

High-Temperature Solution Polymerization of Butyl Acrylate/Methyl Methacrylate: Reactivity Ratio Estimation

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ABSTRACT: Solution copolymerizations of butyl acrylate/methyl methacrylate in toluene were performed over an expanded temperature range (60–140°C) compared to more typical ranges that do not exceed 80°C. From a large amount of data collected independently at two laboratories, reactivity ratios were estimated at five different temperatures. The reactivity ratios were estimated from low conversion copolymer composition data using both the error-in-variables model method and a nonlinear parameter estimation based on the integrated copolymer composition equation. Using all of the available data, temperature-dependent expressions were developed for the reactivity ratios and compared to previously published bulk copolymerization values. No significant differences appeared to exist between the bulk and solution polymerization reactivity ratios. Furthermore, the copolymer composition data conformed to the Mayo-Lewis kinetic model over the entire temperature range. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 602–609, 2000

Key words: butyl acrylate; methyl methacrylate; solution copolymerization; reactivity ratios

INTRODUCTION

A wide variety of polymerization processes are conducted in solution. The principal reason for this is the alleviation of viscosity-related problems that are manifested in the areas of heat transfer, mixing, material handling, and processing. Aside from these reactor design challenges, the chemistry of solvent in free-radical polymerization kinetics is of interest.¹ Solvent effects on propagation rates have been associated with some monomer systems while others show little or no effect. When these solvent effects do occur, deviations from the expected propagation rate and the expected multicomponent polymer composition

and microstructure are detected. A variety of models have been proposed to explain these solvent effects and are reviewed in Coote et al.¹

Typically, free-radical polymerizations of vinyl monomers are carried out in the 40–80°C temperature range. In fact, most of the published studies of polymerization kinetics have been conducted between 50 and 60°C. Compelling reasons exist, however, to explore higher temperature ranges (e.g., 90–150°C). Excursions into higher temperature ranges often occur during polymerizations due to poor heat transfer properties of typical reaction mixtures.^{2,3} As well, polymerizations are often conducted at or taken to higher temperatures (during the latter stages of the reaction) in order to minimize residual levels of monomers or initiators.

Another impetus for studying polymerization kinetics at elevated temperatures relates to the

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development of models for predicting polymer production rates and product quality. Most modeling efforts to date have been focused on a limited temperature range, say, 40–80°C. While these models can be applied beyond this temperature range, it is important to be cautious with regards to the resulting predictions. Thus, efforts should be made to gain confidence in these models outside of “normal” operating conditions.

In multicomponent polymerizations, reactivity ratios are key model parameters that are vital to the prediction of polymer composition and microstructure, and by extension, to the prediction of polymerization rate and molecular weight distribution. According to the terminal model for propagation,⁴ reactivity ratios are parameters in the Mayo–Lewis equation or copolymer composition equation shown below:

$$\frac{F_1}{F_2} = \frac{(r_1 f_1 + f_2) f_1}{(f_1 + r_2 f_2) f_2} \quad (1)$$

where F_1 and F_2 are the overall instantaneous mole fractions of monomer 1 and monomer 2 in the copolymer, respectively, and f_i is the mole fraction of (free) monomer i in the reaction mixture. Reactivity ratios are defined as ratios of homopropagation over cross-propagation rate constants, with a temperature dependence described by the Arrhenius equation:

$$r_1 = \frac{k_{p11}}{k_{p12}} = \frac{A_{11}}{A_{12}} \exp\left(-\frac{E_{11} - E_{12}}{RT}\right) \quad (2)$$

$$r_2 = \frac{k_{p22}}{k_{p21}} = \frac{A_{22}}{A_{21}} \exp\left(-\frac{E_{22} - E_{21}}{RT}\right) \quad (3)$$

The $k_{p_{ij}}$ is the rate constant for addition of monomer j to a “live” polymer chain on which the active radical center is located on a monomer i unit. A_{ij} and E_{ij} are the frequency factors and activation energies for the propagation reactions, respectively. Reactivity ratios are considered to exhibit a negligible temperature dependence over fairly narrow temperature ranges. The weak temperature dependence of the reactivity ratios is due to the similarity in the activation energies for the homopropagation and corresponding cross-propagation reactions. However, a significant change in the reactivity ratios is possible when temperature is varied in a more pronounced way. Often, reactivity ratio estimation experiments are performed around 60°C, and thus when reaction tempera-

tures differ significantly from “normal” operating ranges and the temperature dependence of these reactivity ratios is not accounted for, erroneous model predictions may result.

