

Surfactant concentration effects on the microemulsion polymerization of vinyl acetate

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Abstract

The polymerization of vinyl acetate in oil-in-water microemulsions stabilized with cetyltrimethylammonium bromide (CTAB) is reported here as a function of surfactant concentration. Reaction rate decreases as the CTAB/water ratio is increased in the parent microemulsions. Polymer particles in the latexes grow with conversion; they also become bigger as the initial surfactant content is increased. Number-average molar masses are smaller than those expected by termination by chain transfer to monomer, but weight-average molar masses increased as the surfactant concentration in the parent microemulsion is raised. However, the latter are much smaller than those obtained by polymerization in an emulsion stabilized with the same surfactant. Possible explanations to this unusual behavior are provided here.

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1. Introduction

Even though there are many similarities between emulsion and microemulsion polymerization such as the synthesis of high molar mass polymer particles in the nano-size range dispersed in water (latex) with fast reaction rates, the polymers produced by these processes often have different characteristics. For instance, the emulsion polymerization of tetrahydrofurfuryl methacrylate yields a cross-linked polymer whereas the microemulsion process gives a branched polymer with a large molar mass (ca. 10^7 g/mol) [1]. The free radical microemulsion polymerization of methyl methacrylate produces the isotactic polymer whereas emulsion polymerization yields the atactic form [2]. More recently, we reported that non-branched poly(vinyl acetate) with much lower molar mass and narrower

molar mass distribution can be obtained at high conversions ($\approx 99\%$ conversion) by microemulsion polymerization [3] in contrast to emulsion polymerization that yields highly branched poly(vinyl acetate) with higher molar mass and wider molar mass distribution, as a result of chain transfer reactions to polymer [4,5]. Moreover, we found that both surfactant type and charge appear to have a role on the termination mechanism and, as a consequence, on the poly(vinyl acetate) molar mass distribution [6–8].

The influence of surfactant concentration on the microemulsion polymerization of non-polar [9–11] and polar monomers [12–14] has been studied. For non-polar monomers such as styrene, the reaction rate behavior [9] and particle size evolution [9–11] are similar to those typically observed. However, with more hydrophilic monomers, the kinetic behavior is atypical. For the polymerization of isobutyl methacrylate in microemulsions stabilized with CTAB [12] and for the polymerization of butyl acrylate in microemulsions stabilized with SDS [13], an inverse dependence between reaction rate and surfactant concentration was found, which was attributed to a reduction in monomer concentration within the droplets since the number density of them increases as surfactant

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concentration is raised while maintaining constant the initial monomer content. Tauer et al. invoked an aggregative nucleation mechanism to explain the increase in particle size and the slowing down in reaction rate with increasing initial surfactant concentration for the polymerization of butyl acrylate in microemulsions stabilized with a mixture of sodium dodecylsulfate (SDS) and Aerosol OT [14]. However, most of these articles report the surfactant concentration effects on kinetics (reaction rate) and colloidal aspects but none addresses the effect on the molar mass characteristics of the polymer produced.

In a previous work, we reported the effect of surfactant ratio of CTAB/DTAB on polymerization kinetics as well as in molar mass characteristics (\bar{M}_w , \bar{M}_n and MWD), where it was observed that as the amount of DTAB was increased, \bar{M}_w increased and MMD becomes bimodal due to bimolecular termination by particle coagulation and higher rates of chain transfer to polymer [15].

Here, we studied the effect of surfactant (CTAB) concentration on the microemulsion polymerization of vinyl acetate. We report reaction rates, particles sizes and molar mass distributions (MMD) as a function of conversion and CTAB content in the parent microemulsions. We found unusual kinetic and colloidal behaviors and provided some possible explanations.

