

Recalculation of the Monomer Reactivity and Experimental Differences in Emulsion and Microemulsion Copolymerizations of Partially Water-Soluble Monomers

Sumit Bhawal, Surekha Devi

Department of Chemistry, Faculty of Science, Maharaja Sayajirao University of Baroda, Baroda, 390002, India

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ABSTRACT: On the basis of the copolymerization data for the emulsion and microemulsion polymerizations of ethyl acrylate and methyl methacrylate, the monomer concentrations at the copolymerization loci were calculated, with the assumption that the sum of their concentrations at the polymerization loci was equal to unity. The equivalency of the locus and feed concentrations, as for styrene, was invalid because of the partial water solubility of both the monomers. Consequently, the locus concentration rather than the initial feed concentration was used to recalculate the monomer reactivity at the actual site of polymerization, and this was called the true reactivity ratio. The apparent reactivity ratios

for emulsion and bulk polymerizations were different, whereas those for microemulsion and bulk polymerizations were similar. This difference was attributed to the mode of polymerization in the emulsions and microemulsions, leading to different copolymer compositions for similar initial feed concentrations. This was verified experimentally from the thermal properties and particle size distribution measurements. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2802–2810, 2002

Key words: emulsion polymerization; copolymerization; particle size distribution

INTRODUCTION

The copolymerization of hydrophobic monomers such as styrene/butylacrylate has been studied in microemulsion media.¹ Because polymerization takes place in microemulsified droplets, the very slight solubility of these monomers in aqueous media should result in the microemulsion reactivity resembling the bulk value. However, the reported reactivity ratios calculated from initial feed concentrations are different from the bulk value.^{1–3} Also, in the copolymerization of hydrophobic styrene with a hydrophilic counterpart such as methyl acrylate, methyl methacrylate (MMA), or acrylonitrile in microemulsions,^{1–3} the microemulsion reactivity ratios calculated with the initial feed values as the monomer concentration were significantly different from the bulk values. However, it was reported that re-evaluating the reactivity of styrene/MMA in microemulsions by the nonlinear least-squares (NLLS) error-in-variable method and taking conversion into account led to an insignificant difference in bulk and microemulsion reactivities.⁴ It was also argued that the partitioning of MMA in the aqueous phase led to the styrene concentration at the poly-

merization loci being different than the initial feed concentration. Therefore, the assumption made in earlier reports^{1–3} regarding the equivalency of locus and feed concentrations for styrene with the partition coefficient approach also led to the equivalency of locus and feed concentrations of the other monomer or to their sum at the polymerization site becoming less than unity. We, therefore, calculated the individual monomer concentrations at the polymerization loci from the ratio of the monomer concentrations at the polymerization loci, which were calculated from initial feed and partition coefficients of the monomers under the assumption that the sum of the monomer concentrations at the polymerization loci was equal to unity. In addition, the equivalency of the locus and feed concentrations, as for styrene, led to the determination of the monomer concentrations at polymerization loci for partially water-soluble monomers such as ethyl acrylate (EA) and MMA, which is impossible with the partition coefficient approach. Reactivity ratios were subsequently recalculated on the basis of the monomer concentrations at the actual sites of propagation, the polymerization loci, rather than the initial feed concentrations, and were termed the true reactivity ratios.

Also, very little information is available on the copolymerization of two partially water-soluble monomers such as EA and MMA. Capek and Tuan⁵ reported the kinetics of the emulsion copolymerization of EA/MMA and argued that initiation took place in

Correspondence to: S. Devi (surekha_devi@yahoo.com).

