

Effect of Partitioning of Monomer on the Reactivities of Monomers in Microemulsion

PARESH G. SANGHVI, NAVEEN KUMAR POKHRIYAL, SUREKHA DEVI

Department of Chemistry, Faculty of Science, M. S. University of Baroda, Vadodara, India 390 002

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ABSTRACT: Copolymerization of styrene and 2-hydroxyethyl methacrylate (2-HEMA) was carried out in a microemulsion medium. The composition of the copolymers was estimated using proton $^1\text{H-NMR}$. The reactivity ratios of styrene and 2-HEMA in ternary microemulsions were observed and were considerable different from those reported for solution and bulk polymerization. In monomer pairs with a considerable difference in polarity, partitioning of a monomer between the aqueous phase and the microemulsion droplets develops a concentration gradient, which can be calculated from the distribution coefficient of the monomer between the two phases. This approach has led to more reliable reactivity ratios for the monomers. The study of styrene–2-HEMA copolymerization in a sodium dodecylsulfate-based microemulsion resulted in $r_{\text{S}} = 3.79$ and $r_{\text{H}} = 0.17$ as apparent reactivity ratios and $r_{\text{S}} = 0.57$ and $r_{\text{H}} = 23.24$ as true reactivity ratios for styrene and 2-HEMA, respectively. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1832–1837, 2002; DOI 10.1002/app.10401

Key words: microemulsion; reactivity ratio; copolymerization; polystyrene; 2-HEMA

INTRODUCTION

Unique properties of microemulsions such as lower viscosity, greater stability, and transparency have made them attractive media for polymerization.^{1–5} The increased interest in microemulsion polymerization is due to the production of polymers with a variety of microstructures, which control the properties of the copolymers. Properties of the copolymers depend on the nature of the monomers and their composition and sequence distribution, which are further governed by the reactivities of the monomers. The effect of the medium on the reactivities has been examined by various researchers.^{6–8} Reactivities

of monomers differ significantly in bulk, solution, emulsion, and microemulsions. Recently, we observed that the estimation of reactivity ratios, by considering the concentration of monomers in the feed and the actual concentration at the site of initiation, leads to a wide difference in reactivity ratios. We reported that $r_{\text{S}} = 1.49$ and $r_{\text{A}} = 0.022$ as apparent reactivity ratios for styrene and acrylonitrile, respectively, and $r_{\text{S}} = 0.85$ and $r_{\text{A}} = 0.82$ as true reactivity ratios, respectively.⁹ The diad–triad sequence distribution in the copolymers was better explained by considering the true reactivity ratios calculated from the actual partitioning of the monomers between the aqueous phase and the monomer droplet in microemulsions.

In our extension of this work, we selected styrene and completely water-soluble 2-hydroxyethyl methacrylate (2-HEMA), which also acts as a cosurfactant in microemulsion copolymerization. For this monomer pair, Lebduska et al.¹⁰

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

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showed the effect of solvent polarity on the reactivities. It is known that a solution of monomers strongly differing in polarity can yield apparent reactivity ratios that depend on the solvent used. This can be explained as resulting from the local monomer concentration in the region of the growing radical chains being different from the overall monomer concentration. They reported 0.53 and 0.59 reactivities for styrene and 2-HEMA in dimethylformamide, whereas in a nonpolar solvent like toluene, reactivities were observed to be 0.5 and 1.65, respectively, for styrene and 2-HEMA. In microemulsions containing styrene, 2-HEMA, sodium dodecylsulfate (SDS), and water, 2-HEMA is expected to be completely soluble in water, but due to its cosurfactant nature, part of it will be partitioning at the monomer droplets. The composition drift occurring during copolymerization was determined by the reactivity ratios and by the monomer partitioning between the monomer droplets and the continuous phase. We aimed to determine the effect of this partitioning of 2-HEMA on the reactivity ratios of styrene and 2-HEMA in microemulsions.

EXPERIMENTAL

Chemicals

Styrene from National Chemicals (Baroda, India) was made free from the inhibitor using 2% sodium hydroxide and dried over anhydrous calcium chloride. It was further purified by passing through an alumina column and distilling under a vacuum. It was stored at -2°C until further use. 2-HEMA (Fluka, Switzerland) was purified by vacuum distillation. SDS (Qualigens, Mumbai, India) was used without further purification. Potassium persulfate (KPS; Sisco Chemicals, Mumbai, India) was recrystallized from water.