2. Experimental section

CTAB (99%+ pure from Aldrich) was re-crystallized from a 50/50 (v/v) acetone/ethanol mixture. Vinyl acetate (VA), with purity higher than 99% from Aldrich, was dried with CaCl_2 , distilled at 30 °C under reduced pressure and argon atmosphere, stored at 4 °C in dark vials and used within 30 h after distillation. 2,2'-Azobis(2-amidinopropane) dihydrochloride (V-50) from Wako Chem., was re-crystallized from methanol. Hydroquinone (99% pure from Aldrich) was used as received. Triple-distilled and de-ionized water was drawn from a Cole-Parmer ionic exchange system.

A 100-mL glass reactor with cooling jacket and magnetic stirring was employed for the reactions at 60 °C in microemulsions containing 4 wt% VA and varying weight ratios of CTAB/water. The concentration of V-50 was 0.3 wt% with respect to monomer in all the reactions. Prior to polymerization, the monomer and the aqueous solutions of CTAB and V-50 were degassed by cooling-pumping-and-heating cycles. The reacting system was continuously stirred during the entire reaction and purged with argon each time that a sample was taken. Conversion was determined gravimetrically as detailed elsewhere [15].

Particle size was measured at 25 °C and an angle of 90° in a Malvern 4700 quasielastic light scattering (QLS) apparatus equipped with an Argon laser ($\lambda=488$ nm). Intensity correlation data were analyzed by the method of cumulants. Latexes were diluted up to 100 times and filtered through

0.2 μm Millipore filters before QLS measurements to minimize particle-particle interactions and to remove dust particles.

To measure \bar{M}_w , \bar{M}_n and MWD by gel permeation chromatography (GPC), the surfactant was eliminated from the freeze-dried samples by dialysis. The surfactant-free polymer was recovered and then dissolved in HPLC-grade tetrahydrofuran (Merck), which was used as the mobile phase. The chromatographic equipment consisted of a Knauer HPLC64 pump, two PL-gel MIXED-B columns (Polymer Laboratories) and a Knauer differential refractometer as a detector. The GPC was calibrated with narrow polystyrene standards (Polymer Laboratories); the molar masses were calculated with the viscosimetric equation for poly(vinyl acetate) or PVA in THF, $[\eta] = 3.5 \times 10^{-4} \text{ M}^{0.63}$ [16]. This calibration was verified using PVA standards (Polymer Laboratories).

3. Results

Fig. 1 shows conversion vs. time curves for the polymerization at 60 °C of 4 wt% VA in oil in water microemulsions made with different CTAB/water ratios (4/96, 5/95, 6.25/93.75 and 7.5/92.5). The initially transparent microemulsions evolve into bluish-to-opaque latexes as the reaction proceeds. In all cases, reaction rates are fast and conversions higher than 90% are obtained in 20 min or less. Reaction rate decreases as the CTAB/water ratio is raised (inset in Fig. 1) and exhibits only two intervals, which is typical of microemulsion polymerization [17,18]. Within experimental error, the maximum reaction rate takes place at ca. 20% conversion independently of the CTAB/water ratio.

Fig. 2 shows the evolution of particle size as a function of the CTAB/water ratio. Particles become larger with increasing conversion and with increasing CTAB/water ratio. The biggest particles were obtained with the CTAB/water ratio of 7.5/92.5. From the particle size, the number density of particles, N_p , was estimated with the assumptions that particles are spherical and all have the same size. Fig. 3 reveals that N_p diminishes as reaction proceeds in all the polymerizations regardless of the CTAB concentration in the parent microemulsion. A similar behavior was reported for the polymerization of VA in microemulsions stabilized with CTAB and DTAB, alone or in mixtures of them at different weight ratios [15]. Fig. 3 also shows that N_p decreases with increasing CTAB/water ratio.

