

# High Temperature Bulk Copolymerization of Methyl Methacrylate and Acrylonitrile. I. Reactivity Ratio Estimation

R. Khesareh, N. T. McManus, A. Penlidis

*Institute for Polymer Research, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

Received 14 January 2005; accepted 9 April 2005

DOI 10.1002/app.23226

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

**ABSTRACT:** The copolymerization of methyl methacrylate and acrylonitrile has been studied in the bulk phase. Experiments for estimating reactivity ratios were conducted at 60, 100, 120, and 140°C. Tidwell–Mortimer and the feed composition constraint approaches were used to design the experiments. The error in variables model (EVM) method was employed to evaluate the reactivity ratios and analyze

the error involved. The results show that the reactivity ratios do not vary significantly with temperature up to 140°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 843–851, 2006

**Key words:** copolymerization; radical polymerization; kinetic (polymerization); reactivity ratio

## INTRODUCTION

Methyl methacrylate (MMA) and acrylonitrile (AN) copolymerization has been poorly reported in the literature. Study of this copolymer system over a wide range of temperatures is of much importance for the investigation of terpolymerization of styrene, methyl methacrylate, and acrylonitrile to produce a polymer with improved optical applications.

Styrene–methyl methacrylate copolymer (SMMA) is a transparent polymer, which is used in optical applications. Adding acrylonitrile as a termonomer to this copolymer system improves some desired chemical and mechanical properties, such as solvent resistance and toughness of the product.<sup>1</sup> Also, polymerization under thermal conditions can improve the clarity of the terpolymer.<sup>2</sup>

To study the terpolymer system, it is necessary to investigate the three copolymer pairs of styrene (STY)/MMA, STY/AN, and MMA/AN<sup>3</sup> at elevated temperatures (100–140°C). The STY/MMA copolymer has received much literature attention compared with other copolymer systems at conventional temperatures (40–80°C)<sup>4</sup>; however, the studies at elevated temperatures are scarce. The STY/AN copolymer has also been studied at conventional temperatures and

some studies at higher temperatures have also been reported.<sup>4</sup> Kinetic studies for MMA/AN are very limited and, even in the conventional temperature range (40–80°C), there is not enough information in the literature.

Micro-emulsion copolymerization of MMA/AN at 70°C was studied by Reddy et al.<sup>5,6</sup> The reactivity ratios of MMA/AN copolymer were evaluated by Fineman–Ross (F–R), Kellen–Tudos (K–T), and Mayo–Lewis (M–L) methods. Error analyses were not performed and a simple linear regression was used to determine reactivity ratios. In addition, no experimental design method was employed, leading to questions about the reliability of the estimates obtained.

Brar et al.<sup>7</sup> characterized the stereochemistry of MMA/AN copolymer using different NMR spectroscopic techniques. The reactivity ratios estimated were:  $r(\text{MMA}) = 1.45$ ,  $r(\text{AN}) = 0.17$ .

Also, Brar and Hekmatyar<sup>8</sup> reported the characterization of the sequence distribution of MMA/AN/STY terpolymer using <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy. The terpolymerization was performed by photo-initiation. The reactivity ratios estimated in their work were based on the Alfrey–Goldfinger equation<sup>9</sup> using five data points. Polymerization temperature, conversion levels, and error analysis were not mentioned in the paper, and the reactivity ratios for MMA/AN were the same as those in the earlier work.

Steinfatt and Schmidt-Naake<sup>10</sup> studied micro-emulsion of MMA/AN/STY terpolymer at 60°C. Terpolymer composition data from elemental analysis, infrared, and Raman spectroscopy were used to estimate reactivity ratios. Conversion levels were not reported.

Correspondence to: A. Penlidis (penlidis@cape.uwaterloo.ca).

Contract grant sponsors: Natural Sciences and Engineering Research Council (NSERC), Canada; Canada Research Chair (CRC) Program.

TABLE I  
Summary of Reaction Details for Reactivity Ratio Estimation Experiments for MMA/AN Copolymerization

Run	Experimental design	Temperature (C°)	$f_{10}^0$ (MMA)	$X^a$ (%)	$f_{10}^0$ (MMA)	$X^a$ (%)
1	T-M <sup>b</sup>	60	0.58	9	0.078	9
2	T-M	100	0.64	5	0.085	2
3	T-M	120	0.64	5	0.085	0.5
4	C-D <sup>c</sup>	60	0.612	3	0.118	2
5	C-D	100	0.645	2.5	0.2	3
6	C-D	120	0.675	5.8	0.2	3.8
7	C-D	140	0.675	3.3	0.2	3.1

<sup>a</sup> X: Conversion.

<sup>b</sup> T-M: Tidwell and Mortimer; polymer produced precipitates in the reaction mixture and is not soluble in common solvents.

<sup>c</sup> C-D: Composition constraint design; no precipitation observed in reactions and the copolymer is soluble in common solvents.

