A Kinetic Description of the Free Radical Polymerization of Vinyl Acetate in Cationic Microemulsions

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ABSTRACT: The polymerization of vinyl acetate (VA) in three-component microemulsions stabilized with the cationic surfactant, cetyltrimethylammonium bromide (CTAB), is investigated as a function of concentrations of monomer and initiator (V-50) and temperature. Stable latexes containing small particles (35−50 nm) of poly(vinyl acetate) with average number molar masses of $(4-5) \times 10^5$ g/mol are obtained. Analysis of the molar mass distributions (MMD) indicates that the controlling chain growth termination mechanism is chain transfer to monomer, and *not* to polymer, which is the dominant termination mechanism for the emulsion polymerization of this monomer, especially at high conversions. Deconvolution of the MMD curves and measurement of the radius of gyration as a function of molar mass show that more than 80% of the final polymer is linear, produced by chain transfer to monomer, whereas the rest may be branched, probably formed by chain transfer to polymer or by terminal double bond reactions. The population of linear polymer decreases with decreasing reaction temperature, but it is independent of initiator and monomer concentrations.

Introduction

Emulsion and microemulsion polymerization are processes that are able to produce colloidal polymer particles of high molar mass with fast reaction rates because the reactions happen in compartmentalized loci.[1−5] However, the reaction kinetics of these two processes are different. In batch emulsion polymerization, typically three reaction rate intervals have been reported as a function of conversion.[1,2] In interval I, particles are generated and the reaction rate speeds up as the number of particles increases. This interval ends when the micelles disappear and there is no more surfactant available for stabilization of new particles. Interval II, characterized by a constant reaction rate, takes place until the emulsified monomer droplets—which maintain constant the concentration of monomer in the particles—vanish. In interval III, reaction rate decreases with time because the monomer in the particles diminishes until is depleted, as the reaction proceeds. In microemulsion polymerization, by contrast, reaction rate first increases, goes through a maximum, and then decreases continuously; i.e., there is no constant rate interval.[5] However, the absence of the constant rate period in the emulsion polymerization of styrene has been reported recently by reaction calorimetry.[6,7]

Other important differences are the following: (i) in emulsion polymerization, particles form only in early stages of the reaction whereas continuous particle nucleation is believed to occur in microemulsion polymerization;[5,8,9] (ii) in addition to micellar entry,[9,10] homogeneous nucleation also appears to be important in microemulsion polymerization even for the polymerization of water-insoluble monomers,[11] whereas this mechanism only occurs in the emulsion polymerization of fairly water-soluble monomers, such as vinyl acetate;[12] (iii) emulsion polymerization rate does not depend on overall monomer concentration (it only affects the duration of interval II)[1,2] whereas polymerization rate increases with increasing overall monomer concentration in the parent microemulsions;[10,13−16] and (iv) both latex particle size and average number of chains per particle are considerably smaller in microemulsion polymerization.[5]

There are other subtle differences between these two polymerization processes. For instance, the emulsion polymerization of tetrahydrofurfuryl methacrylate yields a cross-linked polymer whereas a branched poly(tetrahydrofurfuryl methacrylate) with a large molar mass (ca. 10^7 g/mol) is produced in microemulsion polymerization.[15] Also, isotactic poly(methyl methacrylate) is produced by free radical microemulsion polymerization whereas the atactic form is obtained in emulsion polymerization.[17]

The emulsion polymerization of vinyl acetate (VA) has been the subject of extensive research, and nowadays there is a good understanding of the mechanism and the kinetics of this process.[18−25] Experimentally it has been found that (i) interval I is very short probably because particles are generated by both homogeneous and micellar nucleation, which enhances the rate of nucleation; (ii) interval II ends at low conversions (15%);

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and (iii) polymerization rate is fairly constant between 20 and 85% conversion (interval III).[19,21] This unusual feature was explained in terms of the dependence on monomer concentration of chain transfer rate, which is the termination-determining process, that counterbalances the dependence of the overall polymerization rate on monomer concentration.[26] Moreover, in VA emulsion polymerization, transfer reactions to monomer and polymer as well as terminal double bond reactions control the molar mass distribution (MMD) at low radical fluxes, and so, MMD is independent of the number and size distribution of particles and of the initiator and emulsifier concentrations.[21] On the other hand, Badran et al. reported the effect of initiator and emulsifier concentration on MMD at high concentrations of a redox initiation system.[27]

By contrast, the polymerization of VA in microemulsion media has been scarcely examined. Nikitina et al.[28] reported the polymerization of VA in a Windsor type II system (VA/water/nonionic surfactant microemulsion in equilibrium with excess VA) and obtained latex particles between 15 and 55 nm. They claimed that diffusion of monomer from the organic phase to the reacting microemulsion medium was the controlling rate process. Donescu et al.[29−33] polymerized VA in four-component systems made of surfactant, cosurfactant, water, and VA and obtained poly(vinyl acetate) of relatively low molar mass (around 10^4 g/mol), probably because the reaction was carried out in the continuous phase where most of the VA was cosolubilized as a result of the large amount of cosurfactant (1-propanol) used (20−37 wt %).

