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Polymerization of vinyl acetate in microemulsions stabilized with a mixture of dodecyltrimethylammonium bromide and didodecyldimethylammonium bromide

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Summary

Polymerization of vinyl acetate (VA) in three component oil/water (o/w) microemulsions stabilized with a mixture of two cationic surfactants (DTAB/DDAB in a weight ratio of 3), was carried out at 40, 50 and 60°C using a water soluble initiator, V-50. In all cases studied, stable latexes containing particles with diameters between 70 and 110 nm were obtained. Particle size increased with conversion yielding uncommonly large particles for microemulsion polymerization, probably because particle coagulation. Multimodal molar mass distributions with average molar masses between 1.2 to 2.0×10^6 g/mol were obtained. Chain transfer to polymer and bimolecular termination reactions play important roles in the microemulsion polymerization of this monomer.

Introduction

Microemulsion polymerization is an alternative process to emulsion polymerization because is possible to obtain latexes containing polymeric nanoparticles of high molar mass (1). However, the kinetics of these two processes are different (1). In classical emulsion polymerization, three-reaction rate intervals (i.e., nucleation, propagation and termination) are typically observed. Moreover, particles are generated only during the first interval and the final latexes contain particles usually greater than 100 nm (2). In contrast, only two rate intervals have been reported in microemulsion polymerization (1). In addition, continuous nucleation of particles occurs and the final latexes contain particles with diameters smaller than 50 nm (1).

Because of the important applications of the poly(vinyl acetate) latexes, the emulsion polymerization of vinyl acetate (VA) has been investigated exhaustively (3-8). However, the microemulsion polymerization of this monomer has been scarcely studied. Donescu et al., reported the microemulsion polymerization of VA in transparent systems made of VA, water, surfactant and alcohol and obtained polymer of low molar mass ($\approx 10^4$ g/mol) because their systems were not true microemulsions but cosolubilized systems (9-12). Recently, we reported the polymerization of VA in true o/w microemulsions, using cetyltrimethylammonium bromide (CTAB) as surfactant (13). We obtained latexes containing particles with diameters smaller than 50 nm and molar masses around 2.0-4.5×10^5 g/mol. We also found that particle coagulation occurs during the reaction.

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In this work we report the polymerization of VA in o/w microemulsions stabilized with a mixture of dodeciltrimethylammonium bromide (DTAB) and didodecildimethylammonium bromide (DDAB) as a function of initiator (V-50) concentration and temperature.

Experimental

DTAB (Aldrich) was recrystallized from a 50/50 (v/v) mixture of acetone and ethanol. DDAB (Aldrich) was first recrystallized from a 90/10 (v/v) mixture of acetone and ethyl ether and then from ethyl acetate. 2,2′-azobis(2-amidinopropane) dihydrochloride or V-50 (Wako Chem.) was recrystallized from methanol. VA (Aldrich) was distilled at 30°C under reduced pressure and argon atmosphere, stored in dark vials and used within 30 hours after distillation. Water was deionized triple-distilled grade. Microemulsions containing 4 wt% VA, 1.2 wt% DDAB, 3.6 wt% DTAB and 91.2 wt% H_2O, were polymerized in a 100-mL glass reactor with magnetic stirring, at 40, 50 and 60°C, using various V-50 concentrations (0.3, 0.5 and 0.9 wt% with respect to monomer). Prior to the reaction, VA and the aqueous solution of surfactants and initiator were degassed by cooling-and-pumping cycles. Conversion to polymer was determined by gravimetry. Reaction rates, R_p, were calculated by numerical differentiation of the conversion versus time data. Particle size was determined in a Malvern 4700 quasielastic light scattering apparatus. Average molar masses and molar mass distributions (MMD) were obtained in a Perkin Elmer LC30 gel permeation chromatograph (GPC), equipped with a refractive index detector and a multiangle light scattering detector (Wyatt Technology).