Preparation of Microemulsions

The one-phase microemulsion region at 30°C was determined visually by titrating styrene–2-HEMA mixtures with aqueous micellar solutions of SDS. A microemulsion formulation, comprising 5% styrene–2-HEMA mixtures, 14% SDS, and 81% water, was used for the microemulsion polymerization.

Microemulsion Polymerization Process

Polymerization was carried out in a three-neck reaction vessel equipped with a mechanical stir-

rer, nitrogen inlet, and condenser. Microemulsion of the desired composition was loaded into the vessel. The reaction mass was purged with nitrogen. The reactions were carried out by using 0.37 mM of KPS as the initiating system at 70°C . The copolymer was precipitated by using a fourfold excess of methanol.

Characterization

The composition of the copolymer was determined by $^1\text{H-NMR}$. The spectra were recorded on a Bruker DPX 200 spectrometer operated at 200 MHz and 298 K using CDCl_3 as a solvent. D_2O was used for the exchange of $-\text{OH}$ -type protons. The spectra were recorded using a spectral width of 7500 Hz, acquisition time of 2 min 5 s, a pulse decay of 5 s, and accumulation of 16 scans for a 1% w/v sample concentration.

RESULTS AND DISCUSSION

Reactivity Ratios

The copolymer composition, the sequence distribution, and, hence, the polymer properties depend upon the reactivities of the monomers in the given system. Reactivity ratios depend on the microenvironment. Due to partitioning of the monomer, the monomer concentration at the polymerization loci and feed differ widely. The reactivity ratios of styrene–2-HEMA in the microemulsion were determined at less than 10% conversion using the linear graphical method of Finemann–Ross (FR)¹¹ and Kelen–Tudos (KT)¹² as well as a nonlinear least-square (NLLS) method.¹³ The copolymer compositions were determined using $^1\text{H-NMR}$. Figure 1 shows a representative $^1\text{H-NMR}$ spectrum of the styrene–2-HEMA copolymer in CDCl_3 . The aromatic protons show splitting into two broad bands, one centered around 6.5–7.0 ppm, which can be attributed to *ortho* protons, and another between 7.0 and 7.5 ppm, which can be attributed to *meta* and *para* protons. The signals for protons of the $-\text{OCH}_2$ group appeared around 3.1–4.2 ppm. The composition of the copolymer was evaluated from the relative intensities of $-\text{OCH}_2$ (2-HEMA unit) and $-\text{C}_6\text{H}_5$ (styrene unit) proton resonance using the following relationship¹⁴:

$$F_S = \frac{2I(-\text{C}_6\text{H}_5)}{2I(-\text{C}_6\text{H}_5) + 5I(-\text{OCH}_2)} \quad (1)$$

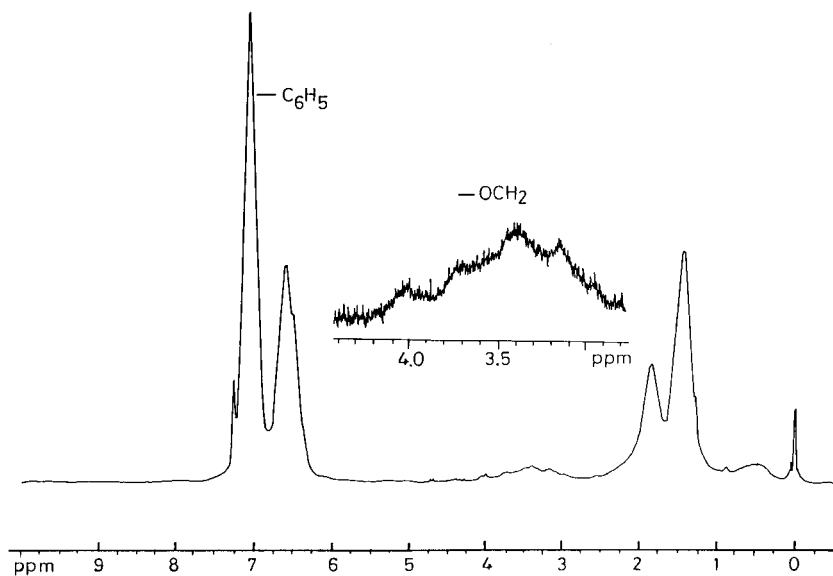


Figure 1 (a) $^1\text{H-NMR}$ spectrum of styrene-2-HEMA copolymer in CDCl_3 .

