LETTER TO THE EDITORS

REACTIVITY RATIOS FOR THE SYSTEM DEAEMA / MMA

We have studied the copolymerization of diethylaminoethyl methacrylate (DEAEMA) and methyl methacrylate (MMA) in solution (DMF) and in bulk. Reactivity ratios were calculated using a series of simultaneous equations based upon the relationship:

$$\frac{dm_1}{dm_2} = \frac{M_1}{M_2} \frac{r_1(M_1 + M_2)}{r_2(M_2 + M_1)}$$

where m_1 and m_2 are the moles of monomer in the final polymer and M_1 and M_2 are the original monomer compositions; r_1 and r_2 are the dimensionless reactivity constants (reactivity ratios). Knowing the relative compositions of the monomer mixture and the final composition of the polymer, a system of simultaneous equations can be solved which yields values for r_1 and r_2.

MATERIALS AND EXPERIMENTAL

The DEAEMA and MMA monomers were distilled to remove polymerization inhibitors and any oligomers present and then copolymerized using the following molar ratios of starting monomers: 20/80 DEAEMA/MMA, 30/70 DEAEMA/MMA, 50/50 DEAEMA/MMA, 70/30 DEAEMA/MMA, and 90/10 DEAEMA/MMA. Each copolymer was prepared by using a total of 0.757 mol of monomer (Exception, the 20/80 copolymer was prepared by using 0.605 mol of distilled monomer). The monomers were added to a flask containing 400 mL of distilled-in-glass dimethyl formamide (DMF) as a solvent. The flask, previously purged with nitrogen, was placed in a heating mantle and continuously flushed with nitrogen throughout the reaction. The temperature was slowly raised to 75°C, 0.2% AIBN initiator (based on monomer) added (t = 0), and the polymerization carried out within the isokinetic range. The reaction mixture was allowed to cool and was precipitated into either distilled water or a water/methanol mixture. The polymers were redissolved in THF (tetrahydrofuran) and collected by dripping the polymer solvent mixture from a separatory funnel into a 40-liter vessel of distilled water/methanol. The drip rate was approximately 2 drops/s, slow enough to insure good washing of remaining monomer away from the polymer as it precipitated. The polymer was then collected by gravity filtration through a lint-free cloth, and was vacuum dried at 30°C for 48 hours.

The bulk polymers were prepared in sealed vials at 50°C using selected monomer molar ratios. Polymer recovery was similar to that described above. The conversion of monomer to polymer was monitored by removing aliquots of samples of the reaction mixture at specific time intervals; the polymer was recovered as described and weighed and the weight percent of monomer consumption recorded as a function of time of reaction. Specific samples from the time series and the final polymer were analyzed for DEAEMA or MMA content by elemental analysis, Kjeldahl analysis, NMR (nuclear magnetic resonance) and FTIR (Fourier transform infrared). The final polymers exhibited M_w's in the range 3.5–4.5 × 10^4 and M_n's of 2.8–3.0 × 10^4. The polydispersity of these polymers was lower than anticipated.