Table 1 reports \bar{M}_n and \bar{M}_w at the end of reaction for the different CTAB/water ratios in microemulsion and those obtained by emulsion polymerization with a CTAB/water ratio of 1/99. Here, \bar{M}_n does not change significantly with CTAB/water ratio, including that in emulsion. However, \bar{M}_w increases as the CTAB/water ratio increases for polymerizations in microemulsion, but it is much smaller than that obtained by emulsion polymerization. Table 2

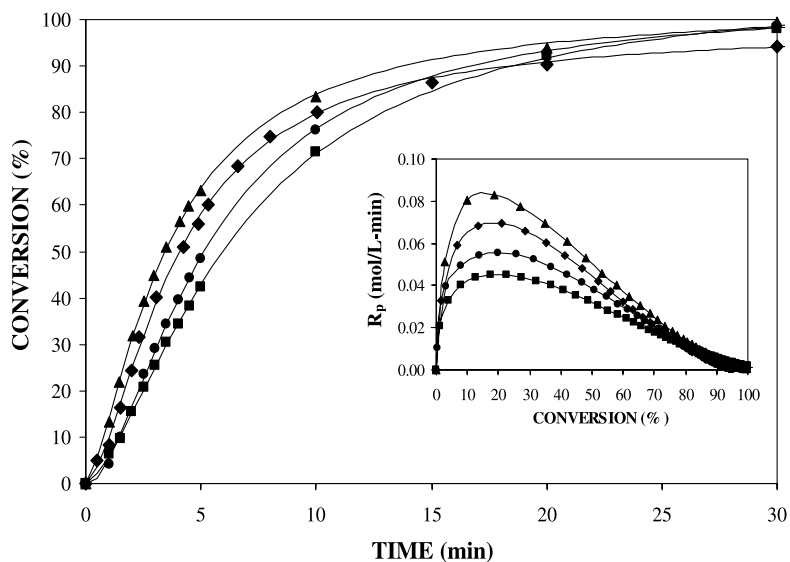


Fig. 1. Conversion vs. time for the polymerization at 60 °C of VA in microemulsions prepared with different CTAB/water weight ratios: (▲) 4/96; (◆) 5/95; (●) 6.25/93.75; (■) 7.5/92.5. Inset: polymerization rate as a function of conversion.

reports \bar{M}_w and the polydispersity indexes ($I_D = \bar{M}_w/\bar{M}_n$) as a function of conversion for the CTAB/water ratio of 5/95 and shows that both \bar{M}_w and I_D increase as reaction proceeds. The poly(vinyl acetate) average molar masses obtained in this work and in other microemulsion systems previously reported by us [3,6,15,19] are much lower than that reported in the polymerization of this monomer in an emulsion stabilized with CTAB in a surfactant/water ratio of 1/99 (Table 1) [20] and those reported elsewhere [4,5].

Fig. 4 displays the molar mass distributions (MMD) of the poly(vinyl acetate) obtained at final conversion for the different CTAB/water ratios, that of the poly(vinyl acetate) obtained by polymerization in the emulsion stabilized with CTAB as well as the theoretical MMD calculated by assuming that chain transfer to monomer is the only chain

growth termination mechanism. In the later case, $P(M)$ is given by [21]

$$P(M) = \exp[-k_{tr}M/(k_p M_0)] \quad (1)$$

where $P(M)$ is the number MMD, M is the polymer molar mass, $k_{tr,M}$ and k_p are the rate constants for chain transfer to monomer and for propagation, respectively, and M_0 is the monomer molar mass. For the calculation of the theoretical MMD, a value of 2.2×10^{-4} for $k_{tr,M}/k_p$ was employed, which is an average of the values at 60 °C reported in the literature [22].

The molar mass distributions of the polymers made by microemulsion polymerization shift to lower molar masses compared to the theoretical curve regardless of the CTAB/water ratio (Fig. 4), indicating that other