The reactivity ratios estimated were:  $r(\text{MMA}) = 1.24 \pm 0.11$  and  $r(\text{AN}) = 0.16 \pm 0.06$  and for micro-emulsion polymerization  $r(\text{MMA}) = 3.53 \pm 0.28$  and  $r(\text{AN}) = 0.09 \pm 0.05$ , for micro-emulsion.

Hatada et al.<sup>11</sup> reported an assessment of MMA/AN copolymers analyses using <sup>1</sup>H and <sup>13</sup>C NMR. The copolymerizations were performed in DMSO solution at 40, 50, and 60°C. The penultimate model was employed to determine reactivity ratios. The reactivity ratios were also calculated for the terminal model by the Fineman–Ross method, which imparts considerable uncertainty ( $r(\text{MMA}) = 1.38$  and  $r(\text{AN}) = 0.32$ ). It was reported that even the existence of a prepenultimate effect is possible; however, the statistical analysis of uncertainty used was not reliable enough to show the effect of experimental error in drawing this conclusion.

Finally, Grassie and Beattie<sup>12</sup> estimated the reactivity ratios at 60°C as  $r(\text{MMA}) = 1.32 \pm 0.05$  and  $r(\text{AN}) = 0.138 \pm 0.037$ .

In the present work, the MMA/AN copolymerization system has been studied in bulk at the conventional temperature range and elevated temperatures (100–140°C) to estimate reactivity ratios over a range of temperatures for this poorly studied copolymer system. Two experimental designs and the error in variables model (EVM) method were employed to obtain reliable reactivity ratio estimates.

## EXPERIMENTAL

### Purification of reagents

Methyl methacrylate (Aldrich, Canada) was washed three times with a solution of 10% by weight sodium hydroxide (NaOH) in water, three times with deionized water and then dried over CaCl<sub>2</sub> for 24 h. The washed monomer was distilled under reduced pressure and the middle fraction of the distillate was collected for polymerization.<sup>13</sup>

Acrylonitrile (Aldrich) was purified by being passed over inhibitor removal resin (Aldrich) and then purged by nitrogen gas. Throughout this work, monomer 1 refers to MMA and monomer 2 refers to AN.

2,2'-Azobisisobutyronitrile (AIBN) (Polyscience Inc., Warrington, PA) was recrystallized three times from cold absolute methanol, dried in a vacuum oven at room temperature and stored in a freezer at -10°C. This initiator was used for experiments at 60°C. Tert-butylperoxy 2-ethylhexyl carbonate (TBEC) (Aldrich) was used without purification in experiments at 100 and 120°C. The purity of TBEC used in these experiments was 95%. Di-*tert*-butyl peroxide or trigonox B (TgB) (AKZO Chemicals Inc., Chicago, IL) was also used without purification for copolymerizations at 140°C.

All solvents for the experimental part and for characterization of the copolymers (dichloromethane, acetonitrile, ethanol, *n,n*-dimethyl-formamide) were used without further purification.

### Methods

Experiments were carried out in borosilicate glass ampoules. The monomers and initiators were weighed and then ~2 mL of solution pipetted into the ampoules. AIBN, TBEC, and TgB were used as initiators for experiments at different temperatures. A standard degassing procedure<sup>14</sup> was used to remove any traces of oxygen. All ampoules were sealed and then stored in liquid nitrogen until needed.

Polymerizations were carried out in a temperature-controlled oil bath, at 60, 100, 120, and 140°C. The ampoules were placed in the bath for a measured time interval, in an attempt to obtain conversion levels of 10% or less (preferably less than 5%). Ampoules were subsequently submerged in liquid nitrogen, thawed, cleaned, dried, and weighed. Then, ampoules were subsequently scored and broken, and the contents

**TABLE II**  
Experimental Results at 60°C Used for Reactivity Ratio Estimation

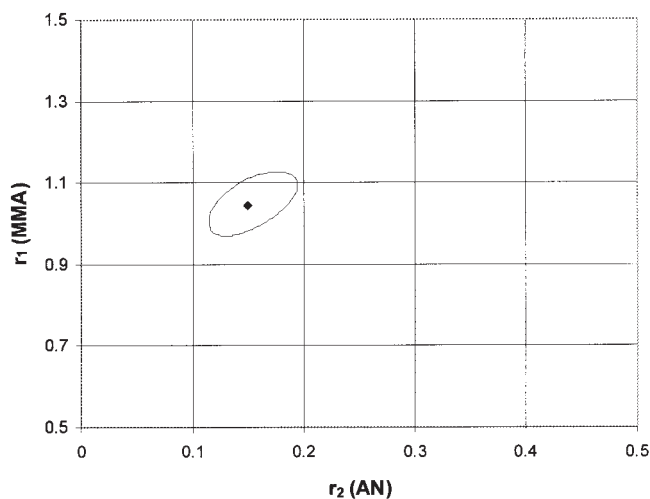
Exp. design	$f(\text{AN})$	Conversion (%)	$N$ (wt %)	$F(\text{AN})$	Standard error (%)
T-M	0.420	8.9	4.84	0.298	1.26
	0.420	8.9	4.95	0.300	
	0.420	9	4.89	0.303	
	0.420	6.1	4.89	0.300	
C-D	0.388	3	5.5	0.332	8.25
	0.388	2.9	4.97	0.300	
	0.388	2.9	4.88	0.304	
	0.388	2.9	4.44	0.276	
	0.388	2.8	4.81	0.296	
	0.388	2.8	4.81	0.296	
C-D	0.882	1.8	13.28	0.656	1.43
	0.882	1.9	13.12	0.651	
	0.882	9	13.07	0.649	

