Reactivity Ratios and Monomer Partitioning in the Microemulsion Copolymerization of Vinyl Acetate and Butyl Acrylate

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ABSTRACT: The true monomer reactivity ratios for the vinyl acetate/butyl acrylate system were determined with experimental data from the cumulative copolymer composition at low, intermediate, and high conversions and with the monomer partitioning among the aqueous, microemulsion droplet, and polymer particle phases taken into account. A mixture of sodium dodecyl sulfate and poly(ethylene oxide) (23) dodecyl ether (Brij-35; 3 : 1 w/w) was used as a stabilizer. Potassium persulfate was used as an initiator. The true values of the monomer reactivity ratios were $0.028 \pm 3.2 \times 10^{-3}$ for vinyl acetate and $6.219 \pm 3.1 \times 10^{-1}$ for butyl acrylate, and these were in agreement with those reported in the literature for bulk copolymerizations but differed from values reported for other compartmentalized copolymerizations. Thus, these results indicate that the monomer partitioning and cumulative copolymer composition throughout the reaction have to be duly accounted for in the determination of monomer reactivity ratios in heterogeneous polymerizations. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 329–337, 2009

Key words: copolymerization; kinetics (polym.); microstructure; modeling; radical polymerization

INTRODUCTION

Microemulsions are thermodynamically stable fluids that are formed spontaneously through the mixing of organic and aqueous phases in the presence of a surfactant in the correct proportions.[1] By microemulsion polymerization, it is possible to obtain polymeric nanoparticles with high molar masses and with a variety of microstructures, which have an influence on their properties.[2] Even though microemulsion polymerization and emulsion polymerization have similarities [both methods allow the synthesis of nanolatexes (<1000 nm) with polymers of high molar masses (typically >10^6 Da)], they dif-

fer in other aspects. A microemulsion polymerization begins in a one-phase thermodynamically stable solution of monomer-swollen micelles, whereas an emulsion polymerization typically begins in a two-phase dispersion with large monomer droplets. Kinetically, the processes differ: in emulsion polymerization, three reaction-rate periods are observed, whereas in microemulsion polymerization, only two periods have been reported. Furthermore, microemulsion polymerization is characterized by continuous nucleation even for poorly water-soluble monomers throughout the reaction because of the excess surfactant used in the formulation of the parent microemulsion; in emulsion polymerization, nucleation typically occurs only during the first period of the reaction, and continuous nucleation has been reported only for the more water-soluble monomers.[3–5]

The properties of copolymers depend on the monomer nature, composition, and sequence distribution, which are related to the monomer reactivity ratios.[6] For this reason, the estimation of copolymerization reactivity ratios is an area of interest in both academia and industry.[7] The traditional methods for the estimation of monomer reactivity ratios in homogeneous copolymerizations (bulk and solution) are based on the assumption that the comonomer composition does not change significantly at low conversions (<5–10%). In microemulsion copolymerization

systems, the determination of the reactivity ratios is more complex because it is clear that there are differences in the comonomer compositions (ratio of monomer 1 to monomer 2) between the aqueous and organic phases (microemulsion droplets and particles), especially when one of the monomers presents high water solubility.[8]

Reactivity ratios in heterogeneous copolymerizations have been determined with data at low conversions with and without monomer partitioning; for example, Bhawal et al.[9] determined the reactivity ratios of ethyl acrylate and methyl methacrylate (MMA) from microemulsion copolymerization data at a low conversion (<10%). These authors estimated the concentrations in the reaction loci using partition coefficients to calculate the true monomer reactivity ratios and found that they were close to those calculated in bulk copolymerization. Guillot's research group[10] determined the reactivity ratios of the MMA/butyl acrylate (BuA) system in conventional emulsion copolymerization with the copolymer composition at low conversions and the initial monomer feed composition data by the Fineman–Ross method. The resulting values of the reactivity ratios were 2.3 ± 0.2 for MMA and 0.23 ± 0.05 for BuA, which are different from those reported for homogeneous polymerization (reactivity ratio for MMA = 1.8 ± 0.1 and reactivity ratio for BuA = 0.37 ± 0.1[11]). Guillot and coworkers used these reactivity ratios to reproduce the copolymer composition throughout the reaction with the Mayo–Lewis equation, observing that the predicted values deviated from the experimental data at low conversions (<20%). However, a better prediction was obtained when they used the monomer reactivity ratios previously reported in the literature for bulk polymerizations and took into account monomer partitioning between the aqueous and organic phases (using partition coefficients).