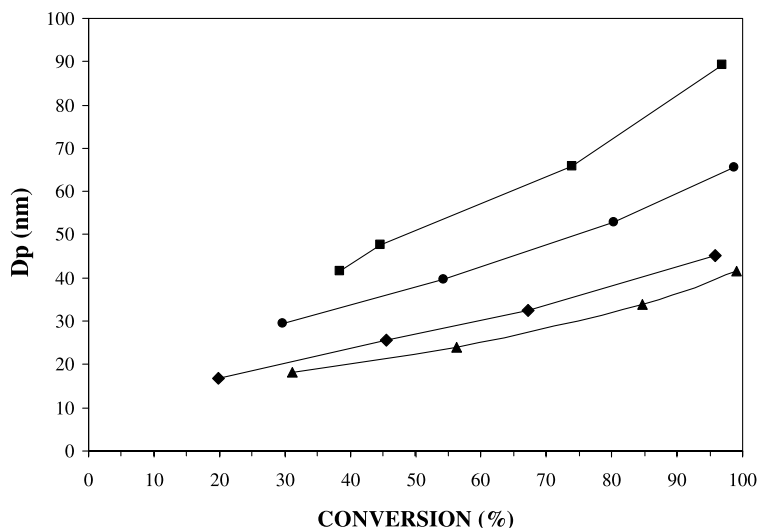


Fig. 2. Particle size as a function of conversion for the polymerization at 60 °C of VA in microemulsions prepared with different CTAB/water weight ratios: (▲) 4/96; (◆) 5/95; (●) 6.25/93.75; (■) 7.5/92.5.

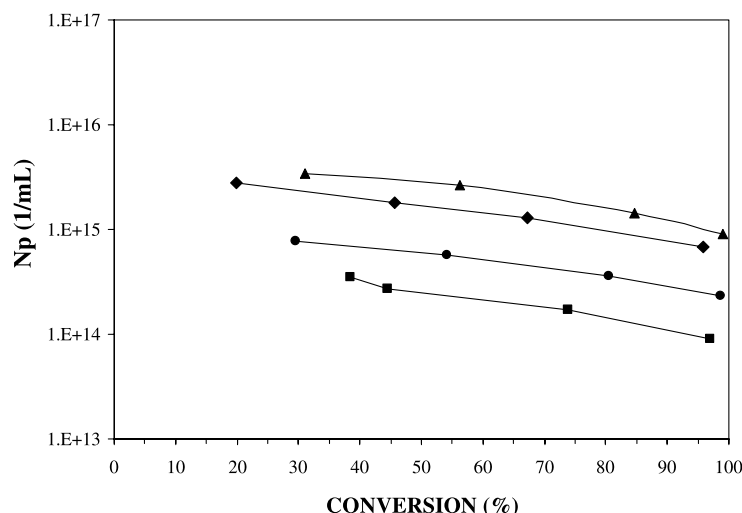


Fig. 3. Number density of particles vs. conversion for the polymerization at 60 °C of VA in microemulsions prepared with different CTAB/water weight ratios: (▲) 4/96; (◆) 5/95; (●) 6.25/93.75; (■) 7.5/92.5.

mechanisms besides chain transfer to monomer are operative in these systems. Moreover, the MMD of the polymer obtained with the lower CTAB/water ratios is unimodal; however, as the CTAB/water ratio is increased, a shoulder develops in the high molar-mass side of the distribution. By contrast, the MMD of the polymer made by emulsion polymerization, as a result of the well-known dominance of chain transfer to polymer in the emulsion polymerization of vinyl acetate [23], shifts to larger molar masses compared to those of the polymers made by microemulsion polymerization and the theoretical one calculated as if chain growth termination is only by chain transfer to monomer. Hence, the development of the shoulder as the CTAB content increases, suggests that chain transfer to polymer also contributes to chain termination in microemulsion polymerization of VA.

Fig. 5 shows the MMD at low, intermediate and high conversions for the CTAB/water ratio of 5/95. This figure reveals that a broadening of the MMD curves occurs as polymerization advances. Also as the reaction evolves, a shoulder develops at the high-molar mass side of the distribution and becomes quite noticeable at the end of the reaction.