poured into a 10-fold excess of methanol. The empty ampoules were then reweighed. The precipitated copolymer was dried in a vacuum oven at 75°C for 7 days to reach a constant weight. The conversion was measured based on total polymer by gravimetry.

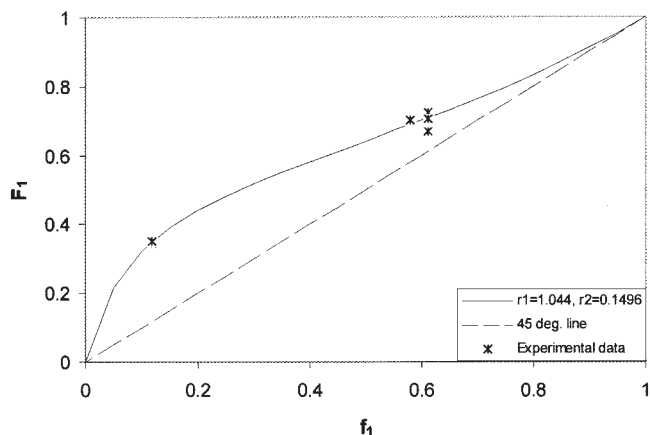
Acrylonitrile dramatically decreases the solubility of the copolymer, therefore for higher amounts of AN in the copolymer, a cocktail of solvents containing acetonitrile was used, whereas for insoluble copolymers containing high levels of AN, filtering was used to isolate the polymer.

### Experimental design

The design of the experiments followed the criteria proposed by Tidwell and Mortimer<sup>15</sup> and Burke et al.<sup>16</sup>



**Figure 1** 95% posterior probability contour for reactivity ratios, for MMA/AN copolymer produced at 60°C.



**Figure 2** Copolymer composition versus feed composition of MMA calculated by Mayo-Lewis model and estimated reactivity ratios at 60°C.

### Tidwell and Mortimer approach

The Tidwell-Mortimer experimental design<sup>15</sup> was employed for preliminary experiments. According to the criterion, the initial mole fractions of the monomer designated as monomer 1 are given by:

$$f'_{10} = 2/(2 + r_1) \quad (1)$$

and

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

Initial guesses for the reactivity ratios  $r_1$  and  $r_2$  needed in the above equations were obtained from Brar and Hekmatyar<sup>8</sup> at 60°C, and based on reactivity ratios estimated at 60°C (in this work), initial guesses at 100 and 120°C were subsequently obtained.

### Feed composition constraint design

The  $f'_{10}$  suggested by the Tidwell and Mortimer approach contains more than 90 mol % of AN. The copolymer produced with that level of AN in the feed precipitates out from the reaction mixture. Therefore, the assumption of homogeneity of polymerization is not applicable. To achieve homogeneous reactions in both sets of pairs used for reactivity ratio estimation ( $f'_{10}$  and  $f'_{10}$ ), the feed composition constraint experimental design<sup>16</sup> was used.

In many cases, reactivity ratios are subject to composition constraints. Burke et al.<sup>16</sup> showed that all the key information contained in the  $D$ -optimal criterion (which is the basis of the Tidwell-Mortimer approach) can be summarized in two equations; one equation is a function of  $r_1$ , and the other a function of  $r_2$ , as follows:

$$0.0 < f_2 < \text{composition constraint}$$

**TABLE III**  
Reactivity Ratios for AN/MMA Copolymerization  
at 60°C

References	$r_1$ (MMA)	$r_2$ (AN)
Brar and Hekmatyar (1999)	1.45	0.17
Steinfatt and Schmidt-Naake (2001)	$1.24 \pm 0.11$	$0.16 \pm 0.06$
Grassie and Beattie (1984)	$1.322 \pm 0.05$	$0.138 \pm 0.037$
This work	1.04	0.15

$$f_{2,1} = \frac{r_1}{2} \left[ 1 - \exp\left(-\frac{f_{2,2}}{r_1}\right) \right], \quad 0.0 < r_1 < 1.5 \quad (3)$$

$$f_{2,2} = 1 - \frac{r_1}{2} \left[ 1 - \exp\left(-\frac{(1-f_{2,1})}{r_2}\right) \right], \quad 0.0 < r_2 < 1.5 \quad (4)$$