where $I(-\text{C}_6\text{H}_5)$ and $I(-\text{OCH}_2)$ represent the total peak area for the aromatic protons and $-\text{OCH}_2$ protons, respectively. F_S is the mol fraction of styrene in the copolymer. The concentrations of styrene and 2-HEMA in the copolymer and the feed are given in Table I. The overall reactivity ratios r_S and r_H calculated for styrene and 2-HEMA were within the limit of $M_S \approx 0.5$. Linear plots were observed in both the FR and KT methods (Fig. 2). The overall reactivity ratios were 3.50 and 3.91 for styrene and 0.03 and 0.41 for 2-HEMA. The overall reactivity ratios r_S and r_H were also calculated by NLLS using the copolymer composition data. The values obtained were $r_S = 3.79$ and $r_H = 0.17$. A 95% joint confidence interval for a styrene-2-HEMA comonomer pair is shown in Figure 3. The dependence of the reactivity ratios on the microenvironment is reflected in the vast difference observed in the re-

Table I Composition of Styrene and 2-HEMA in Feed and Copolymer

M_S	M_H	P_S	P_H	Conversion (%)
0.90	0.10	0.97	0.03	6.3
0.75	0.25	0.92	0.08	4.2
0.67	0.33	0.89	0.11	5.5
0.50	0.50	0.803	0.197	6.1

M_S, M_H : mol fractions of styrene and 2-HEMA in feed, respectively. P_S, P_H : mol fractions of styrene and 2-HEMA in copolymer, respectively.

activity ratios of styrene and 2-HEMA obtained in bulk, solution, and microemulsion polymerization (Table II). There is only one possible reason for the difference among the reactivity ratios of the bulk, solution, and microemulsion polymerization system, namely, that the monomer fraction in the polymerization loci is different although the feed composition is identical.

In the microemulsion medium, it is assumed that the initiation of polymerization takes place in a monomer droplet. Due to very low (0.027%) solubility of styrene and the complete solubility of 2-HEMA in the aqueous phase, the actual concentration of 2-HEMA at the monomer droplet will be smaller than that in the feed. As a result, the copolymers synthesized should show a styrene-rich character in a microemulsion medium. Zang et al.¹⁵ studied the copolymerization of acrylamide, a water-soluble monomer, and styrene, a hydrophobic monomer, in a microemulsion medium. They observed that the molar concentration of styrene in a microemulsion droplet is much higher than is the concentration of acrylamide in the aqueous phase and, hence, at the first stage of copolymerization, styrene is preferentially added to the propagating chain rather than acrylamide. They also suggested that the initiation of polymerization occurs at the interface between the oil phase and the water phase but that the polymerization occurs in the microemulsion droplet. The reactivity ratios of styrene and acrylamide within the limit of $M_S \approx 0.5$ were reported to be 3.9 and