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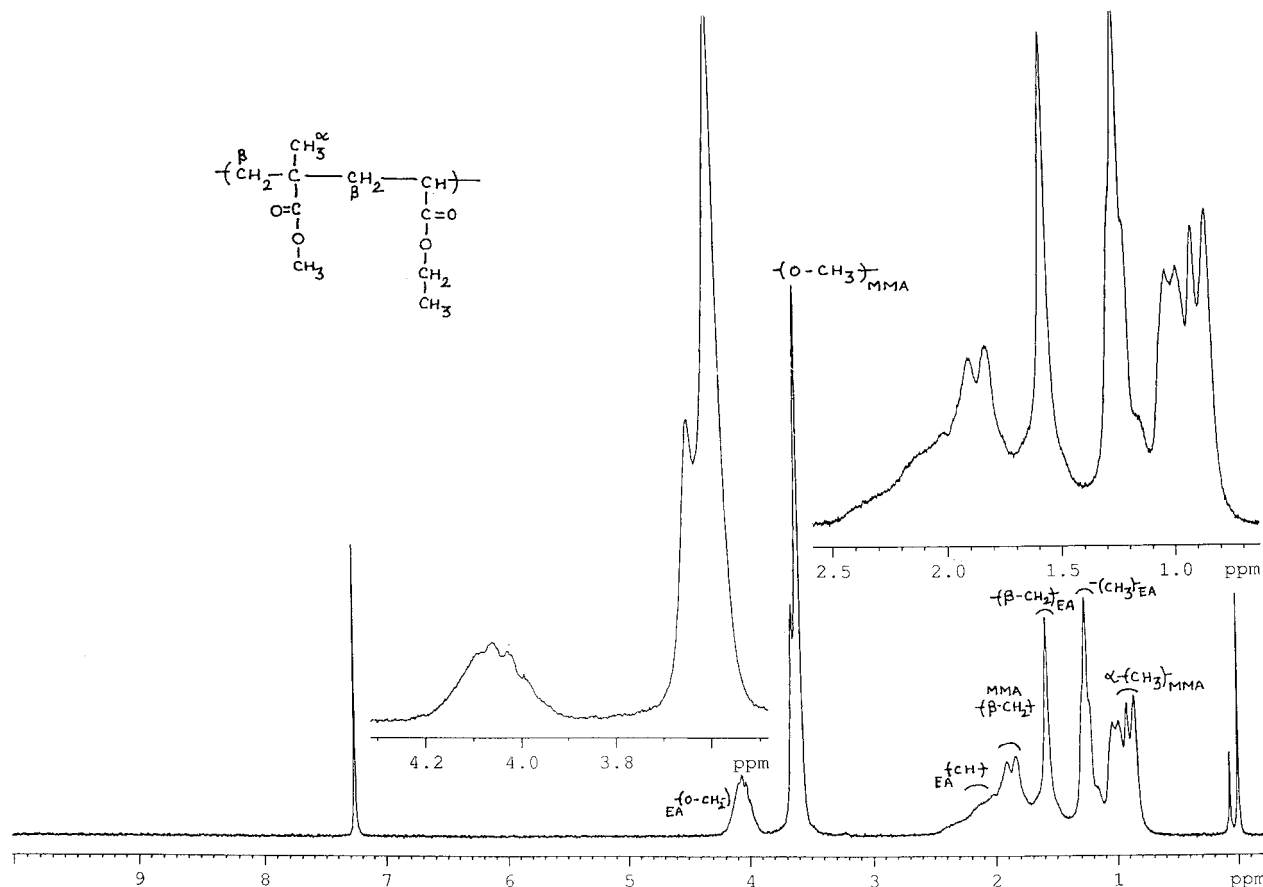


Figure 1 $^1\text{H-NMR}$ spectra of the EA/MMA copolymer produced by microemulsion copolymerization. The molar fraction of MMA in the feed was 0.25, and that in the copolymer was 0.49.

both the monomer-swollen micelles and aqueous phase. However, in microemulsion polymerization, the monomer droplets stabilized by surfactants are the principle loci for polymerization. This difference in the mechanism of polymerization is assumed to influence the thermal properties, particle size distribution, and copolymer composition (for similar initial feed concentrations) for polymers synthesized through emulsions and microemulsions. In this article, we also attempted to correlate these differences in properties with the polymerization mechanism.

EXPERIMENTAL

Materials

EA and MMA from National Chemicals (Baroda, India) were passed through an alumina column, distilled under vacuum, and stored at 4°C until further use. Potassium persulfate (KPS) from Sisco Chemicals (Mumbai, India) was recrystallized from water. Sodium dodecylsulfate (SDS) from S.D. Fine (Baroda, India) was used without further purification.

Emulsion copolymerization

The polymerization of an emulsion consisting of a 25-g monomer mixture, 0.5 g of SDS, and 75 g of water was carried out in a three-necked reaction vessel equipped with a mechanical stirrer, a nitrogen inlet, and a condenser. The reaction mass was purged with nitrogen for 15 min. The reactions were carried out at 70°C with 0.37 mM KPS. The copolymers were precipitated immediately with a fivefold excess quantity of methanol and were washed with water several times. For the complete removal of the emulsifier, the copolymers were dissolved in acetone and reprecipitated in water.

Microemulsion copolymerization

The mixed monomers (10 g) were emulsified with 75 g of an aqueous solution containing 15 g of SDS. Then, the microemulsions were polymerized and processed in the same way as the emulsion polymerization. The total conversion was kept lower than 6% in all cases.