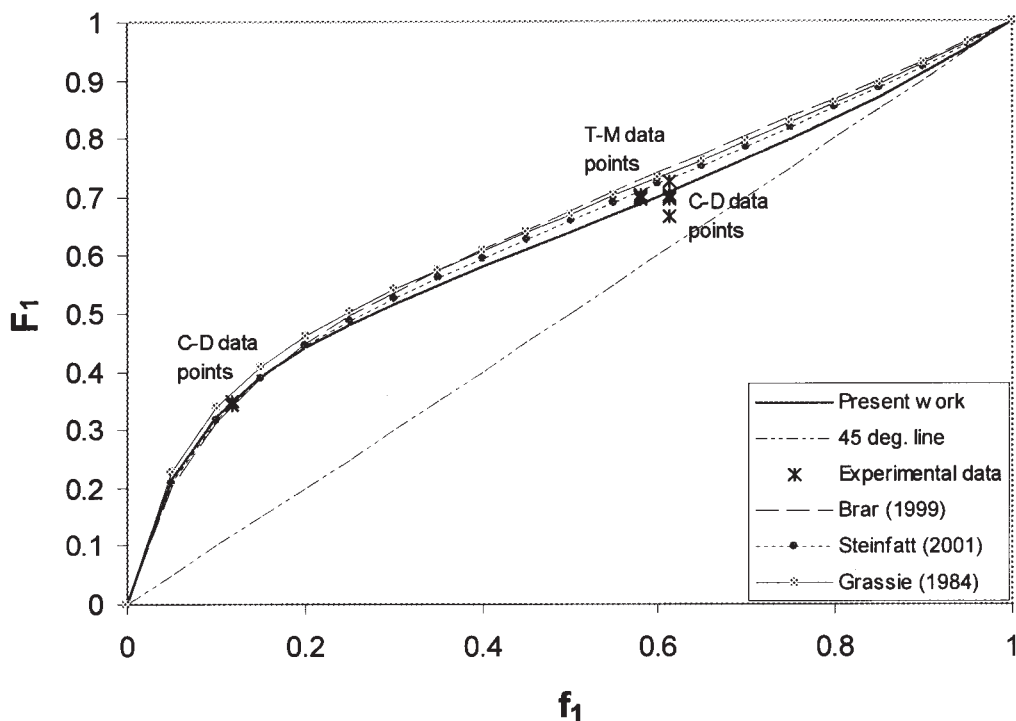
The composition constraint for AN was obtained by performing screening experiments at 60°C with different feed compositions with 0.01 mol/L AIBN, and it was observed that if AN in the feed composition was more than  $f = 0.89$  mol, the polymer precipitated in the reaction mixture. Experiments with  $f = 0.89$  mol AN in the feed showed that there was no polymer precipitation up to 15% conversion. Therefore,  $f = 0.89$  mol AN was chosen as a feed composition constraint for 60°C, and for higher temperatures  $f = 0.80$  mol AN

was considered as the feed composition constraint, to ensure that reactions were homogeneous.

The resulting polymers were isolated as described above and analyzed for cumulative polymer composition by elemental analysis for the weight percent of nitrogen. Elemental analysis was carried out by Guelph Chemical Laboratories Ltd. Guelph, Ontario, Canada.

## RESULTS AND DISCUSSION

The Tidwell–Mortimer method was used in the preliminary design of experiments at 60, 100, and 120°C and the estimated reactivity ratios from these experiments were used as the initial guesses for the composition constraint experimental design. As mentioned above, the polymer produced at  $f'_{10}$  from the Tidwell–Mortimer approach, precipitated out from the reaction mixture during polymerization, therefore data from these experiments were not used for the final reactivity ratio estimation. The reactivity ratios estimated in this work were based on the results of experiments designed by the feed composition constraint approach, and the results from polymers that were soluble from the Tidwell–Mortimer approach (at  $f'_{10}$ ) as additional data points. A summary of the experiments done for reactivity ratio estimation is presented in Table I.



**Figure 3** Comparison of Mayo–Lewis model curves based on different reactivity ratios estimated at 60°C (Table III).

**TABLE IV**  
 Summary of Experimental Data Points from Reactivity Ratio Experiments with Added Initiator at 100, 120, and 140°C

Temp (°C)	Exp. design	$f'_{10}$ MMA	X (%) Ave.	No. of data points	$F_2$ (AN) Ave.	Error (AN) (%)	Error used in EVM
100	T-M	0.641	5	4	0.289	4.08	7%
	C-D	0.646	2.5	4	0.285	6.59	
	C-D	0.201	3	4	0.614	0.84	
120	T-M	0.641	5	3	0.294	11.16	6%
	C-D	0.678	5	6	0.258	2.88	
	C-D	0.198	3.8	6	0.615	0.66	
140	C-D	0.678	3.3	6	0.254	1.75	2%
	C-D	0.198	3.1	6	0.615	0.6	

### Conventional polymerization temperature (60°C)

As mentioned in the introduction, there are some reactivity ratios estimated in the literature for the conventional temperature range (40–80°C). However, the precision of these values is not clear. Therefore, experiments for reactivity ratio estimation were conducted at 60°C to obtain more precise estimates and to learn more about this copolymer system.