In this paper the polymerization of vinyl acetate (VA) in ternary microemulsions stabilized with the cationic surfactant, cetyltrimethylammonium bromide (CTAB), is reported as a function of monomer and initiator concentrations and temperature. The polymer produced here appears to have a low degree of branching even at high conversions, in contrast to the highly branched poly(vinyl acetate) of large molar mass produced by emulsion polymerization. The hypothesis is that because of the small size of the reacting particles, the monomeric radicals produced by chain transfer to monomer can desorb rapidly from the particles, inhibiting in this way chain transfer reactions to polymer.

Experimental Section

CTAB (99% pure from Aldrich) was recrystallized from a 50/50 (v/v) mixture of acetone and ethanol. VA (Aldrich) was distilled at 30 °C under reduced pressure and argon atmosphere, stored at 4 °C in dark vials, and used within 30 h after distillation. Water was distilled and deionized. V-50 [2,2′-azobis(2-amidinopropane) dihydrochloride] from Wako Chem. was recrystallized from methanol.

A 100 mL glass reactor with magnetic stirring was employed to polymerize microemulsions made along a CTAB/H_2O ratio of 5/95 (w/w) and different amounts of VA. The concentration of V-50 was also varied. Prior to polymerization, the CTAB aqueous solution and the monomer were degassed by cooling, pumping, and heating cycles. The reacting system was continuously stirred and purged with argon during the reaction. Conversion was followed by gravimetry.

Particle size was measured by quasielastic light scattering (QLS) in a Malvern 4700 QLS apparatus equipped with an argon laser ($\lambda = 488$ nm). Measurements were performed at 25 °C and at an angle of 90°. Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate, $\langle \Gamma^2 \rangle$ ($=q^2D$), where $q = (4\Pi n/\lambda)\sin(\theta/2)$ is the scattering vector, n the index of refraction, and D the diffusion coefficient, and the variance, ν ($= [\langle \Gamma^2 \rangle - \langle G \rangle^2]/\langle G \rangle^2$), is a measure of the width of the distribution of the decay rate. The measured diffusion coefficients were represented in terms of apparent radii with Stokes' law and the assumption that the solvent has the viscosity of water. Latexes were diluted up to 100 times with water and filtered through 0.2 μm Millipore filters before QLS measurements to minimize particle−particle interactions and to remove dust particles.

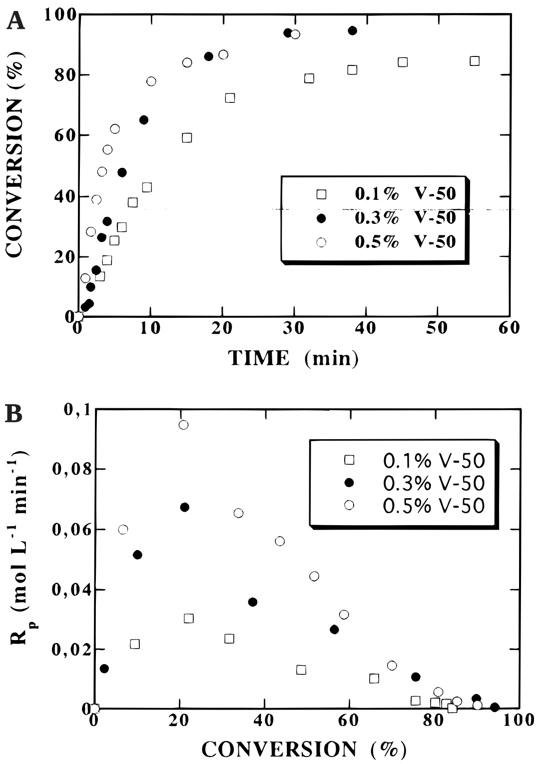

Figure 1. (A) Conversion versus time for the polymerization at 60 °C of microemulsions containing 4 wt % VA, 4.8 wt % CTAB, and 91.2 wt % water as a function of concentration of V-50 (in wt % with respect to monomer). (B) Reaction rate versus conversion as a function of initiator concentration.