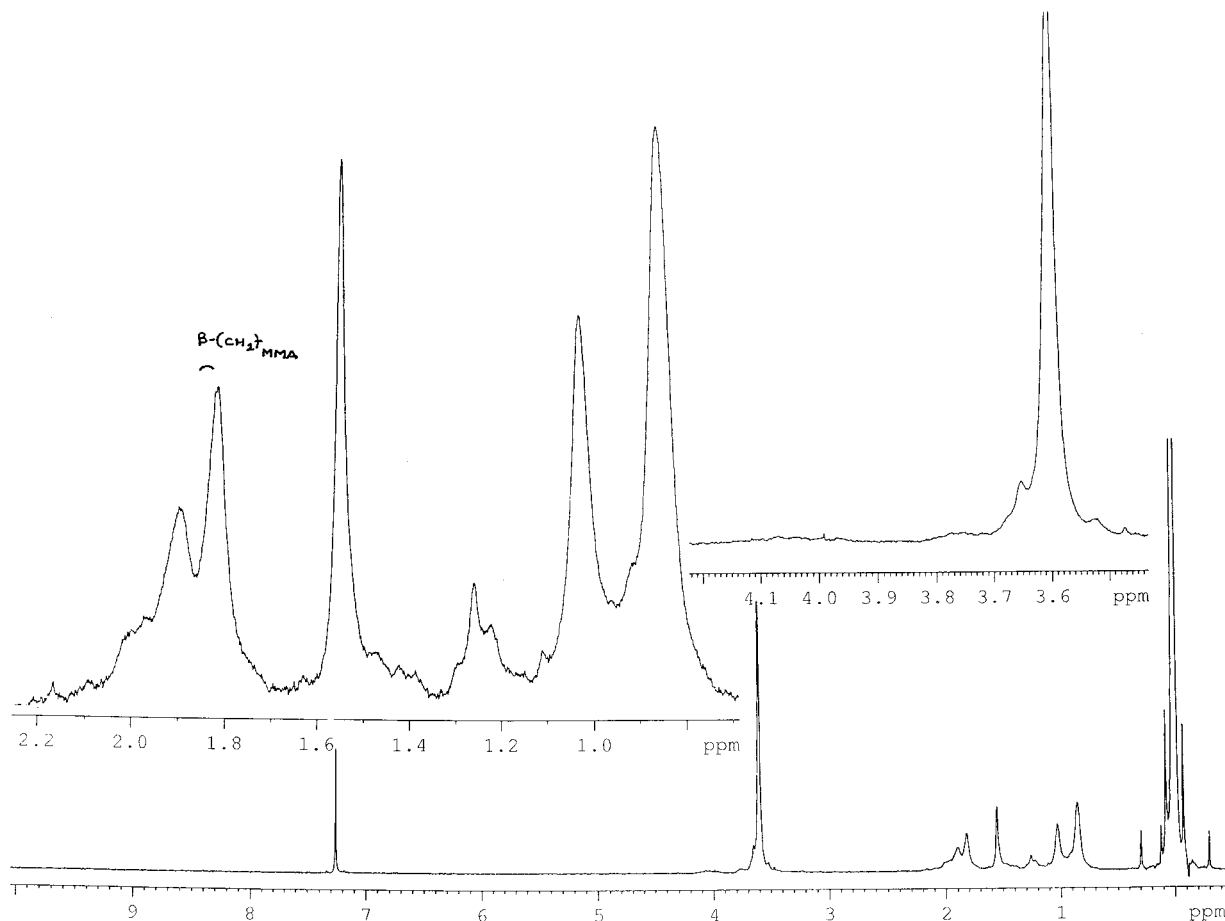


Figure 2 $^1\text{H-NMR}$ spectra of the EA/MMA copolymer produced by microemulsion copolymerization. The molar fraction of MMA in the feed was 0.9, and that in the copolymer was 0.95.

Characterization

The composition of the copolymer was determined from $^1\text{H-NMR}$ spectra recorded on a 200-MHz Bruker DPX 200 instrument (Germany) with tetramethylsilane as an internal reference and a 2% w/v sample solution in CDCl_3 . A differential scanning calorimetry (DSC) analysis was carried out on a Universal V.2. 6D TA at a heating rate of $10^\circ\text{C min}^{-1}$.

Particle size measurements

The size of the polymerized emulsion and microemulsion latexes was measured by dynamic light scattering with a Brookhaven B I 90 particle size analyzer (New York), which had a 5-mW helium-neon laser (623.8-nm wavelength), at room temperature. Before the analysis, the latexes were diluted with distilled and deionized water to minimize the particle-particle

TABLE I
Composition of EA/MMA Copolymers Synthesized in Bulk, Emulsion, and Microemulsion

Feed concentration		Emulsion		Microemulsion		Bulk	
f_{EA}	f_{MMA}	F_{EA}	F_{MMA}	F_{EA}	F_{MMA}	F_{EA}	F_{MMA}
0.9	0.1	0.814	0.185	0.729	0.27	0.72	0.27
0.75	0.25	0.583	0.416	0.52	0.479	0.51	0.49
0.66	0.33	0.478	0.521	0.384	0.615	0.42	0.57
0.5	0.5	0.348	0.651	0.3	0.699	0.30	0.7
0.25	0.75	0.187	0.812	0.136	0.863	0.13	0.86
0.1	0.9	0.102	0.897	0.051	0.948	0.05	0.94

F_{EA} = EA fraction in the copolymer synthesized through emulsion and microemulsion polymerization.