Butyl acrylate/methyl methacrylate (BA/MMA) is a commercially important component in many paints, adhesives, and coatings. Kinetic studies of the BA/MMA system are limited. Bulk copolymerization reactivity ratio estimations at 60°C have been reported by Grassie et al.,⁵ Bevington and Harris,⁶ and more recently by Dubé and Penlidis.⁷ The latter study included a complete kinetic analysis of the copolymerization by examining conversion, copolymer composition, and molecular weight over the full conversion range. In an additional step, we have estimated the reactivity ratios for bulk BA/MMA copolymerizations over an extended temperature range (60–140°C).⁸ Other kinetic studies include solution copolymerizations by Brosse et al.⁹ and emulsion copolymerizations by Emelie et al.,¹⁰ Urretabizkaia et al.,¹¹ and Dubé and Penlidis.¹² Furthermore, a study of solvent effects on reactivity ratios has been published recently for both the BA/MMA and methyl acrylate/MMA systems in benzene at 50°C at two solvent concentrations.^{13,14} For both systems, no conclusive evidence was provided to show a solvent effect on the reactivity ratios. This is not completely unexpected since, for the most part, systems containing MMA tend to exhibit little, if any, solvent effect on the reaction kinetics.¹

In this paper, results will be presented from an extensive body of BA/MMA solution copolymerization reactivity ratio estimation experiments run over an expanded temperature range (60–140°C). An Arrhenius-type temperature dependence of the reactivity ratios will also be determined. Finally, these results will be compared to similar experiments conducted in bulk⁸ in order to possibly identify the existence of any solvent effects on the reactivity ratios.

EXPERIMENTAL METHODS AND DESIGN

Experiments were conducted in an identical way to a previous bulk copolymerization study.⁸ The monomers, butyl acrylate and methyl methacrylate (Aldrich Chemical, Inc.) were washed three times with a 10% sodium hydroxide (NaOH) solution to remove the inhibitor and subsequently thrice washed with distilled deionized water. Calcium chloride (CaCl₂) was added to remove any

residual water. Further purification via rotary vacuum distillation of the monomer solutions was performed 24 h prior to their use. All purified monomers were stored at -10°C when not in use. Di-tert-butyl peroxide (Trigonox B) (Akzo) initiator was used for the experiments at 80, 100, 120, and 140°C , without any purification. Thrice-re-crystallized 2,2'-azobisisobutyronitrile (AIBN) (Polysciences, Inc.) was used as the initiator at 60°C . All other solvents (toluene, acetone, ethanol, chloroform-d) for the experiments and characterization were used without purification.

Monomers and initiators were weighed and pipetted into glass ampoules (approximately 4 mL capacity). The ampoules were then degassed via freeze-thaw cycles and subsequently submerged in a temperature controlled bath for a recorded period of time. Once removed from the bath, the ampoules were opened and the contents were poured into a 10-fold excess of ethanol. Any remaining polymerization mixture was removed from the ampoules using acetone. The precipitated copolymer was dried in a vacuum oven at 60°C until a constant weight was achieved.

Design of Experiments

The selection of the initial monomer feed concentrations was performed, in part, using the Tidwell–Mortimer criterion.¹⁵ This condition is based on the sensitivity of the reactivity ratios to the errors encountered in the determination of the copolymer composition. The initial monomer feed concentrations (monomer 1 refers to BA throughout this paper whereas monomer 2 refers to MMA) were calculated using preliminary reactivity ratio estimates^{5–7} and the following expressions:

$$f'_{10} = 2/(2 + r_1) \quad (4)$$

and

$$f''_{10} = r_2/(2 + r_2) \quad (5)$$

The Tidwell–Mortimer design points were repeated four times each. The remaining monomer feed concentrations were selected at a series of equidistant points with respect to feed mole fraction. The mass conversion for each reactivity ratio experiment was maintained below 10 wt % in order to minimize the effects of composition drift on the reactivity ratio estimates.