Average molar masses and MMD were measured with a LC30 Perkin-Elmer gel permeation chromatograph (GPC) equipped with a refractive index and a Dawn multiangle light scattering detectors. Chromatographic grade tetrahydrofuran (Merck) was used as the mobile phase for MMD. A poly(vinyl) GPC standard from Polyscience ($M_n = 74\,000$ g/mol and $M_w = 234\,500$ g/mol) was used to verify the calibration curve and the response of the light scattering detector.

Results

Phase Behavior. The phase diagram of vinyl acetate (VA), water, and CTAB, reported elsewhere,[34] shows that one-phase microemulsions form near the water-rich corner of the phase diagram at 25 and 60 °C. Within this region, microemulsions are transparent and nonbirefringent (when examined through cross polarizers) and have low viscosities (a few centipoise) up to CTAB concentrations around 20 wt %. Above this concentration and within the one-phase region, samples are transparent and nonbirefringent but highly viscous. Microemulsion conductivities are high, suggesting that they are of the oil-in-water (o/w) type; i.e., they consist of micelles swollen with VA dispersed in a saturated aqueous solution of CTAB and VA.[34]

Kinetics. Plots of conversion versus time as a function of V-50 concentration are shown in Figure 1A. Reaction rates are fast, and conversions near 100% are achieved in a few minutes. The initially transparent microemulsions become bluish at the onset of reaction

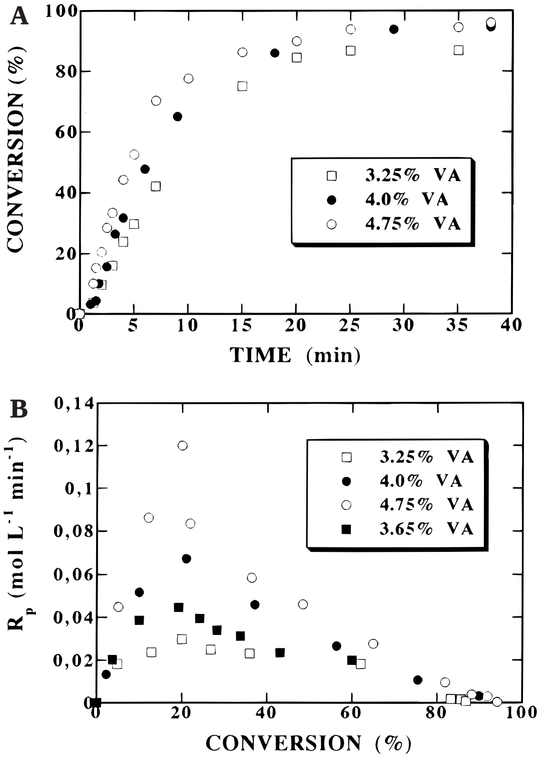

Figure 2. (A) Conversion versus time for the polymerization initiated at 60 °C with 0.3% V-50 of microemulsions made along a CTAB/H_2O weight ratio of 5/95 containing different VA concentrations (in wt %). (B) Reaction rate versus conversion as a function of VA concentration in the parent microemulsions.

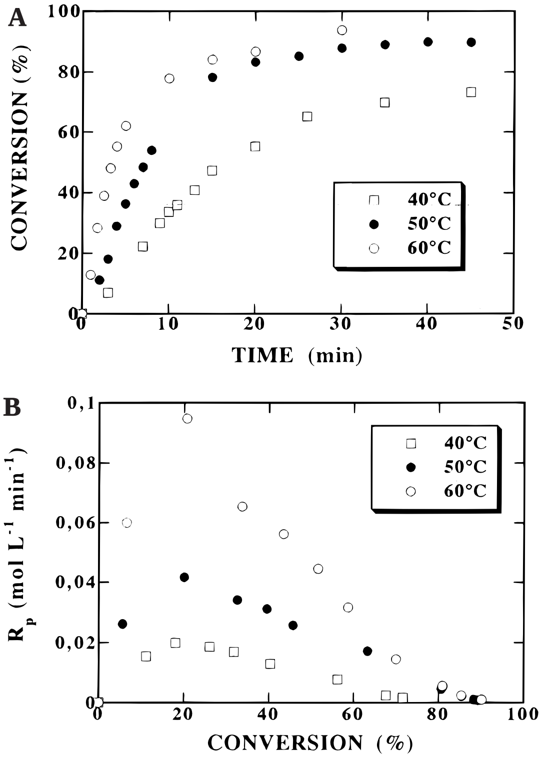

Figure 3. (A) Conversion versus time for the polymerization initiated with 0.5% V-50 of microemulsions containing 4.8 wt % CTAB, 4 wt % VA, and 91.2 wt % water as a function of temperature. (B) Reaction rate versus conversion as a function of temperature.