TABLE II
Composition of EA/MMA in Feed and Copolymerization Loci

Emulsion							
f_{EA}	0.9	0.75	0.66	0.5	0.25	0.10	
f_{MMA}	0.1	0.25	0.33	0.5	0.75	0.90	
f'_{EA}	0.929	0.815	0.746	0.595	0.329	0.140	
f'_{MMA}	0.070	0.184	0.253	0.404	0.670	0.859	
f'_{EA}/f_{EA}	1.032	1.086	1.130	1.19	1.316	1.40	
f'_{MMA}/f_{MMA}	0.70	0.736	0.766	0.808	0.893	0.954	
Microemulsion							
f'_{EA}	0.899	0.749	0.665	0.498	0.249	0.099	
f'_{MMA}	1.0	1.0	1.012	1.002	1.00	1.00	
f'_{EA}/f_{EA}	0.998	0.998	1.007	0.996	0.996	0.990	
f'_{MMA}/f_{MMA}	1.00	1.00	1.012	1.002	1.00	1.00	

interactions until the volume fractions of the particles were 0.01–0.1. Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate.

RESULTS AND DISCUSSION

Both MMA and EA are partially soluble in water. Their solubilities have been reported to be 1.56 and 1.8%, respectively, at 25°C.⁶ Figure 1 shows the typical NMR spectrum of an EA/MMA copolymer. The signals for the methyl protons of the O—CH₃ group from MMA appeared around 3.6 ppm, and those for protons of the O—CH₂ group from EA appeared around 4.07 ppm. The MMA molar fraction (F_{MMA}) in the copolymer was calculated from the area under the peak for the protons of the O—CH₃ group from MMA and from the peak area of O—CH₂ protons from EA in the same way as reported for bulk polymerization by Grassie et al.⁷ with the following relation:

$$F_{MMA} = 2 \times A_{MMA} / 2 \times A_{MMA} + 3 \times A_{EA} \quad (1)$$

The NMR spectrum in Figure 2 shows the configurational effect due to the splitting of the β -methylene protons of MMA in the EA/MMA copolymer synthesized through a microemulsion. The compositions of the EA and MMA in the copolymers synthesized by

emulsion, microemulsion, and bulk polymerizations under similar feed ratios and calculated with eq 1 are given in Table I. From these results, the reactivity ratios were calculated with the Finemann–Ross,⁸ Kelen–Tudos,⁹ and NLLS error-in-variable¹⁰ methods. The concentrations of the monomers in the feed and at the copolymerization loci are given in Table II and were used for the calculation of the apparent and true reactivities, respectively, of the monomers in emulsions and microemulsions. The results, shown in Table III and Figure 3, indicate insignificant differences in the true reactivity ratios for the emulsion, microemulsion, and bulk polymerizations. The apparent reactivity ratios are quite different for the bulk and emulsion. However, they are similar for the bulk and microemulsion. The only possible reason for the difference in the apparent reactivity ratios in the bulk, emulsion, and microemulsion is the difference in the monomer concentration at the polymerization loci, which results in different monomer fractions in the copolymers synthesized through emulsions and microemulsions of identical feed compositions in comparison to the bulk. There are two approaches to predicting the monomer fractions in copolymerization loci. One is Maxwell et al.'s¹¹ semiempirical approach, which considers the partitioning of monomers between different phases in emulsion polymerizations. They developed a simple

TABLE III
Reactivity Ratio of EA/MMA with Various Methods for Emulsion and Microemulsion Copolymerization

Method	Bulk (from ref. 7.)			Emulsion (this work)			Microemulsion (this work)		
	r_{EA}	r_{MMA}	$r_{EA} \times r_{MMA}$	r_{EA}	r_{MMA}	$r_{EA} \times r_{MMA}$	r_{EA}	r_{MMA}	$r_{EA} \times r_{MMA}$
Mayo–Lewis	0.24	2.03	0.48	—	—	—	—	—	—
FR (apparent)				0.44	1.55	0.68	0.26	2.0	0.52
KT (apparent)				0.37	1.41	0.52	0.26	2.02	0.52
NLLS (apparent)				0.37	1.44	0.53	0.25	2.12	0.53
FR (true)				0.30	2.28	0.68	0.26	2.10	0.54
NLLS (true)				0.25	2.13	0.53	0.25	2.11	0.52

FR = Finemann–Ross method; KT = Kelen–Tudos method.