RESULTS AND DISCUSSION

Using elemental and Kjeldahl analysis, the percent DEAEMA in the copolymer was computed based upon the amount of nitrogen in each sample. The percents of DEAEMA and MMA were determined by NMR, by taking a ratio of the DEAEMA quartet at 2.6 ppm over the MMA methoxy singlet at 3.6 ppm. This ratio was plotted against the respective original monomer concentration of DEAEMA, and the copolymer composition was determined from the best-fit curve. The FTIR data were analyed by taking a ratio of the absorbances at 1090 ove 2810
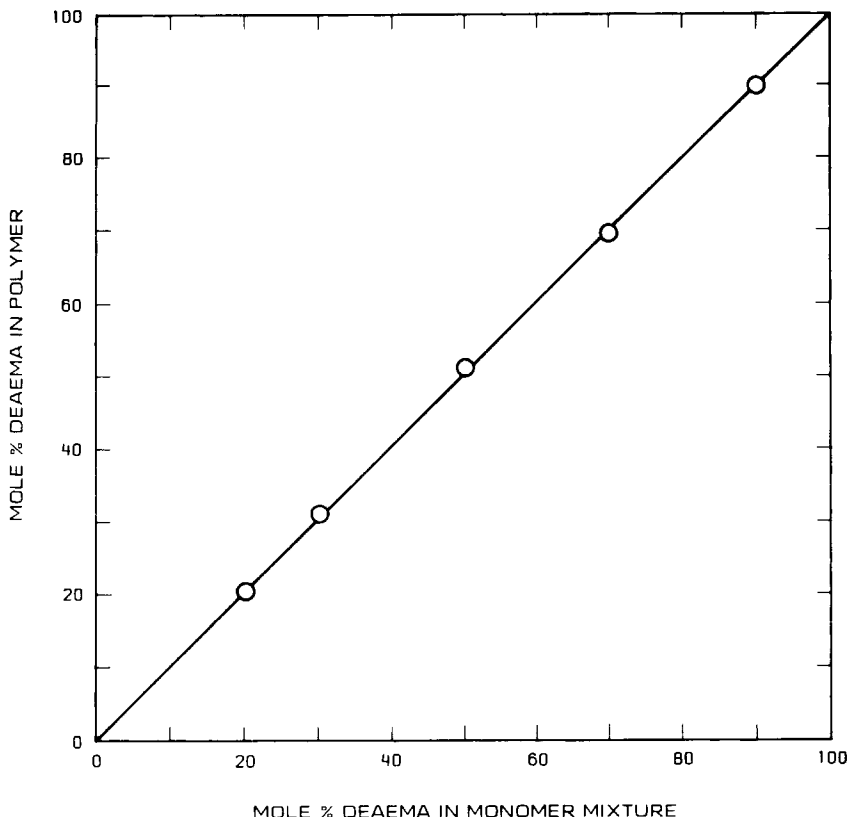
Fig. 1. Mole % DEAEMA in Copolymer vs. mole % DEAEMA in monomer mixture (elemental analysis).

nanometers and treating the data as with the NMR data. From this data, and the known initial monomer ratios, the corresponding reactivity ratios for the polymer were calculated.

Figure 1 plots the mole percent DEAEMA in the monomer mixture versus the mole percent DEAEMA in the copolymer as obtained by elemental analysis. Clearly the relationship is linear, and indicates a reactivity ratio of essentially 1:1. Basedon the solution of ten simultaneous equation pairs, r_1(DEAEMA) was computed to be 0.94 ± 0.12 and r_2(MMA) was computed to be 0.99 ± 0.12.

Figure 2 plots mole percent DEAEMA in the monomer mixture versus the mole percent DEAEMA in the copolymer as obtained by NMR. These values correlate well with the elemental analysis and demonstrate a linear relationship. Based on the solution of the simultaneous equation pairs for the NMR data, r_1(DEAEMA) was computed to be 0.85 ± 0.28 and r_2(MMA) was computed to be 0.97 ± 0.15.

An attempt was made to compute reactivity ratios based upon FTIR spectra. Due to uncertainties in the base line location and therefore the peak area, interpretation of these spectra was difficult. Using estimated peak heights from the various spectra and solving the simultaneous equation pairs r_1(DEAEMA) was computed to be 1.84 ± 0.40 and r_2 (MMA) was 1.65 ± 0.19. The infrared data obtained are deemed less reliable than the other methods. The results are included here for purposes of information and comparison.