Table 1. Number-Average Molar Mass, Particle Size, Number Density of Particles, and Average Number of Polymer Chains per Particle as a Function of Initiator Concentration for Various Conversions

[V-50] (%)	conv (%)	$M_n \times 10^{-3}$ (g/mol)	D_p (nm)	$N_p \times 10^{-15}$ (mL^{-1})	N_c
0.10	21.3	515	34.7	1.86	15
0.10	47.3	509	43.2	0.86	26
0.10	86.4	503	48.7	0.57	72
0.30	38.0	480	35.4	1.57	12
0.30	57.3	494	38.8	1.15	25
0.30	91.4	488	46.1	0.68	67
0.50	22.4	470	37.2	1.43	8
0.50	52.2	483	46.0	0.71	39
0.50	93.8	480	48.3	0.58	84

and then increasingly turbid as the reaction is carried out. At the end of the reaction, the latexes are opalescent and turbid. These latexes are very stable— they have not given signs of precipitation after a few months of storage. Reaction rates increase with increasing initiator concentration and exhibit only two rate intervals (Figure 1B), which is typical of microemulsion polymerization.[5] The conversion (x_{max}) where polymerization rate goes through a maximum, $R_{p_{max}}$, occurs at the same value regardless of the concentration of initiator employed. From the slope of a double logarithm plot of $R_{p_{max}}$ versus initiator concentration, it was inferred that $R_{p_{max}} \propto [V\text{-}50]^{0.69}$.

Conversion versus time is shown in Figure 2A for the polymerization of the parent microemulsions containing different concentrations of monomer. Higher conversions and faster reaction rates are observed as the concentration of VA in the parent microemulsions increases. The plots of polymerization rate versus conversion reveal only two intervals again with x_{max} remaining at the same value, regardless of the monomer concentration in the parent microemulsions (Figure 2B). From a double logarithm plot of $R_{p_{max}}$ against VA concentration, it was found that $R_{p_{max}} \propto [VA]^{3.49}$.

Figure 3A depicts conversion as a function of time for reactions accomplished at three different temperatures. Higher conversions and faster reaction rates are achieved by increasing the temperature of reaction. Again, only two reaction rate intervals are detected (Figure 3B). The plot of the logarithm of $R_{p_{max}}$ versus the reciprocal of the absolute temperature (not shown) gives a straight line (with a correlation index of 0.999), which demonstrates that an Arrhenius behavior is followed. From the slope of this plot, an activation energy (E_a) of 69 kJ/mol was estimated.

Latex Characterization. Particle size (D_p), number-average molar mass (M_n), number density of particles (N_p), and average number of polymer chains per particle (N_c) at various conversions are reported in Table 1 for the reactions initiated with different V-50 concentrations. N_p was estimated from the conversion data and the z-average particle size (measured by QLS) with the assumption that all the particles have the same size; N_c was calculated from N_p and the supposition that all polymer chains have a molar mass equal to M_n. Particles are small and grow as the reaction proceeds regardless of the level of V-50 concentration; however, the final particle size is independent of initiator concentration. Molar masses decrease slightly with increasing initiator concentration. N_p, in turn, diminishes as conversion increases, suggesting that coagulation plays a role in the polymerization kinetics. N_c is small (Table 1), which is a characteristic of microemulsion polymerization,[5] but

Table 2. Number-Average Molar Mass, Particle Size, Number Density of Particles, and Average Number of Polymer Chains per Particle as a Function of Temperature for Various Conversions

T (°C)	conv (%)	$M_n \times 10^{-3}$ (g/mol)	D_p (nm)	$N_p \times 10^{-15}$ (mL^{-1})	N_c
40	26.2	577	32.9	1.32	8
40	43.2	587	29.9	2.05	9
40	73.2	580	35.9	1.33	23
50	25.9	583	29.7	2.15	5
50	48.2	588	34.7	1.48	14
50	89.7	583	42.0	0.88	44
60	22.4	470	37.2	1.43	8
60	52.2	483	46.0	0.71	39
60	93.8	480	48.3	0.58	84

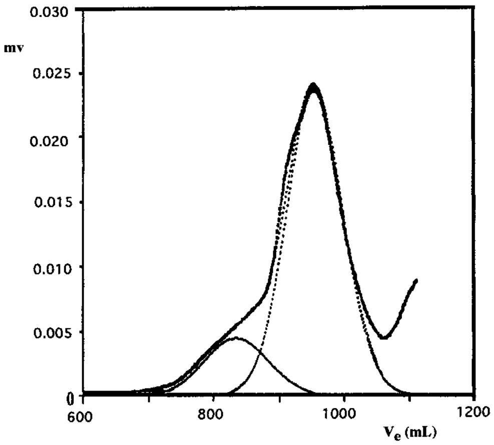

Figure 4. Typical GPC molar mass distribution and Gaussian curves obtained from deconvolution for a poly(vinyl acetate) obtained by polymerization in CTAB microemulsion.

it increases as reaction develops probably as a result of particle coagulation.