The estimation of reactivity ratios is a nonlinear problem, and nonlinear methods should be used. Back in 1965, Tidwell and Mortimer[12] proposed a method using optimally designed experiments in conjunction with nonlinear least squares parameter estimation. This method provides accurate estimates of the reactivity ratios and also allows the construction of a confidence interval. Although laborious, the nonlinear approach to the estimation of reactivity ratios has become straightforward with advances in computing power. An extension of the nonlinear approach is to use the error-in-all-variables method, which accounts for the error in all variables. This method was proposed by Van der Meer et al.[13] and Patiño-Leal et al.[14] and takes into account the error in both the independent and dependent variables (i.e., the monomer feed and copolymer compositions, respectively). The error-in-all-variables method minimizes the weighted sum of squares of the distance from the observed point to the estimated (predicted) value. The weight and the orientation of the distance to be minimized are given by the measurement of the variance–covariance matrix, as pointed out by Polic et al.[7] Although the error-in-all-variables method is widely accepted as the most statistically rigorous procedure for the estimation of monomer reactivity ratios, significant effort is required to determine experimentally the error structure: to obtain a proper statistical estimate of the variance, at least eight replicate measurements for each experimental point are required.[15]

This work reports a method for the calculation of the monomer reactivity ratios for the vinyl acetate (VAc)/BuA system in microemulsion copolymerization that takes into account monomer partitioning between the phases, the cumulative copolymer composition versus conversion data in the entire conversion interval, and a nonlinear parameter estimation approach. To the best of our knowledge, the application of these considerations together has not been reported up to now for reactivity ratio determination in microemulsion copolymerization reactions. The procedure is simpler than the error-in-all-variables method because it does not involve the evaluation of the errors in all variables, which requires either a significant experimental effort or assumptions about the magnitude of the errors that are not or cannot be validated in a realistic way.

The apparent monomer reactivity ratios calculated under the assumption that monomer partitioning does not take place and the true reactivity ratios calculated with the monomer partitioning between the different phases taken into account are reported here. The VAc/BuA system was chosen because the monomers present very different water solubilities and reactivity ratios and there are no reports of their reactivity ratios measured in microemulsion polymerization. Also, VAc and BuA are important monomers for the preparation of useful polymers and copolymers with applications in the paint, coating, and adhesive industries.

EXPERIMENTAL

Materials

VAc, BuA, potassium persulfate (KPS), hydroquinone, and Brij-35 were purchased from Aldrich (St. Louis, MO) (≥99%); sodium dodecyl sulfate (SDS) was purchased from Fluka (Steinheim, Germany) (≥99%). VAc was washed with a 2N NaOH solution, dried with $CaCl_2$ and $MgSO_4$ for 12 h, and subsequently vacuum-distilled at 40°C. BuA was dried with $CaCl_2$ and vacuum-distilled at 40°C. All the other reactants were used as received. Tridistilled-grade deionized water (obtained from a system of

TABLE I
Recipes Used in the Copolymerizations

Run	VAc	BuA	SDS	Brij-35	KPS	Water
1	5.1	0.9	4.5	1.5	0.12	138.0
2	3.0	3.0	4.5	1.5	0.12	138.0
3	0.9	5.1	4.5	1.5	0.12	138.0

All quantities are given in grams.

two ionic interchange columns, Cole–Parmer Instruments Co., Vernon Hills, IL) and argon of ultrahigh purity (Infra, Saltillo, Mexico) were used. Tetramethylsilane (TMS) from Aldrich was used as an internal reference in ^{1}H-NMR.

Copolymerizations

The compositions of the one-phase oil-in-water microemulsions at 60°C in which the reactions were carried out were determined visually by the titration of aqueous solutions of SDS/Brij-35 mixtures (3 : 1 w/w) of different concentrations with the monomer mixture (molar fraction of VAc with respect to BuA: 0.895, 0.598, or 0.207). The compositions of the polymerized microemulsions are given in Table I. Batch reactions were carried out in a 250-mL jacketed glass reactor with magnetic stirring. The surfactant mixture and water were charged to the reactor, cooled to 0°C, and vacuum-degassed, and then the system was saturated with argon. The reactor was heated to 60°C, and the oxygen-free monomer mixture, saturated with argon, was added to the reactor. Then, a KPS solution (2 wt % with respect to the monomer mixture) was added in one shot to initiate the polymerization. The conversion was followed gravimetrically: samples were withdrawn from the reacting system at given times and placed in vials (of known weight) immersed in an ice bath containing 0.5 g of an aqueous hydroquinone solution (0.4 wt %). Then, the samples were weighed and freeze-dried (R45 freeze–dry system, Labconco, Kansas City, MO). The weight of the polymer was estimated by subtraction of the known weights of the surfactants and hydroquinone from the total weight of the freeze-dried samples. Additionally, samples were taken at different time intervals during the reaction to follow the average particle diameter.

Characterization

The freeze-dried samples were purified by washing several times with water to remove surfactants and hydroquinone; washed samples were freeze-dried again and used to determine the copolymer composition by ^{1}H-NMR analysis in a Varian (Palo Alto, CA) Gemini 200 FT-NMR apparatus (200 MHz) with

a 10 mg/mL solution of the copolymer in deuterated chloroform and with TMS as the internal reference.