We subjected our elemental analysis results to data treatment as suggested by Finemann and Ross,[1] and Kelen and Tudos.[2] A comparison of the different data treatments are included in Table I. A plot representing the Finemann and Ross method of data treatment is included as Figure 3.
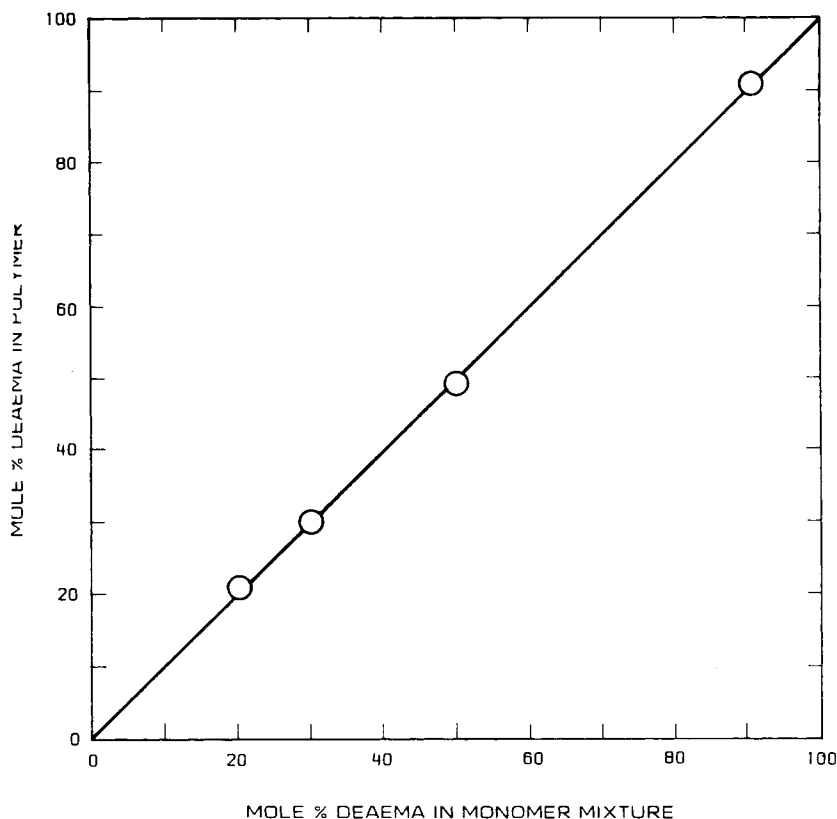
Fig. 2. Mole % DEAEMA in copolymer vs. mole % DEAEMA in monomer mixture (NMR).

We were unsuccessful in our initial efforts to apply the 'Error-In-Variable' method proposed by Chee and Ng.[3] The method has merit and we intend to pursue its applications with those authors.

The only reference of which we are aware that relates copolymerization of DEAEMA with MMA was reported by Tanabe and Nakano.[4] They performed bulk polymerizations of DEAEMA with a series of vinyl monomers including methyl methacrylate and ethyl methacrylate. Values for r_1 and r_2 of 1 (unity) for both methyl methacrylate and ethyl methacrylate were obtained by the Finemann and Ross method. No standard deviations were reported. We also made a limited series of bulk polymerized copolymers of DEAEMA/MMA and analyzed these materials for