A solvent concentration of 30 wt % toluene was used at each reaction temperature (viz. 60, 80, 100, 120, and 140°C) and an additional experiment at 50 wt % toluene was conducted at 120°C .

Characterization

Mass conversion based on the total polymer in the reaction mixture was measured using gravimetry. The resulting isolated copolymers were analyzed for cumulative polymer composition using a Bruker AMX500 and a Bruker MX300 Fourier-Transform NMR spectrometers. The dried polymer was dissolved in deuterated chloroform ($\sim 2\%$ w/v) at room temperature. All spectra exhibited good peak separations for diagnostic signals. The signal at ~ 4.0 ppm was due to the OCH_2 group in BA and another signal at ~ 3.6 ppm was associated with the OCH_3 group of MMA. The relative mole fractions of monomer bound in the polymer (F_{BA} or F_{MMA}) were determined from the areas under the corresponding peaks.

RESULTS AND DISCUSSION

The experimental data contained herein are a combination of work performed independently at the University of Waterloo and the University of Ottawa. The data are presented in Tables I–VI. The mole fraction of the BA monomer in the feed (f_{BA}), mole fraction of BA bound in the copolymer (F_{BA}), and final weight conversion (wt %) for each sample are shown in each table.

A list of the reactivity ratios estimated at various conditions is found in Table VII. The reactivity ratio estimations were performed using two different computational tools, each based on the terminal model for copolymerization. The RREVM program^{16,17} employs the Mayo–Lewis equation⁴ [see eq. (1)]. This form of the copolymer composition equation is used with the assumption of negligible drift in copolymer composition. This factor was addressed in the experimental design wherein the experiments were halted at low monomer conversion levels. A second analysis of the data was based on the integrated form of the Mayo–Lewis model, known as the Meyer–Lowry model¹⁸:

$$x = 1 - \left(\frac{f_1}{f_{10}}\right)^{\alpha} \left(\frac{1 - f_1}{1 - f_{10}}\right)^{\beta} \left(\frac{f_{10} - \delta}{f_1 - \delta}\right)^{\gamma} \quad (6)$$

**Table I BA/MMA (60°C, 30 wt % Toluene)
Reactivity Ratio Estimation Data**

| f_{BA} | F_{BA} | Conversion (wt %) |
|----------|----------|-------------------|
| 0.9500 | 0.8292 | 1.4152 |
| 0.9489 | 0.8343 | 1.1000 |
| 0.8456 | 0.6660 | 1.7300 |
| 0.8456 | 0.6597 | 1.8700 |
| 0.8456 | 0.6698 | 1.9900 |
| 0.7000 | 0.5158 | 0.8784 |
| 0.6830 | 0.4621 | 1.7700 |
| 0.6000 | 0.4069 | 0.7517 |
| 0.5018 | 0.3483 | 1.6900 |
| 0.5018 | 0.3217 | 1.5400 |
| 0.5018 | 0.3228 | 1.8600 |
| 0.4428 | 0.2456 | 2.0337 |
| 0.4428 | 0.2590 | 2.1758 |
| 0.4428 | 0.2598 | 2.2136 |
| 0.3615 | 0.1964 | 3.7273 |
| 0.3615 | 0.2092 | 4.1143 |
| 0.3615 | 0.1940 | 3.6971 |
| 0.3615 | 0.1924 | 5.6210 |
| 0.3500 | 0.2190 | 1.6705 |
| 0.3477 | 0.2224 | 0.8600 |
| 0.2500 | 0.2077 | 2.2991 |
| 0.2499 | 0.1264 | 1.5772 |
| 0.2499 | 0.1258 | 1.4645 |
| 0.2499 | 0.1207 | 1.8032 |
| 0.2499 | 0.1219 | 1.8347 |
| 0.1534 | 0.0956 | 3.0100 |
| 0.1513 | 0.0776 | 1.9559 |
| 0.1513 | 0.0786 | 2.0484 |
| 0.1513 | 0.0731 | 2.1894 |
| 0.1513 | 0.0748 | 1.9809 |
| 0.1500 | 0.1044 | 1.6333 |

where x denotes monomer conversion, f_{1o} is the initial mole fraction of monomer 1, f_1 is the mole fraction of monomer 1, and