The average particle diameter of the latexes was determined by quasi-elastic light scattering with a Nano S90 apparatus (Malvern, UK) at 25°C. Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate (average decay rate $= 2q^2D$, where D is the diffusion coefficient and q is the magnitude of the scattering vector). The measured diffusion coefficients were represented in terms of the apparent radii with Stoke's law and under the assumption that the solvent had the viscosity of water.

THEORY

With the Mayo–Lewis copolymer equation[16] and the definition of the instantaneous copolymer composition (F_1), the following equation can be obtained:

$$F_1 = \frac{dM_1}{dM_1 + dM_2} = \frac{r_1 \frac{M_1}{M_2} + 1}{2 + r_1 \frac{M_1}{M_2} + r_2 \frac{M_2}{M_1}} \quad (1)$$

In the case of a heterogeneous polymerization, M_1 and M_2 correspond to the concentrations of monomers 1 and 2 in the polymerization site (in this case, polymer particles). r_1 and r_2 are the reactivity ratios of monomers 1 and 2, respectively.

If the cumulative copolymer composition ($\overline{F}_1$) is defined as the ratio of the number of moles of monomer 1 to the total number of moles of both monomers incorporated into the copolymer, we can write

$$\overline{F}_1 = \frac{f_{10} - f_1(1 - X)}{X} \quad (2)$$

where X is the total conversion (molar fraction), f_{10} is the molar fraction of monomer 1 at the polymerization site at the beginning of the reaction, and f_1 is the molar fraction of monomer 1 at the polymerization site at a given time.

A material balance for monomer 1 yields the following equation[17]:

$$\frac{df_1}{dX} = \frac{F_1 - f_1}{X - 1} \quad (3)$$

with $f_1 = f_{10}$ at $X = 0$. Deriving eq. (2) with respect to X and combining it with eq. (3), we obtain

$$\frac{d\overline{F}_1}{dX} = \frac{F_1 - \overline{F}_1}{X} \quad (4)$$

Equation (4) can be used as the objective function to estimate the monomer reactivity ratios with

experimental cumulative copolymer composition versus conversion data. However, to be able to estimate the reactivity ratios, it is necessary to know the monomer concentrations at the main site of polymerization (polymer particles). Because in most of the heterogeneous polymerization systems mass transfer rates among the different phases are larger than the polymerization rate, the monomer concentrations in the phases are in thermodynamic equilibrium.[18] In microemulsion polymerization, for the thermodynamic swelling equilibrium behavior, three phases have been considered: the polymer particles, microemulsion droplets (organic phase), and continuous aqueous phase. Because of monomer consumption in the particles (due to the polymerization reaction), there is monomer transport from the microemulsion droplets (or nongrowing particles) through the water phase to the growing particles. In thermodynamic equilibrium, the free energy of mixing of the monomers, $\overline{\Delta G}$, in the different phases is the same. Therefore, the equilibrium condition can be expressed by means of a set of nonlinear equations, which include mass balances as follows:

$$\left(\frac{\overline{\Delta G}}{RT}\right)_i^Q = \left(\frac{\overline{\Delta G}}{RT}\right)_i^k \tag{5}$$

where R is the universal gas constant and T is the absolute temperature. The superscripts Q and k in eq. (5) refer to two different phases: $Q \neq k$.

The free energy of mixing of a given component i in a given phase Q is represented by the Flory–Huggins theory, which was expressed by Ugelstad et al.[19] as follows:

$$\left(\frac{\overline{\Delta G}}{RT}\right)_i^Q = \ln(\phi_{iQ}) + \sum_{j=1}^{n} \left(1 - m_{ij}\right)\phi_{jQ} + \sum_{j=1, j\neq i}^{n} \chi_{ij}\phi_{jQ}^2$$
$$+ \sum_{j=1, j\neq i}^{n-1} \sum_{k=j+1, k\neq i}^{n} \phi_{jQ}\phi_{kQ}\left(\chi_{ij} + \chi_{ik} - \chi_{jk}m_{ij}\right) + 2\gamma\overline{V}_i/r_Q RT \tag{6}$$

where χ_{ij} is the Flory–Huggins interaction parameter, ϕ_{iQ} is the volume fraction of i in phase Q, m_{ij} is equal to $\overline{V}_i/\overline{V}_j$, γ is the interfacial tension, $\overline{V}_1$ is the molar volume of i, and r_Q is the radius of phase Q (polymer particles or microemulsion droplets).