Table 2 reports D_p, M_n, N_p, and N_c at various conversions for the polymerizations carried out at different temperatures. Again, particles are small but grow with increasing conversion or reaction temperature most likely due to coagulation. Moreover, N_p decreases upon increasing temperature since the rate of coagulation is enhanced by raising the temperature. Molar masses are fairly independent of conversion, but they diminish as the temperature of reaction is raised. N_c, in turn, increases with increasing conversion or reaction temperature as a consequence of the decrease in the number density of particles probably due to coagulation.

A representative GPC chromatogram of PVA obtained at high conversions is shown in Figure 4, where a bimodal MMD is observed. By deconvolution, the MMD was fitted to two Gaussian distributions, from which the number-average molar mass, M_{ni}, and the relative areas under each curve, δ_i ($\equiv A_i/A_T$, where A_i is the area of the Gaussian curve i and A_T is the area under the whole MMD), were estimated. Results reported in Tables 3 and 4 show that the relative area of the low MMD curve is larger than that of the high MMD curve and that the average molar masses are fairly independent of conversion and initiator concentration (Table 3). However, average molar masses and δ_i's vary with temperature (Table 4). Notice that the number-average molar mass of the high MMD curve is nearly twice that of the low MMD curve.

Molar mass distributions (MMD) of PVA obtained at different conversions are shown in Figure 5. At low conversions, the MMD is symmetric and narrow. As conversion increases, the MMD broadens and a second peak (seen as a shoulder) appears at the higher molar mass side of the distribution. Also, the high molar mass peak increases with increasing conversion.

Table 3. Relative Areas and Number-Average Molar Masses of the Gaussian Distribution Curves Obtained by Deconvolution of the Whole MMD for Various Initiator Concentrations

[V-50] (%)	conv (%)	δ_2 (%)	$M_{n2} \times 10^{-3}$ (g/mol)	δ_1 (%)	$M_{n1} \times 10^{-3}$ (g/mol)
0.10	86.4	22.7	715	77.3	448
0.30	35.4	18.5	864	81.5	390
0.30	62.1	17.9	846	82.1	427
0.10	91.4	20.2	790	79.8	412
0.50	93.8	14.3	790	85.7	428

Table 4. Relative Areas and Number-Average Molar Masses of the Gaussian Distribution Curves Obtained by Deconvolution of the Whole MMD as a Function of Reaction Temperature

T (°C)	conv (%)	δ_2 (%)	$M_{n2} \times 10^{-3}$ (g/mol)	δ_1 (%)	$M_{n1} \times 10^{-3}$ (g/mol)
40	73.2	37.0	893	63.0	407
50	89.7	34.4	872	65.6	431
60	93.8	14.3	790	85.7	428

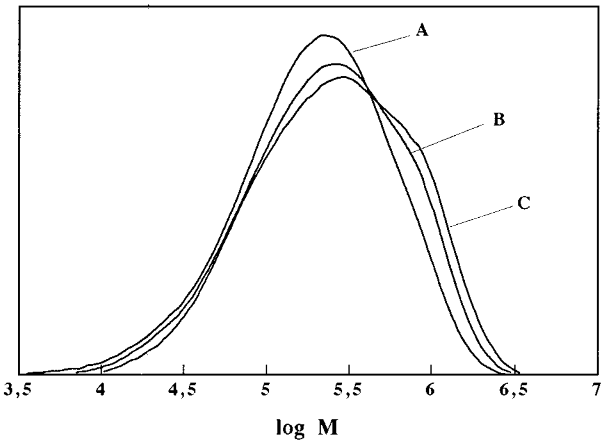

Figure 5. MMD of poly(vinyl acetate) obtained at various conversions from the polymerization in a CTAB microemulsion: (A) 19%; (B) 57%; (C) 93%. Reaction was carried out at 60 °C with 1 wt % V-50 (with respect to VA concentration).

The radii of gyration as a function of the molar mass for the PVA produced in this work and for a commercial PVA standard are shown in Figure 6. The radii of gyration of both samples are similar up to a molar mass close to 8×10^5 g/mol, but then the radii of gyration of our sample become smaller than those of the standard.

