Macromolecules **1997,** *30,* 322−323

Determination of Reactivity Ratios for the System Methyl Methacrylate−*n*-Butyl Methacrylate

Bart G. Manders, Wilfred Smulders,
Annemieke M. Aerdts, and Alex M. van Herk*

Laboratory of Polymer Chemistry, Eindhoven Polymer Laboratories, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received September 17, 1996
Revised Manuscript Received November 14, 1996

Introduction

Copolymers based on (meth)acrylate monomers are an important ingredient in, for example, coating applications. Of these copolymers, the system methyl methacrylate (MMA)−*n*-butyl methacrylate (BMA) is interesting, as both monomers resemble each other closely. A behavior close to ideal can be expected. Nevertheless, a large scatter is found in literature concerning these reactivity ratios,[1−6] as shown in Table 1. Reasons for this scatter may be found in the use of invalid statistical methods[7] during the evaluation of the reactivity ratios as well as in performing experiments without design criteria, leading to large confidence intervals. Linearization of the copolymer composition equation will distort the error distributions associated with the data. Therefore, nonlinear least squares (NLLS) data evaluation is the only valid statistical evaluation method. A simple algorithm for NLLS data evaluation is given by Van Herk.[8] Design of copolymerization experiments was first proposed by Tidwell and Mortimer,[9] who gave a simplification of the D-optimal criterion for copolymer composition determination. The use of this Tidwell−Mortimer criterion will result in the smallest possible confidence interval for the reactivity ratios with a given number of experiments. Experiments have to be performed at two optimal feed compositions f_1' and f_1'' given by

$$f_1' \approx \frac{2}{2 + r_1} \qquad f_1'' \approx \frac{r_2}{2 + r_2}$$

Here we present the reactivity ratios for the system MMA−BMA from new data as well as a reevaluation of the literature data.

Experimental Section

The bulk polymerizations were performed at 50 °C under argon with 50 mL of reaction mixture, with continuous stirring. The monomers (MMA and BMA, both Merck, p.a.) were distilled under reduced pressure under a nitrogen atmosphere and stored at 5 °C. The concentration of α,α′-azobis(isobutyronitrile) (AIBN, Fluka Chemika, >98%) in the reaction mixture was 0.02 (mol/L). To remove oxygen, three freeze−pump−thaw cycles were performed before the start of the reaction. Samples were taken regularly and were mixed with methanol (Merck, p.a.) to check for conversion. The bulk polymerization was quenched with liquid nitrogen when polymer precipitated in the sample−methanol mixture. The reaction mixture was poured in 400 mL of methanol to precipitate the polymer. This polymer was redissolved in THF (Merck, p.a.) and again precipitated in methanol, after which it was dried at 50 °C under vacuum.

A 400 MHz spectrometer (Bruker, AM400) was used for recording ^{1}H NMR spectra at 50 °C. Deuterated chloroform (Janssen Chimika) was used as a solvent and locking agent. Spectra were obtained using a spectral width of 6024 Hz, an acquisition time of 2.7 s, a flip angle of 45° and a pulse delay of 5 s after accumulating 32 scans, using a polymer concentration of 10% (w/v).

Table 1. Literature Reactivity Ratios for the System Methyl Methacrylate (MMA)−*n*-Butyl Methacrylate (BMA)

r_{MMA}	r_{BMA}	temp (°C)	medium	ref
0.96	1.04	70	bulk	Brar and Kapur[1]
0.27	1.01	25	ethanol	Brosse *et al.*[2]
1.27	1.20	60	bulk	Musha *et al.*[3]
0.79	1.27	60	bulk/benzene	Bevington and Harris[4]
0.52	2.11	60	bulk/benzene	Greenley[5]
0.92	1.07			Borchardt[6]

Table 2. Copolymerization Data for the System Methyl Methacrylate (MMA)−*n*-Butyl Methacrylate (BMA) at 50 °C in Bulk

exp no.	f_{MMA}	F_{MMA}	exp no.	f_{MMA}	F_{MMA}
1	0.350	0.33	5	0.700	0.69
2	0.350	0.33	6	0.700	0.69
3	0.350	0.33	7	0.700	0.67
4	0.350	0.33	8	0.699	0.67

Table 3. Reactivity Ratios for the System Methyl Methacrylate (MMA)−*n*-Butyl Methacrylate (BMA) at Different Temperatures Evaluated with the Nonlinear Least Squares Method

r_{MMA}	r_{BMA}	temp (°C)	ref
0.91	1.09	50	this work
0.99	1.06	70	Brar and Kapur[1]
1.30	1.18	60	Musha *et al.*[3]
0.50	2.04	60	Bevington and Harris[4]