Mass balances are given by

$$(1 - x_1)n_{10}\overline{V}_1 = \phi_{1d}V_d + \phi_{1a}V_a + \phi_{1p}V_p \tag{7}$$

$$(1 - x_2)n_{20}\overline{V}_2 = \phi_{2d}V_d + \phi_{2a}V_a + \phi_{2p}V_p \tag{8}$$

$$n_W\overline{V}_w = \phi_{Wa}V_a \tag{9}$$

Parameter	Value	Parameter	Value
χ^*_{AB} [a]	0.15	m^*_{Aw} [a]	0.37
χ^*_{BA} [a]	0.45	m^*_{Bw} [a]	1.31
χ^*_{Aw} [a]	2.1	γ_d [b]	2.0 dyn/cm
χ^*_{Bw} [a]	6.43	r_{d0} [b, d]	2.5×10^{-7} cm
m^*_{AB} [a]	0.33	ρ_{pA} [c]	1.16 g/cm^3
m^*_{BA} [a]	3.03	ρ_{pB} [c]	1.09 g/cm^3

[a] Reference 25.
[b] Reference 24.
[c] Reference 26.
[d] Initial radius of the monomer-swollen micelles.

$$\frac{x_1 n_1 Mw_1}{\rho_{P1}} + \frac{x_2 n_2 Mw_2}{\rho_{P2}} = \phi_{Pp}V_p \tag{10}$$

$$\phi_{1d} + \phi_{2d} = 1.0 \tag{11}$$

$$\phi_{1a} + \phi_{2a} + \phi_{Wa} = 1.0 \tag{12}$$

$$\phi_{1p} + \phi_{2p} + \phi_{Pp} = 1.0 \tag{13}$$

where subscripts 1 and 2 refer to monomers 1 and 2, respectively; subscripts W and P refer to the water and copolymer, respectively; subscripts d, p, and a stand for the microemulsion droplets, polymer particles, and aqueous phases, respectively; n_{i0} is the initial number of moles of monomer i; x_i is the conversion of monomer i; V_i is the total volume of phase i; ρ_{Pi} and Mw_i are the homopolymer density and molecular weight of monomer i, respectively; and n_i is the number of moles of monomer i. The solution to eqs. (5) and (7)–(13) gives the volume fraction of each monomer in each of the three phases. The monomer concentrations in the polymer particles are given by $M_{1p} = \phi_{1p}/\overline{V}_1$ and $M_{2p} = \phi_{2p}/\overline{V}_2$. When all of the monomers in the nonnucleated microemulsion droplets have diffused to the growing particles through the aqueous phase, the terms corresponding to the microemulsion droplet phase are not taken into account anymore. To solve the thermodynamic equilibrium equations, the radius of the microemulsion droplets (r_{d0}) was fixed to 2.5 nm (Table II), and the radius of the polymer particle was obtained by polynomial fitting of the experimental particle diameter versus conversion data.

The following iterative procedure was used for the estimation of r_1 and r_2: for each experiment, eq. (4) was integrated numerically as a function of conversion (the independent variable) and with initial guesses for r_1 and r_2 in eq. (1); in each step of integration, the thermodynamic equilibrium equations were solved to obtain the concentrations of the monomers in the polymer particles to be used in eq. (4). Integration of eq. (4) was achieved with the fifth-

order Runge–Kutta method, and the nonlinear equation system was solved with Newton's method with a line search. This differential–algebraic system was coupled with the parameter estimator subroutine GREG level[20] to obtain improved values for r_1 and r_2; the subroutine minimized the error between the experimental cumulative copolymer compositions and those predicted by eq. (4).

RESULTS

The initially translucent microemulsions turned bluish and slightly opaque when polymerization started and became opaque at the end of the reaction. The final latexes were stable, and no phase separation was observed after 1 year of storage. Figure 1 shows the total conversions as a function of time for VAc/BuA copolymerization in microemulsions with different VAc/BuA ratios. In all cases, high conversions (>90%) have been obtained, and the polymerization rate increases with the BuA content; that is, for a molar fraction of VAc (f_{VAc0}) of 0.895, a conversion of 80% is reached in 15 min, whereas for $f_{VAc0} = 0.207$, the same conversion is reached in less than 2 min. Figure 2 shows the ^{1}H-NMR spectrum for a copolymer of VAc and BuA obtained from microemulsion copolymerization; it agrees with spectra reported by other authors for the same copolymer.[21–23] The molar fraction of VAc in the copolymer was calculated by integration of the peaks at $\sim$ 4.0 ppm corresponding to the BuA units and at $\sim$ 4.9 ppm corresponding to the VAc units and with eq. (14):
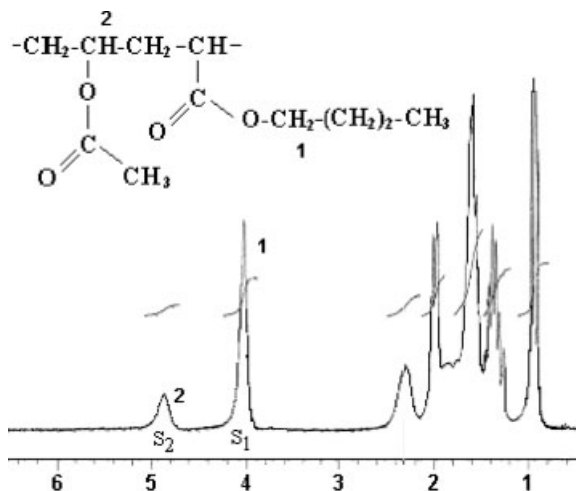

Figure 2 ^{1}H-NMR spectrum of a VAc/BuA copolymer obtained by batch microemulsion copolymerization.

$$\text{Molar fraction of VAc} = \frac{2S_2}{2S_2 + S_1} \quad (14)$$

where S_1 and S_2 are the areas of peaks 1 and 2 shown in Figure 2, respectively.