In the first step, two initial monomer feed compositions were calculated by eqs. (1) and (2) (the Tidwell–Mortimer approach). Four replicates for  $f'_{10} = 0.58$  mol MMA and five replicates for  $f'_{10} = 0.078$  mol MMA were run.

In the next step (run 4 in Table I), the experiments were designed by the composition constraint approach.<sup>16</sup> The composition constraint is found to be:

$$0.0 < f_{AN} < 0.89 \text{ or } f'_{10 \text{ MMA}} > 0.11$$

based on  $f'_{10}$  or  $f'_{10}$  calculated by eq. (3).

Five replicate experiments were run for  $f'_{10}$  and three for  $f'_{10}$ . The products from the eight experiments were analyzed for copolymer composition using nitrogen analysis. The data points obtained under conditions of homogeneous polymerization are presented in Table II. The standard errors shown in this Table (for 95% confidence interval) were calculated based on the mole fraction of AN for each group of data points.

The Error in Variables Model (EVM) method was employed to calculate reactivity ratios based on the Mayo–Lewis equation. The RRVEM program, which works based on the EVM method, was run to estimate reactivity ratios.<sup>17,18</sup> The reactivity ratio point esti-

mates are  $r_1 = 1.044$  and  $r_2 = 0.1496$ , and the 95% posterior probability contour is shown in Figure 1.

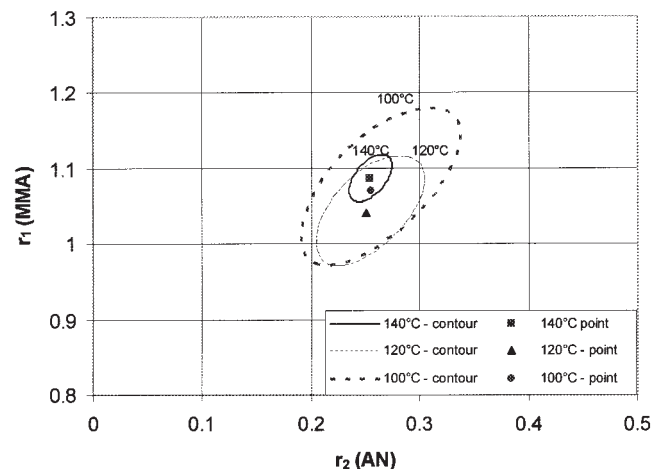
The feed composition errors, used in the EVM program to calculate the 95% probability contours, were 1%, because the purity of AN was +99%. Therefore, 1% error for feed composition covers a sufficient error margin for the reactivity ratio estimation. Analysis of the copolymer composition errors shows that the errors for copolymers containing less AN are larger; the reason being that AN is calculated from elemental analyses for nitrogen and if the amount of AN in the copolymer is low, the experimental error of elemental analysis will be considerably relative to the amount of nitrogen in the samples. The copolymer composition errors used for calculating reactivity ratios by the RREVM program were calculated by pooling the errors of the data points having higher standard errors (lower AN).

The first group of data points includes data from runs where conversion was 9%. This is larger than the normally accepted level for low conversion polymerizations. Therefore, the Meyer–Lowry equation<sup>19</sup> was employed to calculate the polymer composition drift

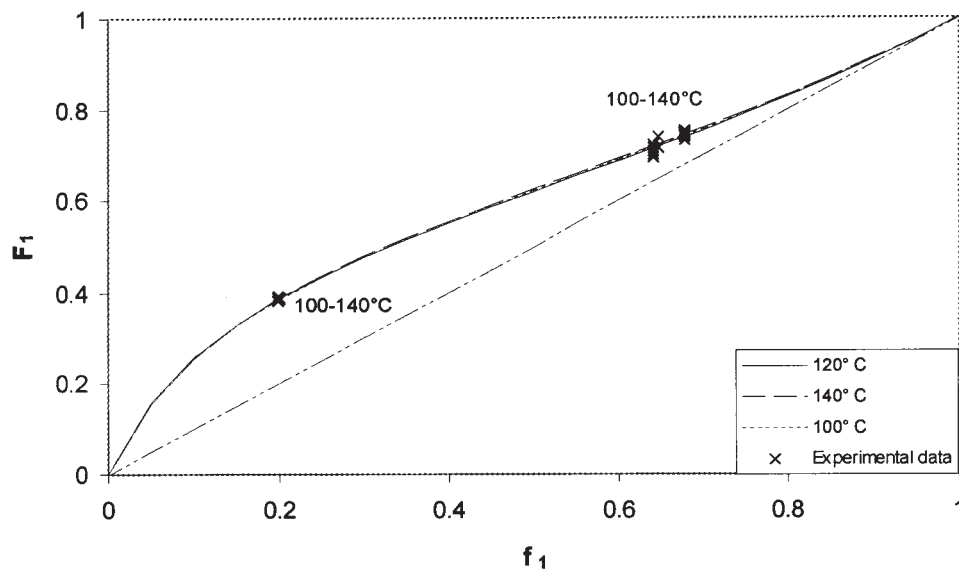
**TABLE V**

Reactivity Ratios Estimated for MMA/AN Copolymer

Temperature (°C)	$r_1$ (MMA)	$r_2$ (AN)
60	1.04	0.15
100	1.07	0.26
120	1.04	0.25
140	1.09	0.25



**Figure 4** 95% posterior probability contours for reactivity ratios estimated by EVM for MMA/AN copolymer at elevated temperatures (100–140°C).