4. Discussion

In all cases, reaction rates are fast and conversions higher than 90% are obtained in 20 min or less for all polymerizations regardless of the CTAB/water ratio (Fig. 1). The reaction rate decreases as the CTAB/water ratio is increased and within experimental error, the maximum reaction rate occurs at around 20% conversion independently of the CTAB/water ratio (inset in Fig. 1). As detailed elsewhere [24], the conversion at which the maximum reaction rate occurs is mainly related to the volume fraction of polymer at equilibrium within the particles.

To explain the inverse dependence of reaction rate with surfactant content let us examine the well-known equation for reaction rate in emulsion and microemulsion polymerization [21,24,25]. For these processes, the reaction rate, R_p , is given by $k_p[M]_p N_p \bar{n} / N_A$, where k_p is the propagation rate constant, $[M]_p$ is the volume fraction of monomer within the particles, \bar{n} is the average number of radicals per particle and N_A is Avogadro's number. Because all reactions reported here were made at the same temperature and with the same monomer, k_p must be the same. Also, the initial monomer content is identical in all reactions, hence the

Table 1
Number-average molar mass (\bar{M}_n), weight-average molar mass (\bar{M}_w) and polydispersity index (I_D) at final conversions

CTAB/water (w/w)	Conversion (%)	$\bar{M}_n \times 10^{-5}$ (g/mol)	$\bar{M}_w \times 10^{-5}$ (g/mol)	I_D
4/96 ^a	94.1	1.03	3.6	3.5
5/95 ^a	96.3	0.80	3.5	4.4
6.25/93.75 ^a	87.7	1.13	4.3	3.8
7.5/92.5 ^a	96.9	1.15	4.7	4.1
1/99 ^b	99.0	1.0	31.0	31

^a For the polymerization at 60 °C of VA in microemulsions.

^b For the polymerization at 60 °C of VA in microemulsions prepared with different CTAB/water ratios and in emulsion.

Table 2

Weight-average molar mass (\bar{M}_w) and polydispersity index (I_D) at different conversions for the polymerization at 60 °C of VA in a microemulsion made with a CTAB/water weight ratio of 5/95

Conversión (%)	$\bar{M}_w \times 10^{-5}$ (g/mol)	I_D
28.4	3.1	2.8
55.3	3.4	3.4
96.3	3.5	4.4

value of $[M]_p$ depends only on conversion; as a result, at a given conversion, $[M]_p$ is the same in all the reactions, independently of the CTAB/water ratio used. Hence, either \bar{n} or N_p (or both) must cause the dependence of reaction rates with CTAB/water ratio.

The average number of radicals per particle depends on the rates of radicals entering and exiting the particles. Assuming that at most only one radical is in a living particle, the probability of a radical entering a particle depends on the number of available radicals, N_p , and particle size. The probability of radical desorption from a particle, on the other hand, depends on the characteristic diffusion time of a monomeric radical on the length scale of the particle size and the time scale of propagation, which means that the probability of radical desorption diminishes as the particle becomes bigger.

Under these circumstances, \bar{n} can be estimated as $\bar{n} = R_p N_A / (k_p [M]_p N_p)$. Values of R_p and N_p at any conversion can be estimated from data in inset of Fig. 1 and those in Fig. 3, respectively. k_p was calculated as 5.04×10^5 l/mol-min from an Arrhenius type relation [26]. The value of $[M]_p$ at any conversion was estimated by assuming that the monomer volume fraction within the particles (ϕ) decreases linearly with conversion from its saturation value ($\phi_s = 0.85$ [27]) at the beginning of the polymerization [28] as follows, $\phi/\phi_s = 1 - x$. Then $[M]_p$ can be estimated from $[M]_p = \phi \rho_m /$

M_0 , where ρ_m (=820 g/l at 60 °C [29]) and M_0 are the density and the molar mass of the monomer, respectively.