Results

The copolymer composition was calculated using the peak areas of the MMA $-OCH_3$ proton signal ($\delta = 3.6$ ppm)[1,10] and the BMA $-OCH_2$ proton signal ($\delta = 3.9$ ppm).[1] The fraction of MMA in the copolymer (F_{MMA}) can be determined using the following relationship:

$$F_{MMA} = \frac{2A(-OCH_3)}{2A(-OCH_3) + 3A(-OCH_2)}$$

where $A(-OCH_3)$ and $A(-OCH_2)$ stand for the total peak areas of $-OCH_3$ and $-OCH_2$, respectively. Results of the copolymerizations are summarized in Table 2. Monomer feed was chosen according to the Tidwell−Mortimer criterion and reactivity ratios from preliminary experiments ($r_{MMA} = 0.87$ and $r_{BMA} = 1.10$). The estimated error in the monomer feed composition is smaller than 1%, and the error in the copolymer composition is estimated at 5%. Gravimetrically determined conversions were below 0.5% to minimize the effect of composition drift. From these data, reactivity ratios have been determined using an NLLS fitting method.[8] The error in the feed composition is so small that we can consider it as the errorless independent variable in the NLLS method. The error-in-variables (EVM) method[11] is not used, because the construction of the confidence intervals in the EVM program is based on the χ^2 distribution, which is not valid for estimated errors, and the available EVM program[11] only gives confidence intervals with approximate shape.[12]

The resulting reactivity ratios as well as reactivity ratios reevaluated from the original literature data with the NLLS method are given in Table 3. In Figure 1 the 95% joint confidence intervals for these reactivity ratios are given. As can be seen in Figure 1, only the reevaluated data from Bevington and Harris[4] deviate

S0024-9297(96)01377-0 CCC: $14.00

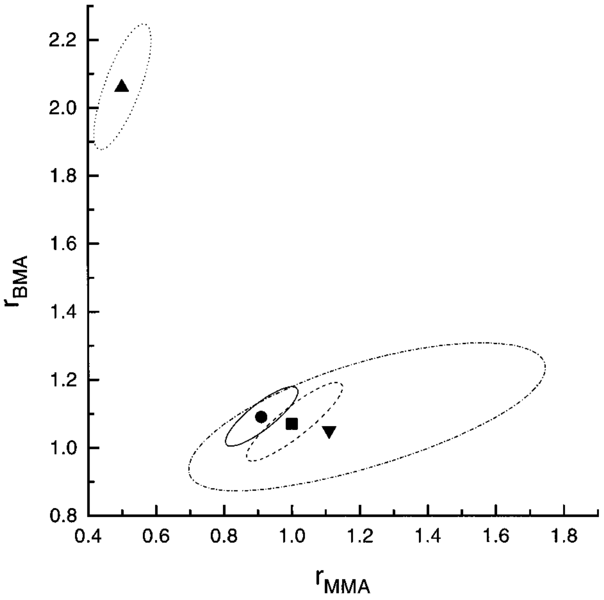

Figure 1. Reactivity ratios and 95% joint confidence intervals for the reactivity ratios for the system methyl methacrylate (MMA)−*n*-butyl methacrylate (BMA) as given in Table 3: (● and — this work; (■ and - - -) Brar;[1] (▲ and ···) Bevington;[4] (▼ and — • —) Musha.[3]

from the other values. They are close to the values presented by Greenley,[5] which result from a reevaluation of the Bevington data with a different linearization method. The reactivity ratios as given by Brosse *et al.*[2] are measured in ethanol, which is not a good solvent for the copolymer, possibly leading to the deviation of the reactivity ratios. Another cause for this deviation might be the bootstrap effect.[13] The data from Musha *et al.*[3] yield a large joint confidence interval due to the small number of data points and the used method of gas chromatographic analysis of pyrolysis products. This joint confidence interval overlaps the intervals resulting from the NMR analysis (this work and ref 1). Also, the resulting joint confidence intervals from the NMR analysis have some overlap. The joint confidence interval for the data from this work is the smallest, indicating the importance of experimental design, which will become more obvious when the reactivity ratios differ from unity.

Conclusions

The resulting reactivity ratios from designed experiments at 50 °C using nonlinear least squares data fitting are $r_{MMA} = 0.91$ and $r_{BMA} = 1.09$. These values coincide with some of the (reevaluated) literature data presented here but have a smaller joint confidence interval.

References and Notes

(1) Brar, A. S.; Kapur, G. S. *Polym. J.* **1988**, *20*, 811.
(2) Brosse, J.-C.; Gauthier, J.-M.; Lenain, J.-C. *Makromol. Chem.* **1983**, *184*, 1379.
(3) Musha, Y.; Hori, Y.; Sato, Y.; Katayama, M. *Nihon Daigaku Kogakubu Kiyo, Bunrui A* **1985**, *26*, 175.
(4) Bevington, J. C.; Harris, D. O. *J. Polym. Sci. B* **1967**, *5*, 799.
(5) Greenley, R. G. *J. Macromol. Sci.-Chem.* **1980**, *A14*, 445.
(6) Borchardt, J. K. *J. Macromol. Sci.-Chem.* **1985**, *A22*, 1717.
(7) O'Driscoll, K. F.; Reilly, P. M. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 355.
(8) Van Herk, A. M. *J. Chem. Educ.* **1995**, *72*, 138.
(9) Tidwell, P. W.; Mortimer, G. A. *J. Polym. Sci., Polym. Chem.* **1965**, *3*, 369.
(10) Aerdts, A. M.; German, A. L.; Van der Velden, G. P. M. *Magn. Reson. Chem.* **1994**, *32*, S80.
(11) Dube, M.; Amin Sanayei, R.; Penlidis, A.; O'Driscoll, K. F.; Reilly, P. M. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 703.
(12) Van Herk, A. M.; Dröge, T. Manuscript in preparation.
(13) Harwood, H. J. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 331.

MA961377L