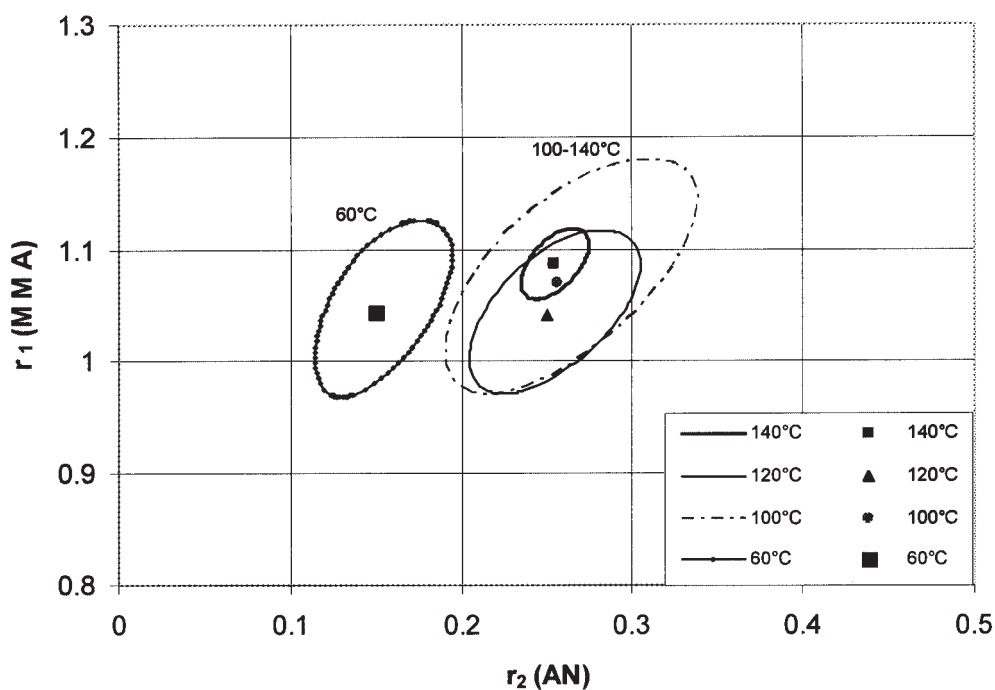
**Figure 5** Comparison of Mayo-Lewis model curves based on reactivity ratios estimated at 100, 120, and 140°C including the experimental data points.

in the range of 0–10% conversion and the result showed a negligible drift. Therefore, these data points can be used in the reactivity ratio estimation with reasonable confidence.

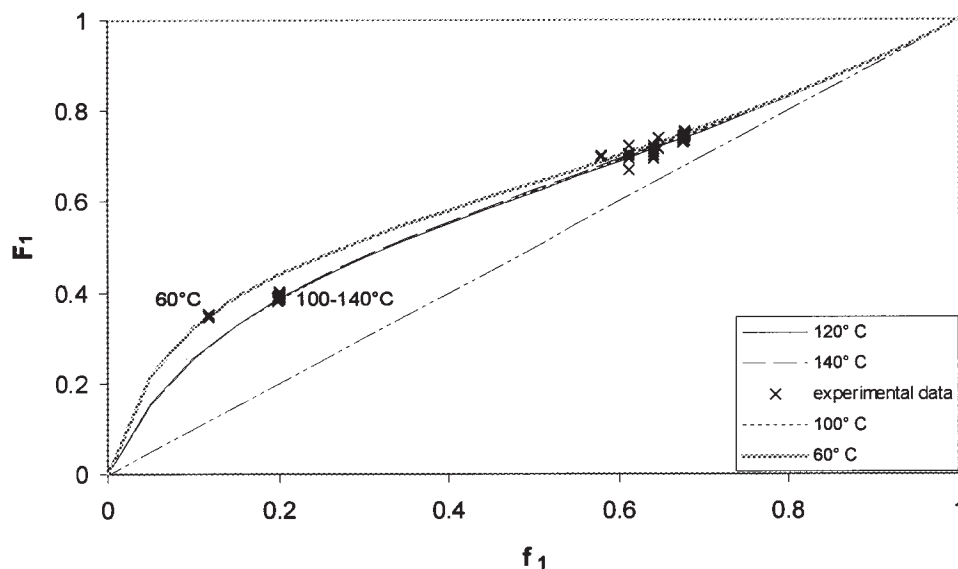
Note that in the elemental analysis, the weight percent of nitrogen is measured and based on that the mole fraction of AN is directly calculated. However, there is no direct measurement and calculation of the MMA mole fraction in the polymer samples. Therefore, to cal-

culate the mole fraction of MMA, it has to be assumed that the rest of the sample is MMA or  $F(\text{MMA}) = 1 - F(\text{AN})$ . Because of experimental errors, this assumption may introduce some error and it wrongly makes the probability contour smaller than the real contour. Therefore, it is preferable to use only the AN copolymer composition in the RREVM program.