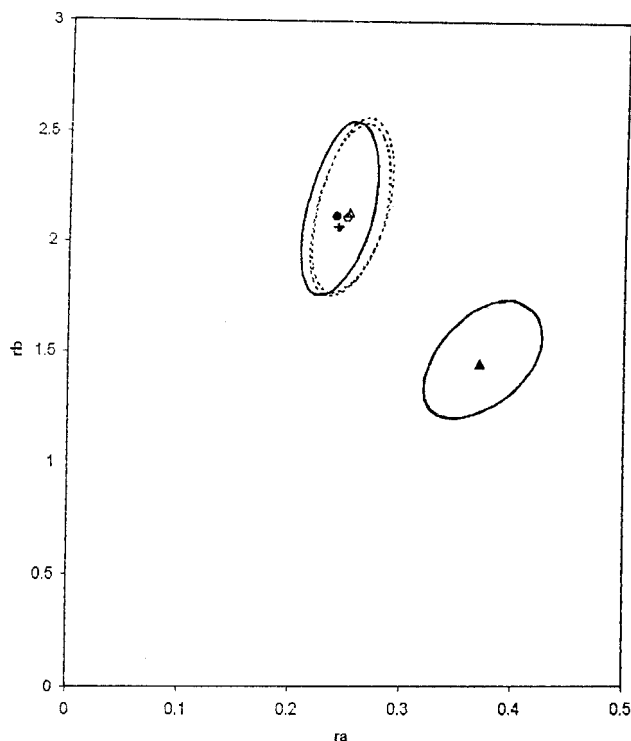


Figure 3 Joint confidence (95%) curves by error in variable method (EVM) based on the monomer concentration (—) in the feed and (···) in the loci. Reactivity ratios are shown based on the monomer concentration in the feed for the EA/MMA (●) microemulsions and (△) emulsions, based on the monomer concentration in loci for EA/MMA (○) microemulsions and (△) emulsions, and in bulk for (+) EA/MMA (r_a = reactivity ratio of EA and r_b = reactivity ratio of MMA).

relationship for the partial swelling of two monomers with limited water solubility to predict the monomer concentrations and fractions within the different phases. The results obtained through their relations agreed well with experimental values. Besides Maxwell et al.'s approach, an approach based on constant partitioning was also adopted. Asua et al.¹² found no obvious difference between Maxwell et al.'s approach and the partition coefficient approach for the determination of the monomer concentration at the polymerization loci for emulsion polymerization. Therefore,

we adopted the partition coefficient approach,¹² in which the monomer reactivities r_{EA} and r_{MMA} from emulsion/microemulsion copolymerizations determined by the NLLS error-in-variable method can be related to those from the bulk copolymerization as follows:

$$r_{EA} = kr'_{EA} \quad (2)$$

$$r_{MMA} = r'_{MMA}/k \quad (3)$$

$$f'_{EA}/f'_{MMA} = k(f_{EA}/f_{MMA}) \quad (4)$$

where r'_{EA} and r'_{MMA} are the reactivities from bulk copolymerization. f_{EA}/f_{MMA} and f'_{EA}/f'_{MMA} are the ratios of the monomer concentrations in the feed and at the loci, respectively. When EA was copolymerized with MMA in both emulsions and microemulsions, the average value of the partition coefficient (k) was taken because of the close solubilities of the two monomers. The partition coefficient values were observed to be 1.47 for emulsion copolymerization and 0.995 for microemulsion copolymerization. The variation in the k values in emulsions and microemulsions arose because of the variation in the mechanism of initiation that led to the monomer concentration drift. Because both monomers are partially soluble in water, the assumption that $f'_{sty} = f_{sty}$, as for a hydrophobic monomer such as styrene, is not valid. Moreover, the correctness of the assumption even for styrene was questioned by Klumperman and Aerdts⁴ for the microemulsion copolymerization of styrene/MMA.² It was argued that if the fraction of styrene at the site of propagation equaled the feed, it would lead to either $f'_{MMA} = f_{MMA}$ or a sum of the fractions at the polymerization loci less than unity. We, therefore, calculated the monomer concentration at the polymerization loci, with $f'_{EA} + f'_{MMA} = 1$ and from the ratio of f'_{EA}/f'_{MMA} calculated with the partition coefficient approach, as in eq 4. The reactivity ratios for bulk, emulsion, and microemulsion polymerizations are given in Table III. The reactivity ratio, being the ratio of the rate constants of homopolymerization to those of copoly-

TABLE IV
Prediction of Copolymer Composition with the Terminal Model (TM)

Feed		Emulsion				Microemulsion			
f_{EA}	f_{MMA}	Experimental		Theoretical (TM)		Experimental		Theoretical (TM)	
		F_{EA}	F_{MMA}	F_{EA}	F_{MMA}	F_{EA}	F_{MMA}	F_{EA}	F_{MMA}
0.9	0.1	0.81	0.19	0.79	0.21	0.73	0.27	0.72	0.28
0.75	0.25	0.58	0.42	0.59	0.41	0.52	0.48	0.51	0.49
0.66	0.33	0.48	0.52	0.50	0.50	0.39	0.61	0.42	0.58
0.50	0.50	0.35	0.65	0.35	0.65	0.30	0.70	0.29	0.71
0.25	0.75	0.18	0.82	0.18	0.82	0.13	0.87	0.13	0.87
0.10	0.90	0.10	0.90	0.93	0.07	0.05	0.95	0.05	0.95

F_{EA} = EA fraction in the copolymer synthesized through emulsion and microemulsion polymerization.