Table 3 reports the estimated values of \bar{n} for the different CTAB/water ratios at conversions of 40 and 55%. The values of \bar{n} increase with increasing CTAB/water ratio but they are much smaller than 0.5 indicating that radical desorption is a frequent event, which is typical of microemulsion polymerization due to the small size of the particles commonly encountered in this process [24]. An increase in \bar{n} as the CTAB/water ratio is augmented should yield faster reaction rates, contrary to the experimental observations (inset in Fig. 1). Hence, only the dependence of N_p on the CTAB/water ratio can explain the decrease in reaction rate as the initial surfactant content is increased.

The increase in particle size (Fig. 2) and the decrease in N_p (Fig. 3) with increasing initial surfactant concentration appear to be counterintuitive because a larger number density of microemulsion droplets should be expected at the beginning of the reaction upon increasing the initial surfactant concentration; hence a larger probability for particle formation by micellar nucleation should be anticipated and, as a consequence, a larger number of particles of smaller size should be produced. However, vinyl acetate is quite soluble in water (2.6 wt% at 60 °C [23]) and because the amount of vinyl acetate in the microemulsions was only 4 wt%, the amount of monomer in the aqueous phase should decrease as the number of microemulsion droplets increases in order to maintain thermodynamic equilibrium. If the monomer concentration in the aqueous phase decreases, the propagation rate in the aqueous phase and the time for reaching the critical size for entering a microemulsion droplet (micellar nucleation) or for attaining the critical size for precipitation (homogeneous nucleation) should increase giving as result slower nucleation rates. Moreover, increasing the surfactant content produces more

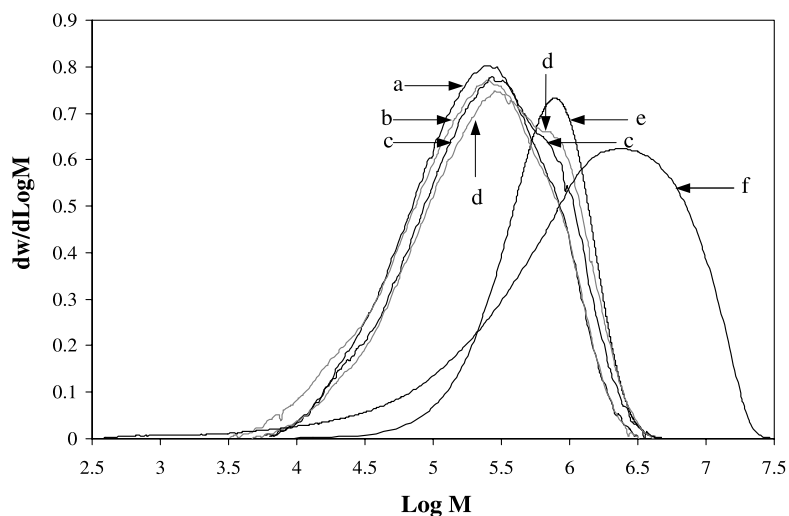


Fig. 4. Comparison of the final MMD's of the PVA polymers obtained by microemulsion polymerization (CTAB/water weight ratios: (a) 4/96; (b) 5/95; (c) 6.25/93.75; (d) 7.5/92.5) with the theoretical MMD calculated by assuming that termination occurs only by chain transfer to monomer (e) and the MMD of the PVA obtained by polymerization in an emulsion stabilized with CTAB (f).

