.; Lowry, G. G. *J Polym Sci Part A* 1965, 3, 2843.
11. McFarlane, R. C.; Reilly, P. M.; O'Driscoll, K. F. *J Polym Sci Polym Chem Ed* 1980, 18, 251.
12. Patino-Leal, H.; Reilly, P. M.; O'Driscoll, K. F. *J Polym Sci Polym Lett Ed* 1980, 18, 219.
13. Dube, M.; Sanayei, R. A.; Penlidis, A.; O'Driscoll, K. F.; Reilly, P. M. *J Polym Sci Part A: Polym Chem* 1991, 29, 703.
14. Van Herk, A. M. *J Chem Ed* 1995, 72, 138.
15. Van Herk, A. M.; Dröge, T. *Macromol Theory Simul* 1997, 6, 1277.
16. Van der Meer, R.; Linssen, H. N.; German, A. L. *J Polym Sci Polym Chem Ed* 1978, 16, 2915.
17. Chee, K. K.; S. C. Ng. *Macromolecules* 1986, 19, 2779.
18. Sünbül, D.; Çatalgil-Giz, H.; Reed, W.; Giz, A. *Macromol Theory Simul* 2004, 13, 162.
19. Kelen, T.; Tüdös, F. *J Macromol Sci Chem A* 1975, 9, 1.
20. Kelen, T.; Tüdös, F.; Turcsanyi, B.; Kennedy, J. P. *J Polym Sci* 1977, 15, 3047.