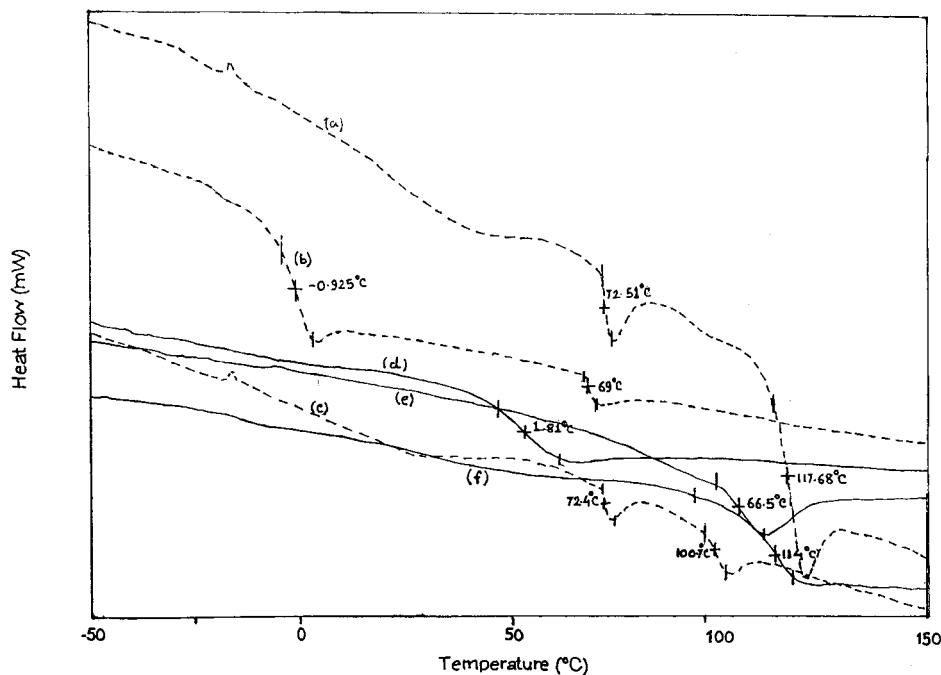


Figure 4 DSC thermograms of the EA/MMA copolymers synthesized through (---) emulsions and (—) microemulsions for three different compositions: (a) 0.1/0.9, (b) 0.9/0.1, and (c) 0.25/0.75 EA/MMA for emulsions and (d) 0.9/0.1, (e) 0.5/0.5, and (f) 0.1/0.9 EA/MMA for microemulsions.

merization, is sensitive to the local monomer concentration at the site of propagation, that is, the polymerization loci. The reactivity ratios were recalculated on the basis of the concentration in the loci rather than in the feed to determine the reactivity ratio at the actual site of propagation, and this was termed the true reactivity ratio. The monomer fraction in the copolymer determined experimentally agrees well with that obtained theoretically with the terminal model¹⁰ and with the application of the true reactivity ratios determined by the NLLS error-in-variable method and the monomer fraction at the copolymerization loci (Table IV). In this study, we observed a significant difference in the true and apparent reactivity ratios for the emulsion copolymerization of EA/MMA, whereas this difference was insignificant for the microemulsion polymerization. This difference in the true and apparent reactivity ratios in the emulsion polymerization can be attributed to the greater concentration of EA at the polymerization loci than in the feed (Table II). The EA fraction in the copolymer synthesized in an emulsion was also observed to be higher than the polymer synthesized through bulk and microemulsion polymerizations for similar initial feed ratios. The copolymers synthesized through emulsion polymerizations showed two glass-transition temperatures (T_g 's; Fig. 4), whereas those synthesized by microemulsion polymerizations showed a single T_g (Fig. 4) for the same feed ratio. This shows that in emulsion polymerizations, two possible mechanisms exist. The polymer obtained by aqueous-phase polymerization (homoge-

neous nucleation) had a greater fraction of the relatively more water-soluble EA, which contributed to the lower T_g . However, the copolymer obtained by micellar polymerization was rich in MMA, which contributed to the higher T_g . The difference was apparent because of the large difference in the T_g 's of the homopolymers (EA, -24°C ; MMA, $+105^\circ\text{C}$).⁶ However, we observed T_g 's of 114 and 117°C for the microemulsion- and emulsion-based copolymers, respectively, synthesized from feed compositions rich in MMA (0.9 MMA/0.1 EA). This might indicate a greater contribution due to the syndiotactic mode of addition of the monomer units in the copolymer, as reported by Wittmann and Kovacs¹³ from the triad analysis of poly(methyl methacrylate) (PMMA). For a copolymer, in addition to the configurational information, the effect of the compositional triads is also important. The possibility of an MMM triad sequence for MMA is expected to be greater than 90% when MMA in the feed is 0.9 because of the greater reactivity of MMA. Figure 2 shows the expected singlet due to the syndiotactic resonance of the β -methylene protons appearing around $\delta = 1.8\text{--}2.0$, although it was broadened and complicated by the residual isotactic resonance for the microemulsion copolymerization of EA/MMA. Similar splitting patterns for β -methylene protons were observed for emulsion systems. Roy and Devi¹⁴ also reported a syndiotactic mode of addition for pure PMMA synthesized in emulsions. The nature of these multiplets for β -methylene protons has been reported to be an absolute measure of the polymer's predomi-