Figure 3 shows the experimental average particle sizes as a function of time for the different molar fractions of VAc in the feed. The particle size increases with increasing conversion, and slightly smaller particles are obtained when a higher VAc molar fraction is used in the feed. In Figure 4, the evolution of the volumes of each of the three phases as a function of conversion for the VAc/BuA system ($f_{VAc0} = 0.207$) is shown. These values were obtained from a simulation solving the thermodynamic and
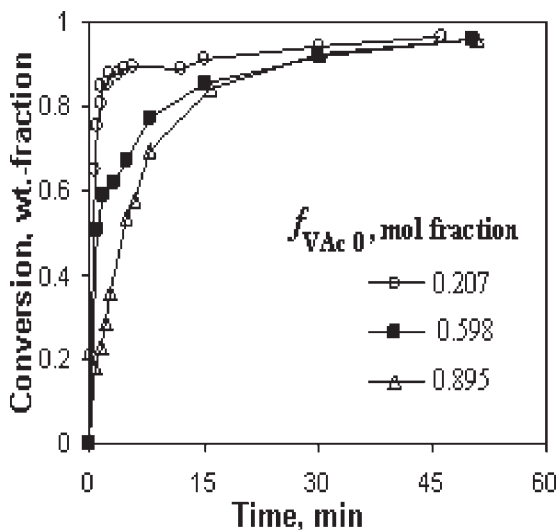

Figure 1 Kinetics of the batch microemulsion copolymerization of VAc and BuA at 60°C with different comonomer compositions used in the feed.
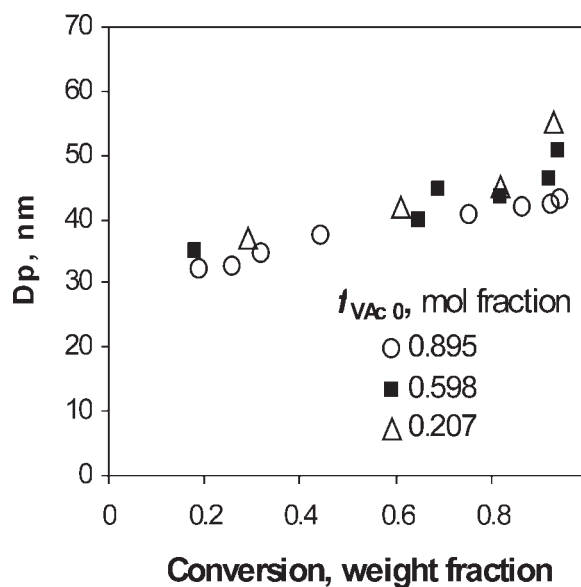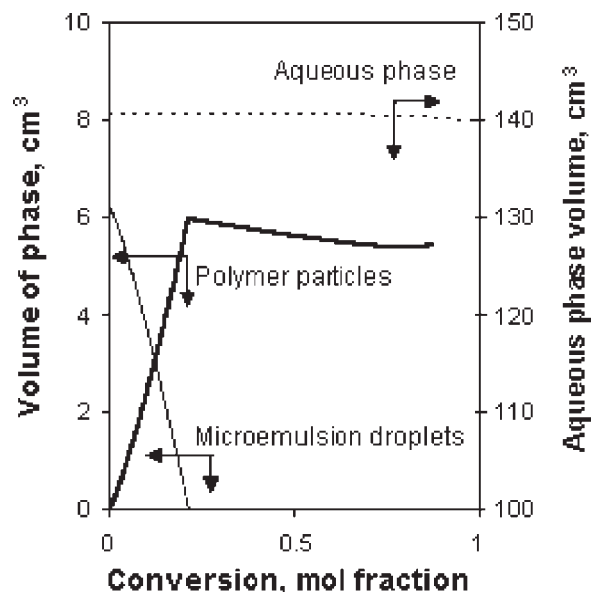

Figure 3 Evolution of the average particle size (D_p) with the conversion in latexes with different comonomer compositions in the recipe.

Figure 4 Model prediction of the total volume of each phase as a function of conversion in the microemulsion copolymerization of VAc and BuA. The molar fraction of VAc in the monomer mixture used in the feed was 0.207.

mass balance equations. The values of the thermodynamic parameters used in eq. (6) were taken from the literature and are given in Table II. The volume of the aqueous phase (which consists of water, the surfactant, and the dissolved monomers) decreases slightly when the microemulsion droplets disappear. Figure 5(a,b) shows the molar ratio of VAc present in the aqueous phase and in the polymer particles, respectively, as a function of conversion for two different molar fractions of VAc in the feed. Because VAc has higher water solubility (≈ 2.5 g/100 g) than BuA (≈ 0.14 g/100 g),[24] the molar fraction of VAc in the particles is lower than that in the feed [Fig. 5(b)].