Results and discussion

Figure 1 shows conversion versus time for the microemulsion polymerization of VA initiated with different initiator concentrations. Final conversions are greater than 95% and practically independent of V-50 concentration. Reaction rates increase with increasing initiator concentration (inset in Fig. 1) because the higher flux of free radicals with increasing V-50 concentration increases the probability of particle generation and of radical entry in non-active particles. Only two reaction rate intervals are detected, with a maximum in reaction rate (R_{pmax}) occurring at about the same conversion, regardless of the level of V-50 used (inset in Fig. 1). Similar results have been documented for the microemulsion polymerization of styrene (14), tetrahydrofurfuryl methacrylate (15), methyl methacrylate (16) and butyl methacrylate (17). R_{pmax} varies with the concentration of V-50 to the 0.5 power. This exponent is smaller than that (0.7) reported for the polymerization of VA in CTAB microemulsions (13). Maximum reaction rates obtained in this work (0.03-0.06 mol/L-min) are smaller than those reported for the CTAB microemulsions (0.060-0.10 mol/L-min) (13).

Table 1 shows that particle size (D_p) decreases with increasing V-50 concentration and increases with conversion independently of V-50 concentration. In the microemulsion polymerization of monomers with rather low water solubility, such as styrene and butyl methacrylate, particle size increases at earlier stages of reaction and then it remains practically constant throughout the reaction (17,18). A slight increase in particle size during the course of reaction has been reported for the polymerization of more water-soluble monomers, such as methyl methacrylate (16). In our case the large increase in particle size with conversion may be caused by coagulation.

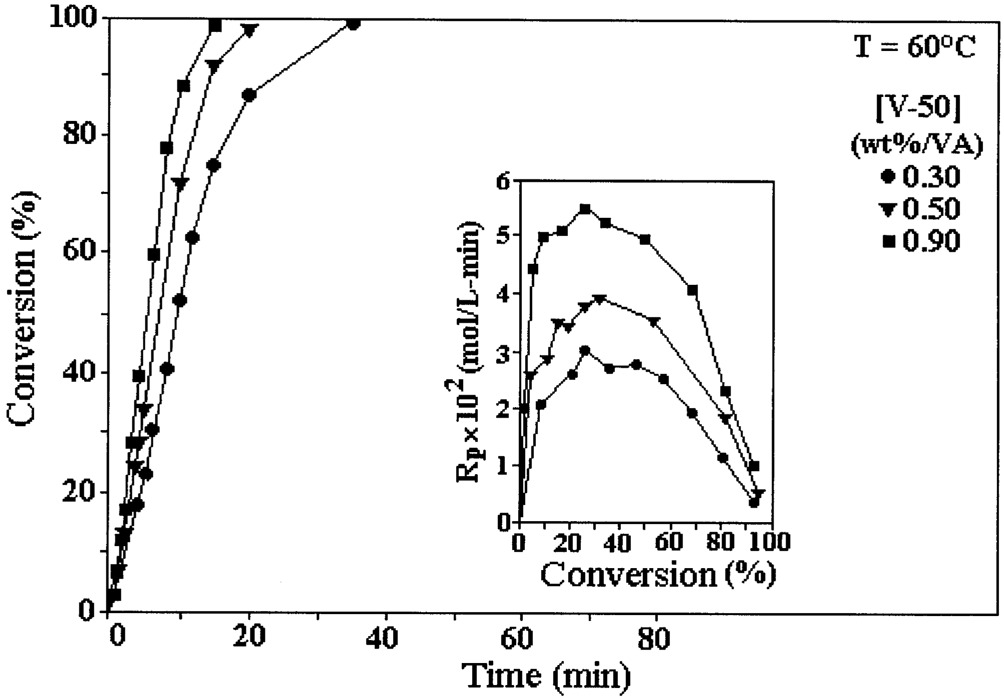

Figure 1. Conversion versus time as a function of V-50 concentration for the micromulsion polymerization of VA. Inset: Polymerization rate versus conversion for data shown in figure.

Table 1. Particle diameter and the number density of particles for the microemulsion polymerization of VA with different V-50 concentrations and different temperatures.