$$\alpha = \frac{r_2}{1 - r_2} \quad (7)$$

$$\beta = \frac{r_1}{1 - r_1} \quad (8)$$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \quad (9)$$

and

$$\delta = \frac{1 - r_2}{2 - r_1 - r_2} \quad (10)$$

Reactivity ratios based on the Meyer–Lowry model were estimated using a nonlinear parameter estimation program. The full conversion range integrated Meyer–Lowry expression excludes the requirement of a negligible composition drift assumption. A comparison of the Meyer–Lowry and Mayo–Lewis based reactivity ratio estimates (Table VII) reveals little difference between the parameter estimates using either method. Thus, we can conclude that the effect of composition drift (if any at all) was negligible.

The RREVM program was used to generate 95% posterior probability contours for reactivity ratios estimated using low conversion data. The contour plots and their point estimates are plotted in Figure 1 at various temperatures. A distinct change in the reactivity ratios may be observed as the temperature is varied. This is further indicated through the nonoverlapping contours in Figure 1.

The reactivity ratios at different temperatures, predicted by the Meyer–Lowry model, were fit to the Arrhenius expressions of eqs. (2) and (3). A nonlinear parameter estimation technique was used and the data were centered about the aver-

**Table II BA/MMA (80°C, 30 wt % Toluene)
Reactivity Ratio Estimation Data**

| f_{BA} | F_{BA} | Conversion (wt %) |
|----------|----------|-------------------|
| 0.9500 | 0.8780 | 11.43 |
| 0.8784 | 0.7335 | 1.52 |
| 0.8784 | 0.7271 | 1.53 |
| 0.8784 | 0.7306 | 1.80 |
| 0.8561 | 0.6649 | 0.79 |
| 0.8561 | 0.6874 | 0.89 |
| 0.8561 | 0.6797 | 1.14 |
| 0.8561 | 0.6827 | 1.40 |
| 0.7000 | 0.4811 | 3.59 |
| 0.6999 | 0.5018 | 1.65 |
| 0.6000 | 0.3927 | 2.32 |
| 0.4910 | 0.3211 | 1.37 |
| 0.4910 | 0.3147 | 2.17 |
| 0.4910 | 0.3050 | 2.14 |
| 0.4910 | 0.3055 | 3.53 |
| 0.4463 | 0.2717 | 2.20 |
| 0.4463 | 0.2684 | 2.16 |
| 0.4463 | 0.2734 | 3.09 |
| 0.4463 | 0.2610 | 2.21 |
| 0.3499 | 0.2107 | 3.25 |
| 0.2780 | 0.1546 | 2.75 |
| 0.2500 | 0.1213 | 3.49 |
| 0.1499 | 0.0926 | 2.45 |
| 0.1010 | 0.0578 | 3.42 |

**Table III BA/MMA (100°C, 30 wt % Toluene)
Reactivity Ratio Estimation Data**

| f_{BA} | F_{BA} | Conversion (wt %) |
|----------|----------|-------------------|
| 0.9500 | 0.8786 | 3.93 |
| 0.8612 | 0.7121 | 0.53 |
| 0.8612 | 0.7143 | 0.20 |
| 0.8612 | 0.7117 | 0.62 |
| 0.8612 | 0.7146 | 0.64 |
| 0.8483 | 0.7029 | 4.01 |
| 0.8483 | 0.6964 | 4.06 |
| 0.8483 | 0.6983 | 4.11 |
| 0.8483 | 0.6951 | 4.52 |
| 0.7197 | 0.5255 | 1.07 |
| 0.7000 | 0.4975 | 1.84 |
| 0.6000 | 0.3987 | 2.01 |
| 0.4862 | 0.3192 | 2.08 |
| 0.4862 | 0.3230 | 2.26 |
| 0.4862 | 0.3310 | 2.08 |
| 0.4862 | 0.3264 | 2.54 |
| 0.4697 | 0.3151 | 3.14 |
| 0.4697 | 0.2976 | 4.19 |
| 0.4697 | 0.3022 | 3.92 |
| 0.4697 | 0.2990 | 3.32 |
| 0.3499 | 0.2126 | 3.76 |
| 0.2500 | 0.1525 | 4.44 |
| 0.2493 | 0.1378 | 2.88 |
| 0.1499 | 0.0826 | 6.83 |
| 0.1014 | 0.0593 | 3.41 |