Table III shows the values of the monomer reactivity ratios obtained from experimental data throughout the reaction as follows: (1) by considering that the monomer concentrations in the polymer particles are equal to the concentrations of the monomers in the reactor (apparent values) and (2) by calculating the monomer concentrations in the polymer particles with monomer partitioning taken into account (true
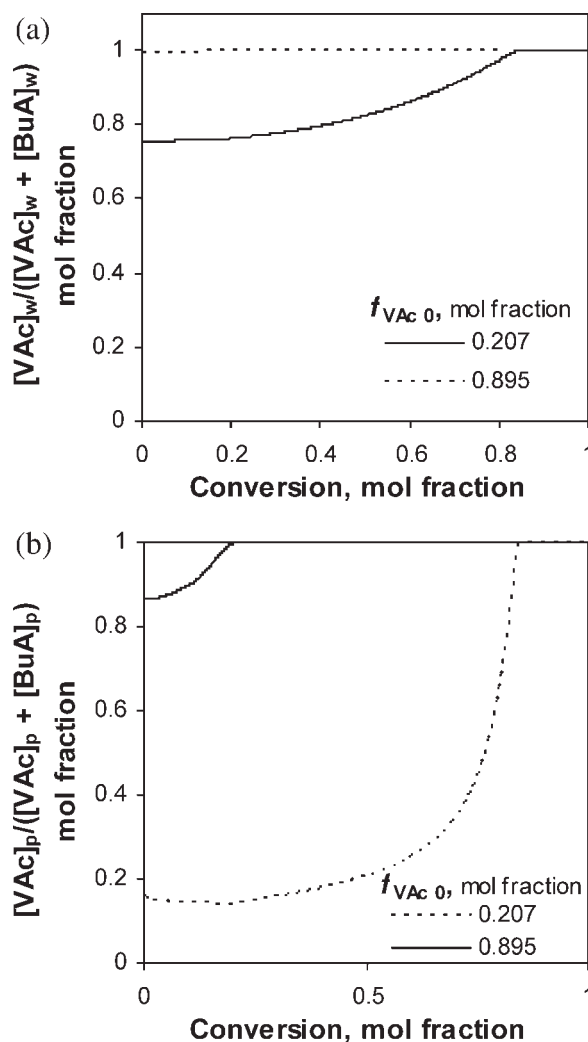
Figure 5 Simulation of the molar ratio of VAc (a) in the aqueous phase and (b) in the polymer particles with different molar fractions of VAc in the feed.

values). The true reactivity ratios are $r_1 = 0.028 \pm 3.2 \times 10^{-3}$ (VAc) and $r_2 = 6.219 \pm 3.1 \times 10^{-1}$ (BuA), which are different from the apparent values. Table IV compares the values of reactivity ratios reported in the literature for the VAc/BuA system with the values obtained here. The values obtained in this work, taking into account monomer partitioning,

TABLE III
Results Obtained for the Calculation of the Reactivity Ratios from the Regression of the Experimental Data for the VAc/BuA System

VAc/BuA	Apparent value[a]	True value[b]
Reactivity ratio for VAc $\pm$ SD	$0.016 \pm 1.8 \times 10^{-3}$	$0.028 \pm 3.2 \times 10^{-3}$
Reactivity ratio for BuA $\pm$ SD	$15.62 \pm 5.9 \times 10^{-1}$	$6.219 \pm 3.1 \times 10^{-1}$
Residual sum of squares	1.16×10^{-2}	1.18×10^{-2}
Overall standard deviation of the fit	2.35×10^{-2}	2.37×10^{-2}

[a] Without monomer partitioning.
[b] With monomer partitioning.

Reference	Conditions	Reactivity ratio for VAc	Reactivity ratio for BuA
25[a]	60°C, bulk	0.037	6.35
22[a]	60°C, bulk	0.026	5.938
23[a]	60°C, emulsion[b]	0.024	10.67
27	60°C, emulsion[c]	0.08 ± 0.005	7.2 ± 0.2
This work	60°C, microemulsion	0.028 ± 0.0032	6.219 ± 0.31

[a] The error is not given in the original source.
[b] Without consideration of monomer partitioning.
[c] With consideration of monomer partitioning and low conversions.

agree with those reported for the VAc/BuA system in bulk polymerization.

Figure 6 shows experimental cumulative copolymer compositions of VAc with different VAc/BuA ratios and model predictions made with the monomer reactivity ratios obtained with consideration of monomer partitioning in the different phases. In this figure, a marked drift in copolymer composition can be observed, as well as good agreement between the experimental data and predictions through the reaction, when true reactivity ratios are used (method A). When the apparent reactivity ratios (method B) are used, the model predictions at low conversions do not agree with the experimental results.