Discussion and Conclusions

The polymerization of vinyl acetate in three-component o/w microemulsions stabilized with CTAB is fast, and high conversions (>90%) are achieved in a few minutes (Figures 1−3). The initially transparent o/w microemulsions become bluish at the onset of particle nucleation and increasingly turbid as the reaction proceeds because of particle growth and the increase in refractive index contrast between the particles and the aqueous phase as monomer changes into polymer. The turbidity of the stable latexes depends on the level of monomer and initiator concentrations employed and on the temperature of reaction.

Faster reaction rates and higher conversions are attained with increasing initiator concentration (Figure

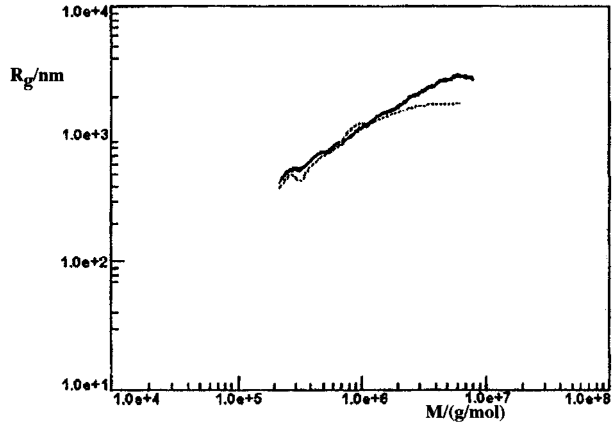

Figure 6. Radius of gyration as a function of molar mass for poly(vinyl acetate) synthesized in this work (- - -) and for a commercial standard one (—).

1) because the larger free radical flux induces a faster particle nucleation rate that speeds up the reaction. Likewise, reaction rate and conversion increase as the concentration of monomer in the parent microemulsion is raised (Figure 2). Inasmuch as the initial aqueous monomer concentration in these microemulsions is at saturation, the probability of radical capture by the monomer molecules in the aqueous phase should be about the same. Then, the increase in overall reaction rate with increasing monomer concentration should be the result of the increase in size and number of the initial microemulsion droplets, which enhances the probability of radical capture by the droplets.

Temperature has a strong effect on reaction rate and conversion because both the initiator decomposition rate constant (k_I) and the VA propagation rate constant (k_p) increase with increasing temperature (Figure 3). The activation energy (69 kJ/mol), obtained from an Arrhenius plot, is similar to the value reported by Badran et al. (65.6 kJ/mol) for the emulsion polymerization of VA initiated with a redox system.[27]

In contrast to emulsion polymerization, only two reaction rate intervals are observed here, which is a typical feature of microemulsion polymerization.[5] The polymerization rate first increases rapidly because of the fast particle nucleation rate, and then it decreases steadily after passing through a maximum, because monomer concentration within the particles begins to diminish as a result of the disappearance of the microemulsion droplets and/or the monomer dissolved in the aqueous phase—the latter is important for the polymerization of more water-soluble monomers such as VA.

Within the experimental error, the maximum reaction rate ($R_{p_{max}}$) occurs at similar conversions ($x_{max} \approx 20 \pm 2\%$) regardless of the V-50 concentration (inset in Figure 1), VA concentration (inset in Figure 2), or reaction temperature (inset in Figure 3). In addition to the experimental error, another uncertainty in the position of x_{max} is introduced by the numerical differentiation process due to the small number of data points taken at low conversions, where the reaction rate increases rapidly. Nevertheless, for the microemulsion polymerization of several other monomers, x_{max} does not depend on the level of initiator or monomer concentration.[9–11,13–16,35]

The maximum reaction rate for the polymerization of VA reported here depends on initiator and monomer concentration as $R_{p_{max}} \propto [\text{initiator}]^{\alpha}$ and $R_{p_{max}} \propto [\text{monomer}]^{\beta}$, where $\alpha = 0.69$ and $\beta = 3.49$. A power dependency of $R_{p_{max}}$ on initiator and monomer concentrations has also been documented for the microemulsion polymerization of styrene and various acrylic and methacrylic monomers.[10,13,14,35,36] The value of α (=0.69) is similar to those reported for other monomers;[35,36] however, the value of β (=3.49) is much larger than those reported in the literature for styrene ($\beta = 1$)[10,35] and methyl methacrylate ($\beta = 1.3$).[13]

Table 5. Particle Size and Number Density of Particles Measured at Intermediate Conversions for the Polymerization of VA in Microemulsions Containing Different Initial Monomer Content