The Mayo-Lewis model<sup>20</sup> is plotted in Figure 2 using the reactivity ratios estimated from the elemen-



**Figure 6** 95% posterior probability contours for reactivity ratios for MMA/AN copolymer at 60–140°C.



**Figure 7** Comparison of Mayo–Lewis model curves based on reactivity ratios estimated over the entire temperature range including experimental data points.

tal analysis data (Table II) and the RREVM program. This figure shows that the copolymer composition drift, with higher mole fractions of MMA in the feed, is negligible and, among three groups of data points shown in the figure, only the group that has  $f_{\text{MMA}} = 0.118$  has a significant copolymer composition drift.

Some of the reactivity ratios reported in the literature are presented in Table III to compare with the values estimated in this work. As shown, the  $r_1$  obtained in this study is different from the values reported in the literature but  $r_2$  is similar.

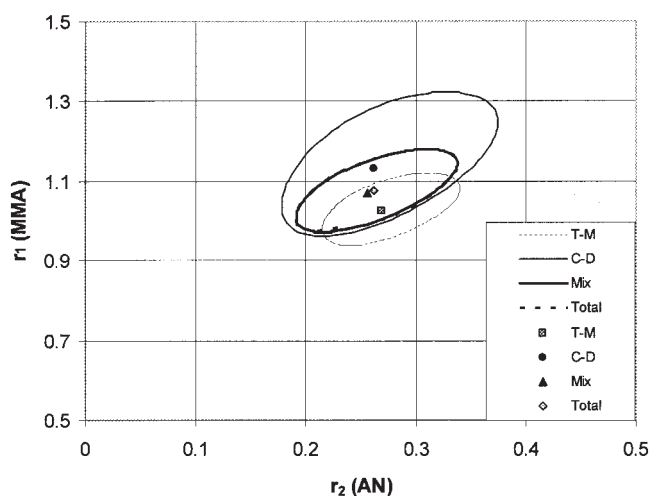
Figure 3 shows the Mayo–Lewis model curve using the reactivity ratios presented in Table III. As shown

in Figure 3, the data points with  $f_{\text{MMA}} = 0.118$  agree with all the curves plotted. But the data points that have 8.25% error,  $f_{\text{MMA}} = 0.612$  (see Table II), cover a broader range of reactivity ratios; (however the other set of data points (T-M) narrows down this range). Therefore, if it is assumed that there was no systematic problem in elemental analysis within the second group of data points, the reactivity ratio for MMA is reliable. These points will be considered further after the assessment of results from subsequent elevated temperature experiments.

#### Elevated temperature range (100–140°C)

There are no reactivity ratios for MMA/AN reported in the literature for elevated temperatures. Therefore, the initial guesses to calculate  $f'_{10}$  and  $f''_{10}$  were based on the preliminary results at 60°C. Runs 2 and 3 in Table I present the preliminary reactivity ratio experiments at 100 and 120°C.  $f'_{10}$  and  $f''_{10}$  were calculated by eqs. (1) and (2). As with experiments at 60°C,  $f'_{10}$  has  $f_{\text{AN}} = 0.915$  mol and the polymer produced at this feed ratio precipitated in the reaction mixture. Thus, the reactivity ratios estimated in these experiments were simply used as initial guesses for the feed composition constrained design (C-D). However, the data points produced at  $f'_{10}$  feed composition of the Tidwell–Mortimer approach, in which homogenous polymerization was achieved, were employed as additional data points to C-D data points in the final reactivity ratio estimation.

The feed composition constraint for all experiments carried out at the elevated temperature range (100–140°C) was considered as 80 mol % of AN:



**Figure 8** Comparing reactivity ratios estimated at 100°C with data points produced by T-M and C-D experimental designs and different combinations of data points from both approaches.

TABLE VI  
Reactivity Ratios Estimated for MMA/AN Copolymer System at Various Temperatures with Different Initiators and Different Combinations of Data Points

Temperature (°C) and initiator	T-M approach	C-D design	Combination of soluble polymers from both approaches	All data points from both approaches
60	$r_1 = 1.24$ $r_2 = 0.23$	$r_1 = 0.98$ $r_2 = 0.15$	$r_1 = 1.04$ $r_2 = 0.15$	$r_1 = 1.09$ $r_2 = 0.19$
100	$r_1 = 1.02$ $r_2 = 0.27$	$r_1 = 1.13$ $r_2 = 0.26$	$r_1 = 1.07$ $r_2 = 0.26$	$r_1 = 1.08$ $r_2 = 0.26$
120	$r_1 = 0.90$ $r_2 = 0.16$	$r_1 = 1.07$ $r_2 = 0.25$	$r_1 = 1.04$ $r_2 = 0.25$	$r_1 = 1.02$ $r_2 = 0.22$
140		$r_1 = 1.09$ $r_2 = 0.25$		

1 = MMA and 2 = AN

$$0.0 < f_{AN} \leq 0.8 \text{ or } f'_{10, MMA} \geq 0.2$$

Runs 5 to 7 (Table I) were used for the reactivity ratio estimations at 100, 120, and 140°C. A summary of these data, used for reactivity ratio estimation, is presented in Table IV.