DISCUSSION

Before polymerization starts, a microemulsion system consists of a monomer dissolved in an aqueous phase and a monomer inside the microemulsion droplets. When polymerization is initiated, some of the microemulsion droplets become particles by capturing radicals propagating in the aqueous phase (micellar nucleation). Particle formation also occurs by homogeneous nucleation when radicals in the aqueous phase grow until a critical size is reached, precipitating from the aqueous phase; these precipitated radicals can absorb surfactant and self-stabilize, producing a stable polymer particle.[25] Because the particles recruit monomers from the microemulsion droplets to continue the polymerization reaction, the volume of the microemulsion droplet phase decreases and eventually disappears, whereas the total volume of the polymer particles (the copolymer plus the monomers) increases (Fig. 4). The conversion at which microemulsion droplets are totally depleted of monomers will depend on the comonomer composition used in the microemulsions.[29] When microemulsion droplets disappear, the total volume of the polymer particles starts to decrease slightly because of the density difference between the monomers and the copolymer and because there is not a monomer reservoir to replenish the particles. Because BuA has lower water solubility than VAc

[practically all of the BuA is present inside the particles; Fig. 5(a)] and the reactivity ratio for BuA is much greater than the reactivity ratio for VAc, faster reaction rates are obtained when monomer mixtures with higher BuA contents are used (Fig. 1).

To understand the composition drift behavior, the molar ratios of VAc present in the aqueous phase and in the polymer particles have been calculated with consideration of thermodynamic equilibrium. Because of the differences in the water solubility of the monomers, f_{VAc0} in the water phase is higher than the molar fraction in the feed [Fig. 5(a)], and f_{VAc0} in the particles is lower than the molar fraction in the feed [Fig. 5(b)]. Because BuA polymerizes preferentially, the BuA present in the aqueous phase is transferred to the particles, causing an increase in the conversion of the molar fraction of VAc in the
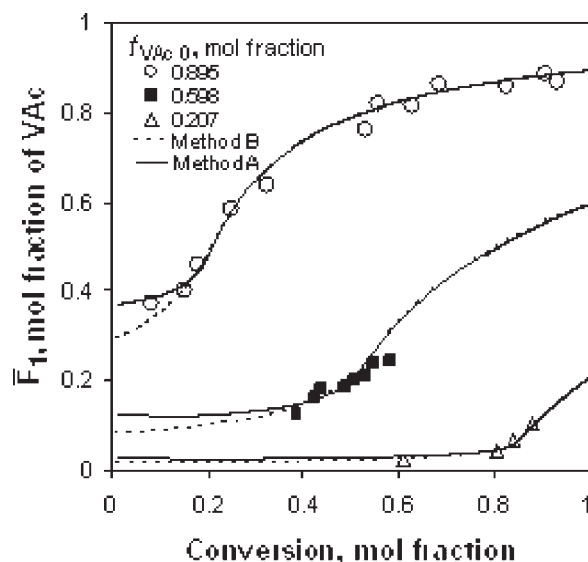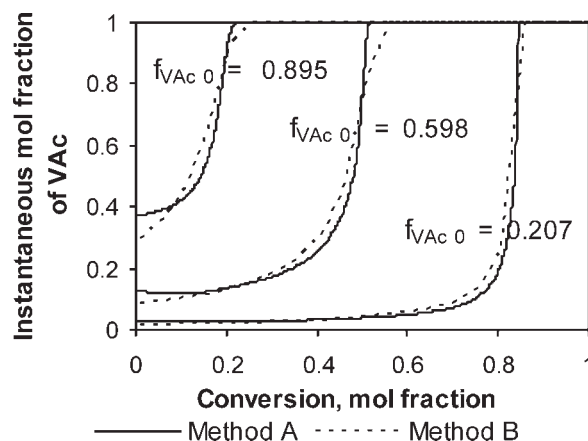

Figure 6 Cumulative molar fraction of VAc in copolymers with different monomer ratios initially charged to the reactor. Method A consists of predictions with the reactivity ratios (calculated with monomer partitioning taken into account), and method B corresponds to predictions obtained with the reactivity ratios calculated without monomer partitioning.

water, and it becomes practically 1.0 before 100% conversion [Fig. 5(a)]. Furthermore, with a higher value of f_{VAc0} (0.895), from the beginning of the reaction, the molar fraction of BuA in the aqueous phase is practically zero (≈ 0.01). The molar fraction of VAc in the particles increases as the reaction progresses because, as mentioned before, BuA is consumed faster than VAc [Fig. 5(b)].