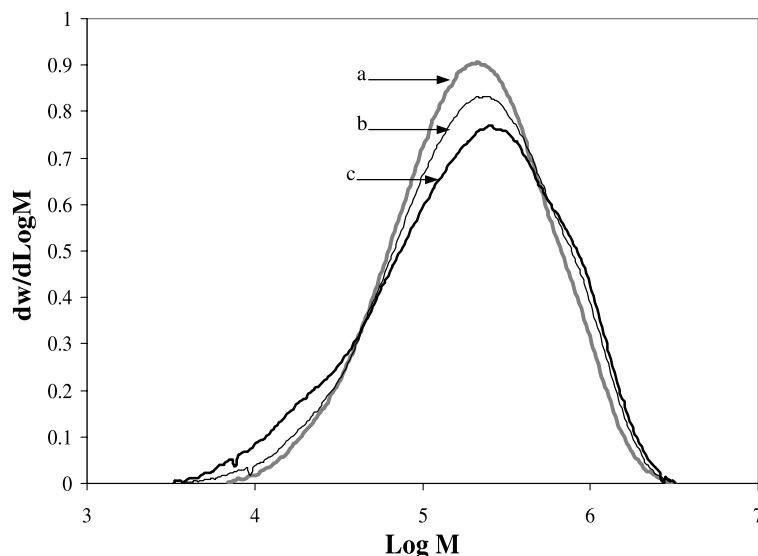


Fig. 5. MMD of PVA obtained by microemulsion polymerization with a CTAB/water weight ratio of 5/95. Conversion: (a) 28.4%; (b) 55.3%; (c) 96.3%.

micelles but since the monomer content is fixed, the swelling of each droplet is smaller. Hence, the probability that a non-initiated droplet with a small amount of monomer becomes empty is larger since according to Laplace's equation [30], the exiting flux of monomer from these non-initiated droplets becomes larger as the droplet size diminishes. This, in turn, increases the number of empty micelles and hence, it reduces the number of nucleation sites during the polymerization; as a consequence, a smaller number density of bigger particles should be obtained throughout the reaction. A lower number density of particles will give as a result a slower reaction rate. However, because in microemulsion polymerization, R_p is proportional to N_p , the decrease in reaction rate with decreasing N_p , should be two to three times smaller than the values reported in Fig. 1. Hence, the combining effects of \bar{n} and N_p on reaction rate can explain the decrease in reaction rate as the CTAB/water ratio is raised.

The observed N_p drop as the polymerization evolves, regardless of the amount of surfactant used, suggests a coagulation process. In fact, coagulation has been reported during the microemulsion polymerization of VA [15] and in emulsion polymerization of polar monomers [31,32].

Table 1 shows that within experimental error \bar{M}_n is nearly invariant to the CTAB/water ratio and that \bar{M}_w increases

with increasing CTAB/water ratio. Furthermore, \bar{M}_w of the polymers obtained by microemulsion polymerization is much smaller than that of the polymer obtained by the polymerization in an emulsion stabilized with CTAB (Table 1). The increase in \bar{M}_w can be explained by the larger particles obtained when a larger CTAB/water ratio was used, which causes the event of chain transfer to polymer to be more frequent because the characteristic exiting diffusion time of a monomeric radical increases with particle size; moreover, the number of polymer chains per particle (N_C) increases with increasing particle size (Table 4). Notice that both particle size and N_C increase with conversion and with CTAB/water ratio, which explains the increase in \bar{M}_w and the development of the shoulder with increasing CTAB/water ratio (Fig. 4) and with conversion, especially for the higher CTAB/water ratios (Fig. 5) since the probability for chain transfer to polymer increases. Of course, bimolecular termination by coagulation of two active particles can also lead to an increase in \bar{M}_w . In addition, \bar{M}_w is more sensible to changes in high molecular weights than \bar{M}_n , and so the latter does not change appreciably in our systems. When the poly(vinyl acetate) is obtained by emulsion polymerization, particles are bigger and N_C is also much larger and so, chain

Table 3

Average number of radicals per particle (\bar{n}) at two conversions for the polymerization at 60 °C of VA in microemulsions prepared with different CTAB/water ratios

CTAB/water (w/w)	\bar{n} (rad./part.)	
	$X=40\%$	$X=55\%$
4/96	0.005	0.006
5/95	0.007	0.009
6.25/93.75	0.017	0.021
7.5/92.5	0.030	0.041

Table 4

Particle diameter (D_p) and average number of polymer chains per particle (N_C) for the polymerization at 60 °C of VA in microemulsions prepared with different CTAB/water ratios at various conversions