The reactivity ratios estimated are listed in Table V. The results show that the reactivity ratio estimates at 100, 120, and 140°C are very similar. The 95% posterior probability contours for the point estimates are shown in Figure 4. This shows that the 95% probability contours of reactivity ratios at all three temperatures are strongly overlapping and all point estimates are inside the 95% probability contours for 100 and 120°C. Therefore, the reactivity ratios over this temperature range (100–140°C) are not significantly different, and the differences between point estimates for reactivity ratios are the result of experimental uncertainty (error estimates shown in Table IV).

The invariance of reactivity ratios with respect to temperature points to the fact that the activation energies for  $k_{11}$  and  $k_{12}$  and activation energies for  $k_{22}$  and  $k_{21}$  are almost the same.

The Mayo–Lewis model curves for reactivity ratios obtained at the elevated temperatures are shown in Figure 5 (Table V). This figure shows that the model curves obtained for the three pairs of reactivity ratios at elevated temperatures do not have a visible difference in terms of feed and copolymer composition. A total of 39 data points (see Table IV) were used to estimate reactivity ratios at 100, 120, and 140°C.

Finally, the reactivity ratios estimated at conventional and elevated temperature ranges (Table V) may be compared to find a possible trend. The 95% probability contours of these reactivity ratios are replotted in Figure 6. Also, the mole fraction of MMA in copolymer versus feed for the entire temperature range is plotted in Figure 7. As shown in Figure 6, the 95% probability contours for reactivity ratios estimated at the elevated temperature range (100–140°C) are strongly overlapping and as discussed, we cannot

prove that the point estimates for reactivity ratios at the elevated temperature range are separate points. Therefore, the reactivity ratios of MMA/AN at the elevated temperature range are either constant or too close to each other to be distinguished due to error effects. However, this trend is not apparently followed by reactivity ratios estimated at 60°C. As shown in Figure 6, there is no overlap between reactivity ratios for copolymerization at 60°C and the reactivity ratios at the other temperatures.

Considering  $r_1$  and  $r_2$  individually as shown in Table V or Figure 6, it is seen that the  $r_1$  at 60°C is in the same range as  $r_1$  at elevated temperatures. The  $r_2$  at 60°C is different from the values estimated at elevated temperatures. Looking at Figure 7 ( $F_1$  vs.  $f_1$  based on Mayo–Lewis model), it can be seen how this difference occurs. Most data points at the higher level of MMA ( $f'_{10}$ ) over the entire temperature range are almost matched with the curves created by reactivity ratios at elevated temperatures. However, only the data points at the lower level of MMA ( $f'_{10}$ ) at 60°C shift the Mayo–Lewis curve towards higher  $F_1$  at lower feed compositions ( $f_1$ ), and this results in the smaller reactivity ratio value for AN.

The reactivity ratios estimated from data produced with the Tidwell–Mortimer approach (T–M) and the feed composition constraint design (C–D) for 100°C are plotted in Figure 8. In addition, the reactivity ratios were estimated by different combinations of data points from experiments with both approaches. The combinations of the data points from soluble polymers (mix), which were employed to calculate reactivity ratios (soluble and insoluble samples), are plotted as well. The results of point estimates for reactivity ratios for all temperatures are presented in Table VI. As shown in Figure 8, the 95% probability contours for reactivity ratios estimated at 100°C from C–D and T–M and the other combinations are overlapping. This means that the T–M approach at this temperature is reliable at low conversions for  $f'_{10}$ . The copolymer composition drift for  $f'_{10}$



calculated by the Tidwell–Mortimer approach is considerable, therefore the data points produced at  $f'_{10}$  are strongly sensitive to conversion. Hence, if one wants to apply this approach, one should try controlling the conversion at  $f'_{10}$  to very low levels.

### CONCLUSIONS

The reactivity ratios of MMA/AN copolymerization system at 60°C were estimated as  $r_1 = 1.04$  and  $r_2 = 0.15$ . Also, these reactivity ratios at 100–140°C did not show a meaningful variation ( $r_1 = 1.04$ – $1.08$  and  $r_2 = 0.25$  at this temperature range). Therefore,  $r_1$  are not varying with temperature but  $r_2$  increases at higher temperatures. The Tidwell–Mortimer approach is reliable for this copolymerization system at very low conversion (preferably less than 3% for  $f'_{10}$ ), whereas handling of the samples produced by the C-D approach is much easier, which, in turn, decreases the possibility of experimental errors.

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