[VA] (%)	conv (%)	D_p (nm)	$N_p \times 10^{-15}$ (mL^{-1})
3.25	43	37.7	1.05
4.0	38	35	1.57
4.75	24.6	33.6	2.31

According to models forwarded for microemulsion polymerization,[9,11,37] reaction rate can increase by increasing one or a combination of the following factors: (i) number of particles, (ii) concentration of monomer within the active particles, and (iii) the average number of free radicals per particle. It is unlikely that the last two factors can change significantly with the initial content of monomer, particularly at the conversions (ca. 20%) where $R_{p_{max}}$ occurs. However, the number of particles may depend on the initial monomer content, especially at low conversions, since the number and size of the droplets depend on the monomer concentration in the parent microemulsions.[38] To examine the role of this factor, we estimated the number density of particles at intermediate stages of reaction for the polymerization of microemulsions containing different initial monomer concentrations (Table 5). A double logarithm plot of N_p versus VA concentration (not shown) reveals that $N_p \propto [\text{VA}]^2$. Inasmuch as the actual number density of particles is underestimated because of the approximations made in calculating N_p—mainly that QLS weighs more larger particles than smaller ones—then the power dependency of N_p on VA concentration may be larger than 2. That β augments as the monomer solubility in the aqueous phase increases (1.0 for styrene, 1.3 for MMA, and 3.49 for VA) suggests that both micellar (microemulsion droplets) and homogeneous nucleation mechanisms play important roles in microemulsion polymerization. With water-insoluble monomers, such as styrene, most of the monomer is solubilized within the microemulsion droplets, and as the initial monomer concentration in the parent microemulsion increases, the number and size of such droplets become larger, which increases the probability of micellar nucleation rate. This, of course, leads to faster reaction rates. However, with more water-soluble monomers, such as methyl methacrylate and vinyl acetate, an important amount of the total content is dissolved in the aqueous phase. Hence, we postulate that for this type of monomer, even though homogeneous nucleation dominates, the role of micellar (droplets) nucleation becomes increasingly more important as the initial monomer concentrations in the parent microemulsions increase, since the concentration of monomer dissolved in the aqueous phase is insensitive to the initial monomer content.

Another unusual feature of the microemulsion polymerization reported here is the much lower M_w's and narrower MMD's obtained even at high conversions, contrary to findings in emulsion polymerization of VA.

In the batch emulsion polymerization of this monomer, transfer reactions to monomer and polymer as well as terminal double bond reactions control the MMD. At low conversions, termination reactions are mainly due to chain transfer to monomer which produce a $M_n \approx (3-5) \times 10^5$ g/mol and a low MMD polydispersity; however, at conversions larger than about 30%, chain transfer to polymer and terminal double bond reactions lead to a high polydispersity ($M_w/M_n \approx 10-15$) and a branched polymer structure, particularly at high conversions, where the reacting particles contain a high number density of macromolecules.[19−22]

The number-average molar mass of a polymer produced in a free radical polymerization can be estimated from the ratio of the propagating to the terminating events, as follows:[39]

$$\frac{1}{X_n} = \frac{k_t[M^\bullet]}{k_p[M]} + \frac{k_{tr,M}}{k_p} + \frac{k_{tr,A}[A]}{k_p[M]}$$

where X_n is the number-average degree of polymerization, k_p, k_t, $k_{tr,M}$, and $k_{tr,A}$ are the rate constants for propagation, bimolecular termination, transfer to monomer, and transfer to a transfer agent, respectively, and [M], [M$^\bullet$], and [A] are the concentrations of monomer in the particles, of radicals, and of transfer agent, respectively. Bimolecular termination reactions are rare events in emulsion and microemulsion polymerization,[2,9,11] and since no transfer agent was used in this work, the above equation reduces to

$$\frac{1}{X_n} = \frac{k_{tr,M}}{k_p}$$

With the values of $k_{tr,M}$ [$=(4.03-6.44) \times 10^{-4}$ m^3/(mol s)] and of k_p [$=2.3$ m^3/(mol s)] for VA at 60 °C taken from the literature,[39,40] M_n was estimated to be $(3.1-4.9) \times 10^5$ g/mol. The number-average molar masses obtained in this work (Tables 1 and 2) fall within this range, suggesting that chain transfer reactions to monomer control chain termination in the microemulsion polymerization of vinyl acetate, *even* at high conversions. In fact, we reported recently that the average molar masses and the MMD polydispersities of poly(vinyl acetate) synthesized in CTAB microemulsions were independent of the concentration of initiator (V-50), and from a plot of the instantaneous number MMD, $P(M)$, versus the molar mass, M, we concluded that chain transfer to monomer was the controlling mechanism for chain termination, even at high conversions.[34]