CTAB/water (w/w)	Conversion (%)	D_p (nm)	N_C (chains/part.)
4/96	94.1	41.5	256
5/95	28.4	19.3	24
5/95	56.3	28.6	78
5/95	96.3	45.3	425
6.25/93.75	87.7	65.6	939
7.5/92.5	96.9	89.2	2160

transfer to polymer is more viable given as a result larger molar masses (Table 1). In fact, in the polymerization of vinyl acetate in emulsions and microemulsions stabilized with AOT [33], the MMD were narrower and the \bar{M}_w smaller in the latter process because the frequency of chain transfer to polymer was lower at high conversions than that in emulsion polymerization as a consequence of the smaller particle size (30 nm vs. >100 nm in diameter) and the smaller number of chains per particle (100 vs. 3920).

The average number molar masses obtained in the microemulsion polymerizations made with the different CTAB/water ratios are smaller than that expected if chain transfer to monomer were the only mechanism for chain termination (Table 2). Moreover, all the MMD are displaced to lower molar masses compared to that predicted if only chain transfer to monomer was operative regardless of CTAB/water ratio (Fig. 4) and degree of conversion (Fig. 5). This suggests that other mechanisms of termination that yield lower molar masses may be functioning. Termination in 0–1 systems with smaller \bar{M}_n than that expected from chain transfer to monomer can occur either by entry of a second radical to an active particle or by chain transfer to a chain transfer agent. Termination by the entry of a second radical to an active particle can be ruled out here because simple calculations indicate that the number of chains per radical in the polymerizations is large (≈ 100) and the probability of annihilation is very small. Hence, transfer to a chain transfer agent is the only possibility. Water is ruled out as a chain transfer agent and this leaves the surfactant as the possible responsible for chain termination.

Lee and Mallinson documented the possibility of chain transfer to surfactant in the polymerization of VA [34]. These authors found that the molar masses obtained when the emulsions were stabilized with AOT were lower than those obtained when SDS was employed. They concluded that the long hydrophobic tails of AOT probably provide a radical transfer site generating short polymer chains. In the case that the hydrophobic tails were the sites for chain transfer, this reaction would be also probable for CTAB as its tail is 16 C-atoms in length. Nevertheless, we cannot rule out the possibility that the site for chain transfer to be one of the methyl groups bonded to the polar head of CTAB. In any case, \bar{M}_n is practically constant for all the CTAB/water ratios. To explain this result, we calculated the local concentration of tails per particle for the different CTAB/water ratios. For these calculations values of 3 nm for the surfactant chain length of the tail (l) and 0.2 nm^2 for the interfacial area stabilized by one surfactant molecule (a_s) were taken from the literature [35]. The results showed that the local concentration of tails in the particles decreases only a little with increasing CTAB/water ratio: 3.2 and 3.0 mol/l for 4/96 and 7.5/92.5 ratios, respectively. So, if chain transfer to CTAB is real, it is expected that \bar{M}_n should practically remain constant with CTAB content as its local concentration in the particles is practically the same regardless of the CTAB/water ratio employed. The fact

that the value of \bar{M}_n obtained in the CTAB-emulsion polymerization of this monomer is similar to those obtained in microemulsion polymerization (Table 1) gives support to this hypothesis.

5. Conclusions

CTAB/water ratio on the parent microemulsion influences final particle size, average weight molar mass and MMD. Contrary to the expected, increasing CTAB concentration gives as a result bigger particles throughout the reaction. Furthermore, reaction rate decreases as the CTAB/water ratio is increased but the conversion at which the maximum reaction rate occurs does not change. Weight average molar masses are much lower than those obtained with emulsion polymerization, which indicates that chain transfer to polymer plays a smaller role in microemulsion polymerization of this monomer as a result of the smaller particle size. An unexpected result is that the \bar{M}_n obtained in microemulsion (regardless of the CTAB/water ratio) and emulsion polymerizations are lower than the value expected if chain transfer to monomer was the only termination mechanism. We speculate that the surfactant may act as a chain transfer agent. Particle coagulation and radical desorption are important events in the polymerization of VA in microemulsions stabilized with CTAB.

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