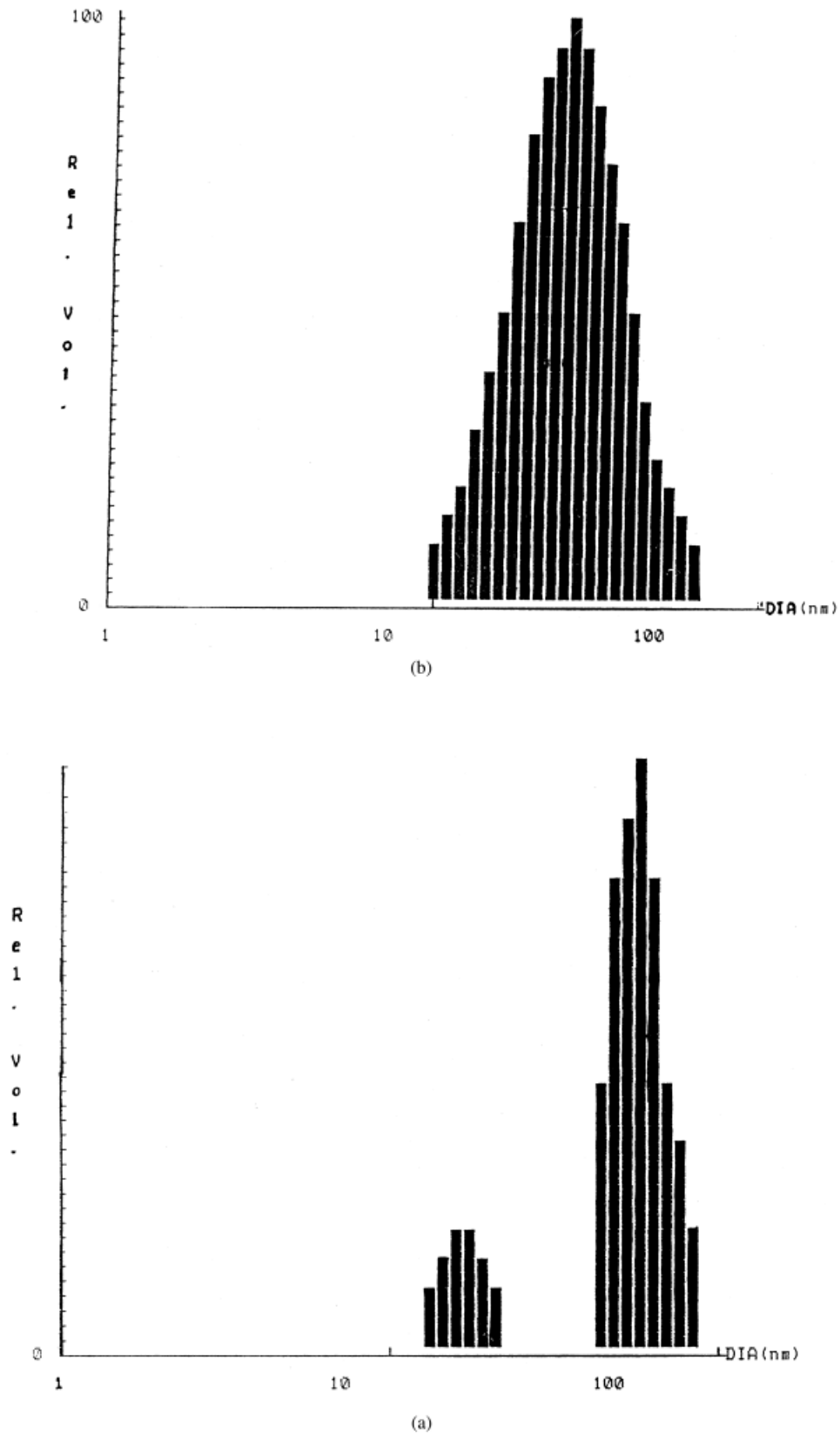


Figure 5 Particle size distribution of the copolymers synthesized through (a) emulsions and (b) microemulsion.