**Table IV BA/MMA (120°C, 30 wt % Toluene)
Reactivity Ratio Estimation Data**

| f_{BA} | F_{BA} | Conversion (wt %) |
|----------|----------|-------------------|
| 0.9500 | 0.8920 | 9.69 |
| 0.8470 | 0.7049 | 4.21 |
| 0.8470 | 0.7036 | 4.04 |
| 0.8470 | 0.7047 | 3.66 |
| 0.8470 | 0.7066 | 4.19 |
| 0.8385 | 0.7029 | 5.37 |
| 0.8385 | 0.7052 | 5.25 |
| 0.8385 | 0.7036 | 4.69 |
| 0.8385 | 0.7049 | 6.44 |
| 0.7000 | 0.5184 | 5.16 |
| 0.6000 | 0.4097 | 3.88 |
| 0.5882 | 0.4255 | 5.31 |
| 0.4592 | 0.3034 | 3.44 |
| 0.4592 | 0.3206 | 3.38 |
| 0.4592 | 0.3379 | 3.14 |
| 0.4592 | 0.3000 | 3.30 |
| 0.4555 | 0.2958 | 5.80 |
| 0.4555 | 0.3031 | 5.67 |
| 0.4555 | 0.3045 | 5.84 |
| 0.4555 | 0.3057 | 5.72 |
| 0.3499 | 0.2456 | 6.13 |
| 0.3005 | 0.1974 | 6.47 |
| 0.2500 | 0.1886 | 6.01 |
| 0.1516 | 0.0894 | 7.27 |
| 0.1499 | 0.0901 | 6.51 |

age temperature (100°C in this case). This was performed in order to provide a reliable assessment of the adequacy of the fit of the data to the Arrhenius model.¹⁹ The resulting temperature-dependent reactivity ratio expressions (at 30 wt % toluene) are

$$r_{BA} = 1.5815e^{-1123.99/RT} \quad (11)$$

$$r_{MMA} = 0.8268e^{+561.31/RT} \quad (12)$$

where R is the gas constant (cal/mol K) and T is the temperature (K). These expressions are plotted along with the Meyer–Lowry based reactivity ratio data in Figure 2. Bulk BA/MMA reactivity ratio data⁸ and their corresponding Arrhenius expressions are also shown in Figure 2 in order to compare the bulk and solution parameter estimation results. Approximate error bars (based on the 95% posterior probability contours of Fig. 1) for the point estimates are also shown. It is clear from Figure 2 that the temperature dependence of the reactivity ratios estimated using the terminal

model, is well described by these two expressions [eqs. (11) and (12)]. Similar to the case for bulk copolymerization, as temperature is increased, the cross-propagation reaction with the BA mono-

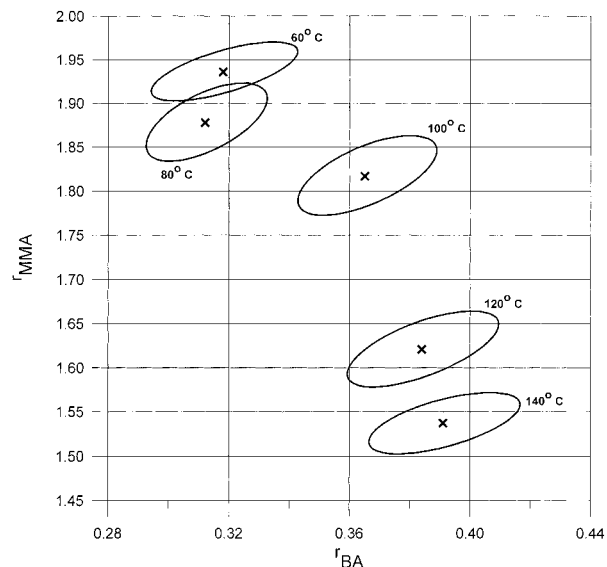
**Table V BA/MMA (120°C, 50 wt % Toluene)
Reactivity Ratio Estimation Data**