Table III shows that the true reactivity ratios are $r_1 = 0.028 \pm 3.2 \times 10^{-3}$ (VAc) and $r_2 = 6.22 \pm 3.1 \times 10^{-1}$ (BuA), and these are different from the apparent values. Table IV compares the values of reactivity ratios reported in the literature for the VAc/BuA system with the values obtained here. The values obtained in this work, taking into account monomer partitioning during microemulsion copolymerization and using data throughout the reaction, are in agreement with those obtained for the VAc/BuA system in bulk polymerization. It can be observed in Table IV that the reactivity ratios obtained in emulsion polymerization without monomer partitioning being taken into account are very different from the ones obtained here and in bulk polymerization and that the reactivity ratios obtained with monomer partitioning and low-conversion data taken into account still are different from the ones obtained here, although they are closer. Montgomery and Fry[30] pointed out that the constraint of stopping the reactions at very low conversions may result in experimental difficulties and that the assumption that there is no change in the comonomer composition at low conversions may be a source of error when the monomers have very different reactivity ratios. Therefore, an improvement in the estimation of the reactivity ratios will result from using an integrated form of the copolymer composition equation with data obtained throughout the reaction (low, medium, and high conversions). It has been reported that when the Maxwell approach[31] or partition coefficient methods are used to determine monomer partitioning for the styrene/BuA system, there is a good agreement with the reactivity ratios obtained with Morton's rigorous theory (thermodynamic equilibrium) only at high monomer contents (>30 wt %); a deviation occurs at low monomer contents.[28] Therefore, Morton's theory is recommended to determine monomer partitioning, which is the approach used in this investigation.

Figure 6 shows that there is a marked drift in the cumulative copolymer composition through the reaction and that the copolymer becomes richer in VAc monomeric units with conversion. The initial copolymer composition is much richer in BuA than the monomer composition in the particles because of the preference of BuA to react with its monomer (reactivity ratio for BuA = 6.2) and the preference of VAc to react with BuA (reactivity ratio for VAc = 0.028).

Figure 7 Simulation of the instantaneous composition of VAc in copolymers with different monomer ratios initially charged to the reactor. Method A consists of predictions with the reactivity ratios (calculated with monomer partitioning taken into account), and method B corresponds to predictions obtained with the reactivity ratios calculated without monomer partitioning.

At low conversions, there is a difference in the compositions calculated with the apparent reactivity ratios and the true reactivity ratios. This difference is greater as the initial composition is richer in VAc. At medium and high conversions, both model predictions agree with the experimental values (methods A and B). Guillot et al.[10] for the emulsion polymerization of the MMA/BuA system reported that when apparent reactivity ratios are used, at low conversions the predicted values deviate from the experimental data. At low conversions, it can be observed that in the case of $f_{VAc0} = 0.895$, the experimental composition is similar to the value calculated with monomer partitioning. For the other two compositions studied, it was not possible to obtain samples at the conversions at which both predictions diverge because the reactions are very fast and results would carry significant errors (Fig. 1).

Figure 7 shows that the instantaneous copolymer compositions calculated with and without monomer partitioning when there is still BuA in the polymer particles are different, although the cumulative compositions are similar at medium and high conversions. With an increase in the initial molar ratio of VAc, at lower conversions, the polymer that is formed is composed practically of only monomeric units of VAc. Because the instantaneous copolymer composition plays an important role in the properties of the final copolymer, care should be taken when reactions using monomers with different water solubility and reactivity ratios are being planned. It is clear from the results obtained in this work that r_1 and r_2, when calculated with monomer partitioning among the phases taken into account and with experimental data taken throughout the

polymerization reaction, produce results in agreement with those calculated for bulk copolymerization, and this corroborates the idea that in radical copolymerization the monomer reactivity ratios are independent of the reaction medium, provided that monomer partitioning between the phases is taken into account.[32] This can be explained because microemulsion polymerization belongs to a class of compartmentalized polymerizations (including suspension polymerization, emulsion polymerization, and miniemulsion polymerization) in which the reactions are carried out in enclosed containers (beads or particles) and thus in essence are bulk polymerizations. To the best of our knowledge, no other works have been reported explaining this behavior in microemulsion copolymerization systems.

The procedure reported here could be further improved by the incorporation of the error-in-all-variables method for the estimation of the reactivity ratios, provided that an experimental determination of errors is carried out. In relation to this observation, it should be pointed out that microemulsion copolymerization is a heterogeneous process, and thus, because of the errors in the determination of monomer partitioning, it should be considered in addition to errors usually involved in the application of the error-in-all-variables approach (feed composition, copolymer composition, and molar conversion).

CONCLUSIONS

Reactivity ratios in heterogeneous systems must be calculated with the thermodynamic equilibrium and mass transfer between the phases and composition data throughout the reaction taken into account. For the VAc/BuA comonomer microemulsion system studied here, good agreement was obtained between the values for the monomer reactivity ratios calculated in this work when the effects of thermodynamic equilibrium and mass transfer were considered and the values reported for the bulk copolymerization of the same monomers. The procedure reported here can be used for the calculation of true monomer reactivity ratios in other compartmentalized copolymerizations.

When copolymers are being synthesized by microemulsion polymerization, it is necessary to consider monomer partitioning to calculate how the instantaneous copolymer composition evolves throughout the reaction.

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