nant configuration.¹⁵ In addition, light scattering experiments for medium-conversion samples showed two distinct particle size distributions for emulsion systems, whereas microemulsion polymerizations show a single particle size distribution plot (Fig. 5) with mean diameters of 52 and 33 nm, respectively. This also indicates simultaneous particle formation by two different nucleation mechanisms for emulsion systems, whereas there is only a single nucleation mechanism for microemulsion polymerizations of EA/MMA. These results show that in emulsion polymerizations, the degree of aqueous-phase polymerization is higher than that in microemulsion polymerizations. However, an increase in the f'_{EA}/f_{EA} ratio with a decrease in the feed concentration of EA and a simultaneous increase in the f'_{MMA}/f_{MMA} ratio with an increase in the feed concentration of MMA mean that the principle loci of polymerization have a smaller concentration of the relatively more hydrophilic monomer EA and, therefore, a greater concentration of the relatively more hydrophobic monomer MMA. The principle loci of polymerization are, therefore, expected to be monomer-swollen micelles rather than the aqueous phase for emulsion polymerizations involving partially water-soluble monomers. In fact, Capek and Tuan⁵ reported the kinetics of emulsion copolymerizations of EA/MMA and argued that initiation took place in both the micelles and aqueous phase.

Unlike for emulsion polymerizations, we observed a single T_g for the copolymers synthesized by microemulsion polymerizations. This indicated a single copolymerization locus. It is well established that microemulsion polymerizations predominantly takes place in microemulsified droplets.^{16,17} The observed negligible difference in the locus and feed concentrations of monomers in microemulsions resulted in the true reactivity ratio matching the apparent value (Table III). Because of the close solubility and polarity of the monomers, there should not be any preferential site of polymerization within a droplet. The negligible internal partitioning of the monomers is also indicated by the constancy of f'_{MMA}/f_{MMA} and f'_{EA}/f_{EA} values. Therefore, homogeneous polymerization in the droplet should be equivalent to a compartmentalized bulk system. The true reactivity ratio in microemulsions, therefore, matches the bulk values (Table II). These arguments are supported by the matching of the monomer fraction in the copolymer synthesized through microemulsions and in the bulk (Table I). This results in the superimposition of copolymer composition plots for the microemulsion and bulk (Fig. 6). The 95% joint confidence curves for emulsions and microemulsions or bulk systems show considerable differences in the values, regardless of the similarity in the solubilities of EA and MMA in water, as shown in Figure 3. The difference arises because of the higher degree of polymerization in the aqueous phase, lead-

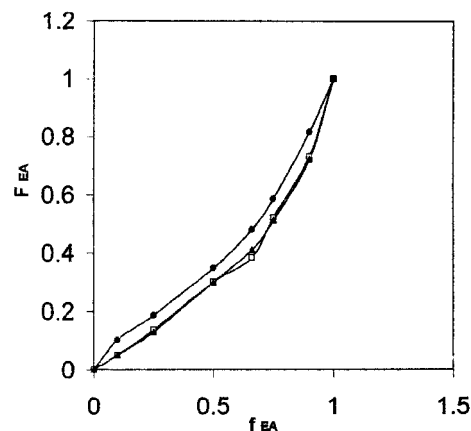


Figure 6 Effect of the monomer feed on the copolymer composition: (●) emulsion, (■) microemulsion, and (△) bulk.

ing to a different copolymer composition than that in the bulk or microemulsion, whereas the true reactivity ratio matches the bulk values for both emulsions and microemulsions. This implies that the multiplication of the initial feed ratio with a suitable constant, that is, the partition coefficient (which includes the effect of the partitioning of both monomers), gives the monomer concentration corresponding to the copolymer obtained, as for bulk polymerization, in which the initial feed corresponds closely to the copolymer composition at very low conversions. Moreover, the close values of the true reactivity ratios in the emulsions, microemulsions, and bulk, especially for the EA/MMA system, are expected because of the very small difference in the comonomer concentrations in both the aqueous phase and micelles due to the close aqueous-phase solubilities of the monomer pairs. An insignificant difference in the true and bulk reactivity ratios was also observed for the microemulsion copolymerizations of styrene/methyl acrylate (MA) and styrene/butylacrylate.¹⁸

CONCLUSIONS

The following three points can be made:

1. There is a difference in the ways in which initiation takes place in emulsions and microemulsions. Emulsion polymerization involves initiation in both the aqueous phase and micelles, whereas aqueous-phase polymerization for microemulsion polymerization is less significant. This was concluded on the basis of the two T_g 's obtained for emulsion-based systems and the single T_g obtained for microemulsion-based systems. Also, the fraction of the relatively more hydrophilic monomer EA in the polymer was higher for the emulsion system-based copolymers than for microemulsion-based polymers

synthesized with similar feed ratios. The particle size distribution also shows a bimodal nature for the emulsion system.

2. The recalculation of the monomer reactivity on the basis of the monomer concentration at the polymerization loci rather than in the feed gives a reactivity ratio similar to that of the bulk for both emulsion and microemulsion polymerizations.
3. The monomer concentration at the polymerization loci, to be calculated with the partition coefficient approach, requires the assumption $f'_A + f'_B = 1$ because of the partial water solubility of both monomers.

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