| f_{BA} | F_{BA} | Conversion (wt %) |
|----------|----------|-------------------|
| 0.9500 | 0.8859 | 6.81 |
| 0.8387 | 0.6925 | 3.15 |
| 0.8387 | 0.6993 | 3.87 |
| 0.8387 | 0.7062 | 3.72 |
| 0.8387 | 0.7003 | 3.65 |
| 0.7000 | 0.5141 | 4.95 |
| 0.6000 | 0.4188 | 3.64 |
| 0.4591 | 0.3128 | 3.21 |
| 0.4591 | 0.3111 | 3.85 |
| 0.4591 | 0.3124 | 4.01 |
| 0.4591 | 0.3111 | 3.27 |
| 0.3499 | 0.2418 | 4.43 |
| 0.2500 | 0.1642 | 5.58 |
| 0.1499 | 0.1011 | 3.85 |

Table VI BA/MMA (140°C, 30 wt % Toluene) Reactivity Ratio Estimation Data

| f_{BA} | F_{BA} | Conversion (wt %) |
|----------|----------|-------------------|
| 0.9500 | 0.8875 | 4.34 |
| 0.8401 | 0.7274 | 11.91 |
| 0.8401 | 0.7271 | 10.16 |
| 0.8401 | 0.7282 | 10.40 |
| 0.8401 | 0.7264 | 11.20 |
| 0.8369 | 0.6899 | 6.90 |
| 0.7000 | 0.5262 | 2.00 |
| 0.6999 | 0.5301 | 5.38 |
| 0.6000 | 0.4358 | 1.58 |
| 0.5491 | 0.3937 | 3.92 |
| 0.5491 | 0.3813 | 4.01 |
| 0.5491 | 0.3769 | 4.19 |
| 0.5491 | 0.3902 | 4.19 |
| 0.4584 | 0.3074 | 4.92 |
| 0.4489 | 0.3098 | 9.27 |
| 0.4489 | 0.3109 | 9.23 |
| 0.4489 | 0.3135 | 8.61 |
| 0.4489 | 0.3100 | 9.80 |
| 0.3499 | 0.2476 | 4.51 |
| 0.2500 | 0.1913 | 4.55 |
| 0.1500 | 0.0993 | 4.00 |
| 0.1500 | 0.0938 | 4.18 |
| 0.1500 | 0.0878 | 4.01 |
| 0.1500 | 0.0974 | 3.42 |
| 0.1499 | 0.1139 | 3.14 |

mer becomes more favored over the homopropagation reaction of MMA monomer. In other words, the reactivity of an MMA-ended radical toward its own monomer appears to decrease with temperature. Most importantly, however, one can see the absence of differences between the solution and bulk copolymerization reactivity ratios as indicated by both the experimental data points and the Arrhenius models in Figure 2.

**Figure 1** The 95% posterior probability contours and point estimates (x) of reactivity ratios for BA/MMA solution polymerizations (30 wt % toluene).

In eqs. (11) and (12), no confidence intervals have been given for the parameter estimates (i.e., activation energy and preexponential factor). This is because the errors in the reactivity ratio estimates are highly correlated and form a joint confidence region as opposed to a linear confidence interval (see Fig. 1). However, using the extremes of the reactivity ratio joint confidence intervals, one could arrive at the following *rough* estimates of the confidence intervals: $A_{BA} = 1.5815 \pm 0.0650$, $E_{BA} = -1123.99 \pm 83.35$ cal/mol, $A_{MMA} = 0.8268 \pm 0.0268$, $E_{MMA} = +561.31 \pm 11.27$ cal/mol. Although not shown in Figure 2, these intervals easily overlap with both the bulk and solution reactivity ratio estimates shown in Figure 2 and further confirm the

Table VII BA/MMA Reactivity Ratio Estimation Results

| Temperature (°C) | Toluene (wt %) | Mayo–Lewis/RREVM Estimation | | Meyer–Lowry/Nonlinear Estimation | |
|------------------|----------------|-----------------------------|-----------|----------------------------------|-----------|
| | | r_{BA} | r_{MMA} | r_{BA} | r_{MMA} |
| 60 | 30 | 0.318 | 1.936 | 0.291 | 1.871 |
| 80 | 30 | 0.312 | 1.878 | 0.313 | 1.917 |
| 100 | 30 | 0.365 | 1.817 | 0.352 | 1.803 |
| 120 | 30 | 0.384 | 1.621 | 0.375 | 1.649 |
| 120 | 50 | 0.357 | 1.543 | 0.374 | 1.639 |
| 140 | 30 | 0.391 | 1.537 | 0.401 | 1.627 |

lack of significant differences between the bulk and solution estimates.