However, the MMD curves for the poly(vinyl acetate) obtained at final conversions in this work are bimodal (Figure 4). By deconvolution, two Gaussian distribution curves were obtained from the MMD. By considering that each distribution is independent of the other, an average-number molar mass for each curve was calculated. Results shown in Tables 3 and 4 suggest that at least two different chain termination mechanisms are taking place. The number-average molar mass of the low MMD curve (M_{n1}) is clearly within the molar mass range which should be produced by chain transfer to monomer. By contrast, the number-average molar mass of the high MMD curve (M_{n2}) is outside the theoretical range of termination by chain transfer to monomer. In fact, the MMD is almost unimodal at low conversions with average molar masses expected from termination by chain transfer reactions to monomer (Figure 5). However, as conversion increases, the MMD becomes bimodal, and the relative area under the high MMD curve (δ_2) increases from 8% at 57% conversion to 18% at 93% conversion (Figure 5). Moreover, the radii of gyration of the PVA produced in this work are similar to those of a PVA standard for molar masses close to 8×10^5 g/mol (Figure 6). That the radii of gyration of our samples are smaller than those of the standard above this limit indicates that the high molar mass poly(vinyl acetate) is in a more compact, probably branched, structure. Branching in poly(vinyl acetate) occurs mainly by chain transfer reactions to polymer, whereas the polymer formed by chain transfer reactions to monomer exhibits a very low degree of branching.[41] We propose that chain transfer to polymer and termination reactions by combination induced by particle coagulation are responsible for the high MMD curve and branching.

Our hypothesis is the following: due to the small size of the polymer particles, there is a large probability that a radical produced by chain transfer to monomer escapes. In fact, Guo et al. reported that the exiting probability of a monomeric radical is much larger in the microemulsion polymerization of styrene than that observed for the emulsion polymerization of the same monomer.[9] However, as particles grow because of coagulation between active and nonactive particles, the exiting probability of the monomeric radicals diminishes, and hence, the probability of termination by chain transfer to polymer increases. Of course, the collision and coagulation of two active particles should lead to a dead chain by instantaneous combination.

That the population of the high molar mass species decreases as the temperature of reaction is increased (Table 4) suggests that chain transfer to polymer plays a more important role than bimolecular termination reactions since the latter should be enhanced by an increase in temperature because of the increase in the rate of collision of active particles, and this should cause a growth of the population of the high MMD curve. However, the opposite behavior is observed (Table 4). On the other hand, the values of the activation energies of the rate constants for chain transfer to monomer (E_a = 41.6 kJ/mol) and for chain transfer to polymer (E_a = 37.7 kJ/mol) indicate that the former is more sensitive to temperature, and hence, reactions of chain transfer to polymer become more important as the reaction temperature is decreased. Hence, the rise in the value of M_{n2} and of δ_2 with decreasing temperature demonstrates that chain transfer to polymer also contributes to chain termination, but to a lesser degree than in emulsion polymerization.

The key factor in this behavior appears to be the smaller size of the microemulsion-made particles compared to the emulsion-made particles. In fact, when VA is polymerized in AOT microemulsions, the particle size is even smaller (20−30 nm) than those achieved here, and the MMD is symmetric with a M_n of $(3-4) \times 10^5$ g/mol.[42,43] On the other hand, when VA is polymerized in microemulsions stabilized with a mixture of dodecyltrimethylammonium bromide (DTAB) and didodecyldimethylammonium bromide (DDAB) in a weight ratio of 3, larger particles (70−110 nm) and a bimodal MMD were obtained, but the population of the high MMD, using the criterion of the area under the curve, was larger than that of the low MMD curve.[44] The latter one has values of M_n around 5×10^5 g/mol, indicating than chain transfer to monomer still plays a role, but a minor one, in chain termination for the microemulsion polymerization of this monomer.

In conclusion, the synthesis of poly(vinyl acetate) with a low degree of branching can be achieved by free radical polymerization in CTAB microemulsions. Stable latexes containing small particles (35−50 nm) of polymer with a number-average molar mass of 5 × 10^5 g/mol are obtained. From the analysis of the MMD, we propose that reactions of chain transfer to monomer are the main mechanism for chain termination and that chain transfer to polymer, induced by particle coagulation and growth, is the secondary mechanism of chain termination. To prove conclusively that chain transfer to monomer and not to polymer controls the MMD and that the poly(vinyl acetate) produced here contains a small degree of branching, even at high conversions; ^{13}C NMR analyses are underway following the method reported elsewhere.[41]

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