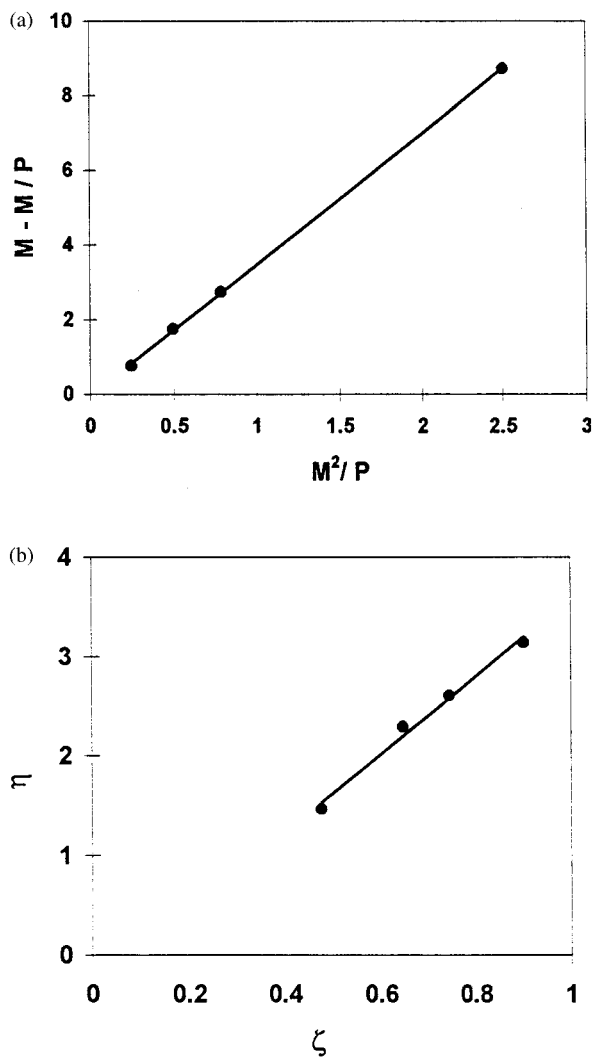


Figure 2 (a) FR method; (b) KT method.

0.04, respectively, which are very much different from those reported for solution polymerization.

Although the difference in the reactivities of the monomers in solution, bulk, emulsion, and microemulsion is attributed to the microenvironment, in the case of monomers with different polarities, variation in the concentration in the feed and at the polymerization loci is not considered, so far, in the calculation of reactivity ratios. Due to solubility of the monomer in water, the distribution of the monomer between the microemulsion droplets and the aqueous phase plays an important role in governing the reactivities of the monomers. Hence, true reactivities can be calculated by considering the distribution coefficient of the monomers. This can be calculated by the following equations¹⁶:

$$r_S = r'_S K_S \quad (2)$$

$$r_H = r'_H / K_H \quad (3)$$

and

$$M'_S/M'_H = K_{SH} M_S/M_H \quad (4)$$

where r'_S (0.27) and r'_H (0.49) are, respectively, the reactivity ratios of styrene and 2-HEMA in bulk polymerization.¹⁴ r_S and r_H are, respectively, the reactivity ratios of styrene and 2-HEMA in a microemulsion, which were observed to be 3.79 and 0.17 by NLLS. M_S/M_H is the styrene/2-HEMA mol ratio in the feed. M'_S/M'_H and K_{SH} are the styrene 2-HEMA mol ratio in the polymerization loci and their distribution coefficient, respectively. In styrene-2-HEMA copolymerization in a microemulsion medium, the distribution coefficient of 2-HEMA, calculated from eq. (3), was 2.88. Using eq. (2), the distribution coefficient for styrene was 14.0. Hence, the average distribution coefficient for the styrene-2-HEMA system was calculated to be 8.46. In a similar way, Gan et al.¹⁷ and Xu et al.¹⁸ reported the distribution coefficient of methyl methacrylate (MMA) and methyl acrylate (MA) in a microemulsion system. Gan et al.¹⁷ reported that the

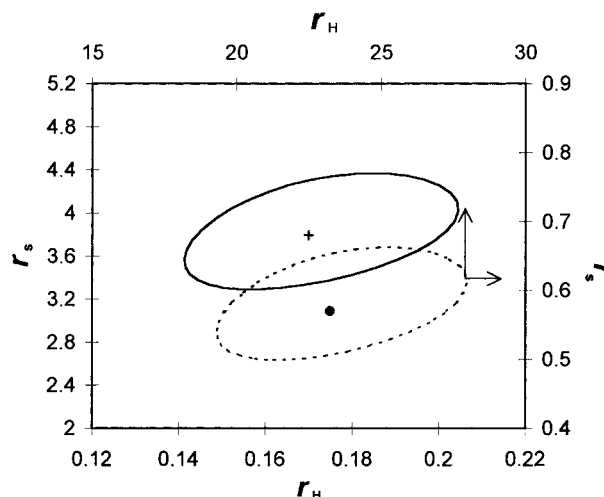


Figure 3 Ninety-five percent joint confidence curve of styrene-2-HEMA reactivity ratio using the NLLS method: (+) estimated values of r_S and r_H based on monomer concentration in the feed; (●) estimated values of r_S & r_H based on monomer concentration in the polymerization loci; (—) curve based on concentration of monomer in the feed; (---) curve based on concentration of monomer in the polymerization loci.