TABLE I
Summary of Reactivity Ratios Values for Three Methods

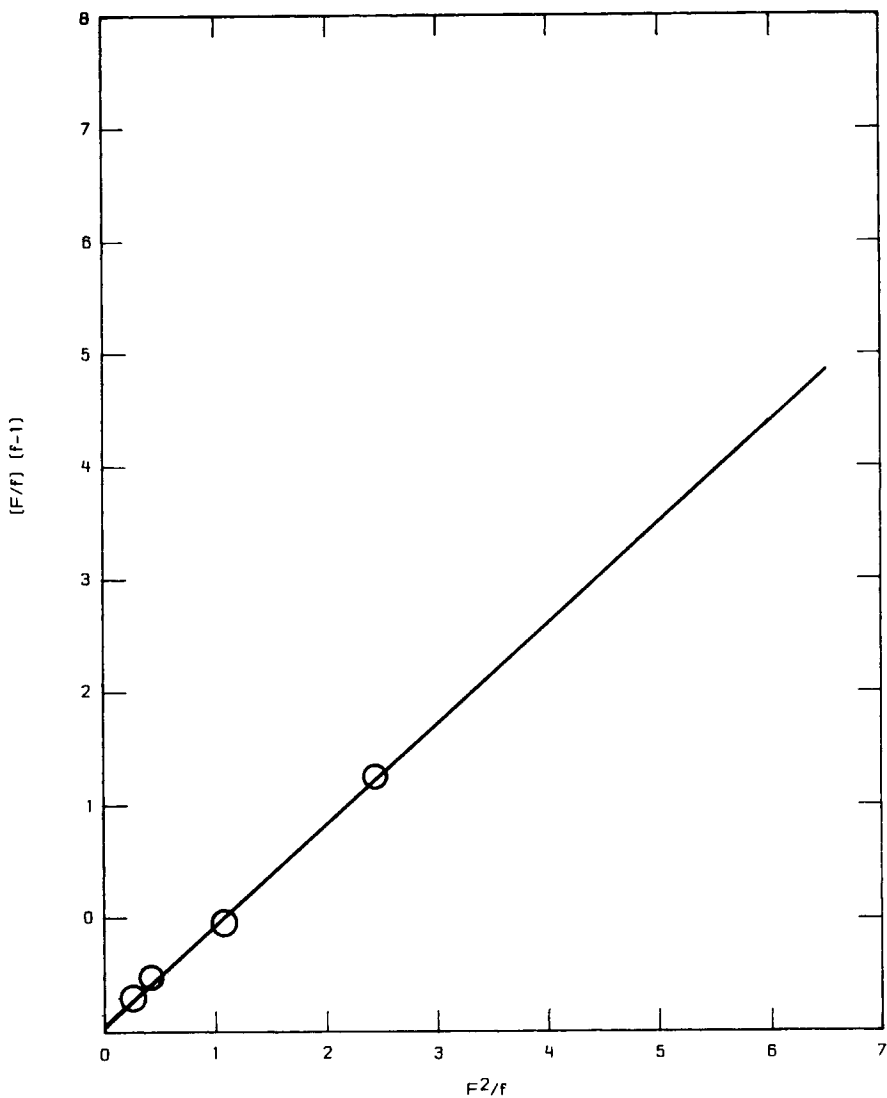| Data source	Method	DEAEMA	MMA
Elemental analysis			
	Simultaneous equation pairs	0.94 ± .12	0.99 ± .12
	Finemann and Ross	0.93	0.92
	Kelen and Tudos (alpha = 1.486)	1.09	0.97
NMR			
	Simultaneous equation pairs	0.85 ± .28	0.97 ± .15
FTIR			
	Simultaneous equation pairs	1.84 ± .40	1.65 ± .19

Fig. 3. Finemann and Ross linear method for determining monomer reactivity ratios in copolymerization.

TABLE II
% Nitrogen for Bulk Polymerized Copolymers

	% Conversion	% N(Kjeldahl)	%N Theoretical for $r_1 = r_2 = 1$
30/70 (bulk)	13	3.38, 3.16	3.34
50/50 (bulk)	10	4.86, 4.89	4.90
70/30 (bulk)	15	6.08, 5.94	6.13
70/30	84	5.93, 6.02	6.13
70/30 (solution)	12	6.11, 6.02	6.13
70/30 (solution)	28	6.10, 6.04	6.13

nitrogen via Kjeldahl's method. Several solution polymers were also analyzed for comparison. The results are shown in Table II.

The values for percent nitrogen for the bulk copolymers are in reasonable agreement with the reactivity ratio of one reported here and by Tanabe and Nakano. The values for percent nitrogen for the 70/30 solution copolymers are consistent with the values obtained from elemental analysis for our copolymers, within the isokinetic range.

In view of the results by Tanabe and Nakano and those reported here, we conclude that the values for r_1 and r_2 for the copolymerization of DEAEMA/MMA are essentially unity for both solution and bulk polymerization.

References

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3. K. K. Chee and S. C. Ng, *Macromolecules*, **19**, 2779–2787 (1984).
4. H. Tanabe and K. Nakano, *Yakozaigaka*, **22**, 193–196 (1982).

S. J. MIRAGLIA
K. G. MAYHAN

Baxter Technology & Ventures
Biomaterials Technology Group
Irvine, California