Due to the elevated temperatures being used in our experiments, depropagation reactions at temperatures near the ceiling temperature for MMA might be expected.⁸ In light of the fact that the Arrhenius expressions did not exhibit lack of fit to the solution reactivity ratio values in Figure 2, the suitability of the terminal model for the BA/MMA solution copolymerization at the reaction conditions shown for the prediction of copolymer composition is deemed acceptable. In other words, no significant depropagation or solvent effects are evident over this wide temperature range.

In an additional experiment at 120°C, an increase in the toluene solution concentration from 30 to 50 wt % did not appear to have a significant effect on the reactivity ratio estimates (see Table VII and Fig. 3). This conclusion was made because the 95% posterior probability contours for these point estimates overlapped one another in Figure 3.

CONCLUDING REMARKS

In this study, BA/MMA solution copolymerization reactivity ratios were estimated over an extended temperature range. Experiments were performed to estimate reactivity ratios at 60, 80, 100, 120, and 140°C with 30 wt % toluene, and 120°C with 50 wt % toluene.

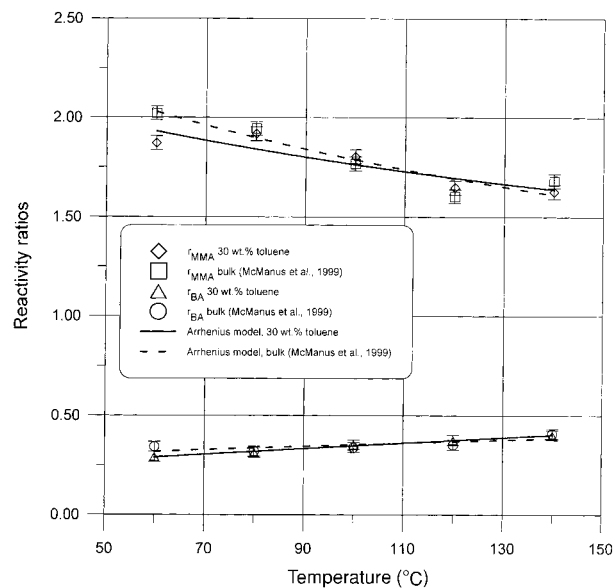


Figure 2 BA/MMA bulk and solution (30 wt % toluene) reactivity ratios vs temperature.

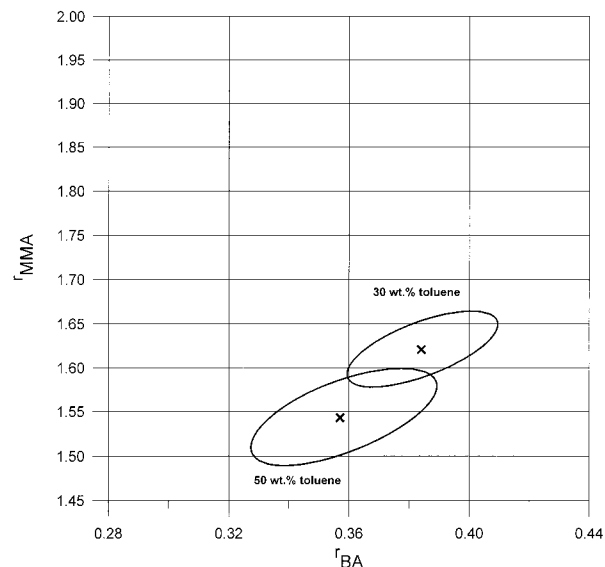


Figure 3 The 95% posterior probability contours and point estimates (x) of reactivity ratios for BA/MMA solution polymerizations (30 and 50 wt % toluene at 120°C).

Reactivity ratios, based on the Meyer–Lowry and Mayo–Lewis models, were successfully fit to Arrhenius expressions. Effects of composition drift during the polymerizations seemed negligible. Also, no significant solvent or depropagation effects seemed to exist under the conditions studied.

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