Table II Effect of Microenvironment on Reactivity Ratios

Polymerization Method	r_S	r_H	$r_S r_H$	Ref.
Bulk	0.27	0.49	0.13	14
Solution	0.41	0.53	0.21	8
Solution	0.50	1.65	0.82	10
Solution	0.45	0.54	0.24	10
Microemulsion	3.79	0.17	0.64	Present work

r_S and r_H are reactivity ratios of styrene and 2-HEMA, respectively.

distribution coefficient for MMA (1.07% water solubility) in a microemulsion is 1.33. In our earlier studies, we reported a 1.81 distribution coefficient for acrylonitrile (7.35% water solubility) in a microemulsion containing SDS. As the solubility of a monomer in the aqueous phase increases, the distribution coefficient increased. The 2-HEMA fraction in the polymerization loci and aqueous phase was calculated using eq. (4), assuming that all the styrene added goes to the microemulsion droplets; hence, $M_S = M'_S$. The concentrations of styrene and 2-HEMA calculated in the polymerization loci are given in Table III. It is observed that the molar ratio of 2-HEMA in the polymerization loci to the feed remains almost constant (0.118) for all the systems, indicating that, due to the higher solubility of 2-HEMA (100%), only 11.8 % of added 2-HEMA is present in the polymerization loci and the remaining 88.2% is solubilized in the aqueous phase of the microemulsion system. Xu et al.¹⁸ reported distribution coefficients of 1.86 and 1.23 for MA in a microemulsion and emulsion, respectively. They also observed that, in a microemulsion medium, only 54% of added MA is present in the polymerization loci and the remaining 46% is solubilized in the aqueous phase. Gan et al.¹⁷ reported that 75% of the added MMA was present in the polymerization loci. In our

earlier work, we reported that only 54% of the added acrylonitrile was present in the polymerization loci.

Hence, following the concept of the distribution of monomers between the aqueous phase and the microemulsion droplet, we calculated the true reactivities for styrene and 2-HEMA from their concentrations at the polymerization loci (Table III). The values obtained are $r_S = 0.57$ and $r_H = 23.24$ and are considerably different from the apparent reactivities calculated from the feed concentrations. Ninety-five % confidence limits calculated for both the true and apparent reactivity ratios are given in Figure 3. It is observed that the apparent reactivity ratios lie very much outside the 95% confidence limit of the true reactivity ratios.

CONCLUSIONS

Reactivity ratios depend upon the microenvironment of the monomer. Reactivity ratios were calculated by considering the concentration of the monomer in the feed and in the copolymer at <10% conversion. For hydrophilic monomers, consideration of the monomer concentration in the feed as being equivalent to that at the monomer droplet leads to inaccurate reactivity ratios. Hence, it is necessary to consider partitioning of the monomer and to calculate the actual concentration of it at the polymerization loci for the calculation of the true reactivity ratios. A vast difference was observed in the reactivity ratios of styrene and 2-HEMA in bulk, solution, and microemulsion. The apparent reactivity ratios, based on the monomer feed composition, were evaluated by an NLLS method and were observed to be $r_S = 3.79$ and $r_H = 0.17$. The partition coefficient of 2-HEMA in the microemulsion medium was 8.46. The true reactivity ratios of styrene and 2-HEMA, based on the actual concentra-

Table III Composition of Styrene and 2-HEMA in Feed and Polymerization Loci

M_S	M_H	M'_S	M'_H	M'_S/M'_H	$M_H - M'_H$	M'_H/M_H
0.90	0.10	0.988	0.012	83.60	0.088	0.118
0.75	0.25	0.970	0.029	32.84	0.220	0.118
0.67	0.33	0.961	0.039	24.40	0.294	0.118
0.50	0.50	0.941	0.059	15.92	0.440	0.118

M_S, M_H : mol fractions of styrene and 2-HEMA in the feed, respectively. M'_S, M'_H : mol fractions of styrene and 2-HEMA, respectively in polymerization loci calculated from eq. (4) considering $K_{SH} = 8.46$.

tion of the monomers in the polymerization loci, were 0.57 and 23.24 for styrene and 2-HEMA, respectively.

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