T (°C)	[V-50] (wt %/VA)	Conversion (%)	D_p (nm)	$N_p \times 10^{-15}$ (particle/mL latex)
60	0.3	23.2	49.9	--
60	0.3	52.3	68.6	--
60	0.3	98.8	110.0	0.05
60	0.5	20.9	44.9	--
60	0.5	41.2	54.6	--
60	0.5	97.6	102.0	0.07
60	0.9	18.3	41.0	--
60	0.9	32.9	48.0	--
60	0.9	98.3	101.8	0.06
50	0.9	35.1	49.6	--
50	0.9	52.9	58.5	--
50	0.9	86.4	79.7	0.13
40	0.9	56.7	57.8	--
40	0.9	80.1	69.5	0.19

Because of the high propagation rate constants and the higher monomer concentrations at equilibrium in the particles of polar monomers, Yeliseyeva (19) postulated that the surface area of the particles grows at a rate that may exceed the rate of surfactant adsorption causing instability and coagulation during emulsion polymerization. VA is a polar monomer with a especially high propagation rate constant (k_p = 2300 dm^3/mol-s) (2) and a high monomer concentration within the particles - the volume fraction of VA in the particles at equilibrium is 0.85 at 60°C when the aqueous phase is saturated with monomer (2). Hence, from the arguments of Yeliseyeva, it is expected coagulation to occur during the microemulsion polymerization of VA. Moreover, in our case, the total surface area of the particles decreases as they grow, changing the composition of the adsorbed surfactant layer due to the differences in water solubility of DTAB and DDAB. This factor also may contribute to instability and particle coagulation.

Figure 2 depicts conversion versus time for the polymerization of VA carried out at different temperatures. Conversion reaches 100% in less than 10 minutes at 60°C; however, at 40°C, conversion is only 80% after 40 minutes of reaction. Reaction rates become faster as temperature increases; moreover, only two intervals are detected at all temperatures (inset in Fig. 2). The increase in reaction rate with temperature is a consequence of the increase in both the V-50 decomposition rate constant and the VA propagation rate constant. Maximum reaction rate follows an Arrhenius behavior with temperature. The overall activation energy is 64.0 kJ/mol, which is similar to those reported for the polymerization of VA in CTAB microemulsions initiated with V-50 (69.0 kJ/mol) (20) and for the polymerization of VA in emulsions stabilized with poly(vinyl alcohol) and initiated with a redox system (65.6 kJ/mol) (21).

Table 1 shows that particle size increases with increasing temperature. Inasmuch as the rate of coagulation is enhanced with increasing temperature (22), the increase in particle size with reaction temperature also gives support to the coagulation hypothesis.

A representative molar mass distribution curve (MMD) is shown in Figure 3. Clearly, the distribution is, at least, bimodal. The number average molar masses ($\overline{M}_n$) range from 1.2-2.0x10^6 g/mol, depending on reaction temperature (Table 2). The average molar masses obtained here are smaller than those typically obtained in emulsion polymerization of this monomer, especially at high conversions. The high molar masses in emulsion polymerization are the result of chain transfer reactions to polymer due to the large size of the particle and the high number density of polymer molecules within the particles, which lead to highly branched macromolecules (5,6). By contrast, poly(vinyl acetate) of lower average molar mass (2.0-4.5x10^5 g/mol) was synthesized by polymerization in CTAB microemulsions initiated with V-50 (13). In this case, we argued that because of the high probability of desorption of the monomeric radical due to the small size of the particles and the lower number density of polymer particles, compared to emulsion-made particles, chain transfer to monomer (and desorption) becomes the dominant mechanism of chain termination. Here, because the larger particle size of our particles, the monomeric radicals stay longer within the particles and so, the probability of chain transfer to polymer increases. Nevertheless, we can not distinguish whether chain transfer is to the same macromolecule ("selfbitting") or to a different macromolecule. Bimolecular termination caused by collision and coagulation of active particles can not be ruled out. In fact, the increase in molar mass with increasing temperature (Table 2), suggests that bimolecular termination after coagulation is taking place, since the rate of coagulation increases with increasing temperature (22).

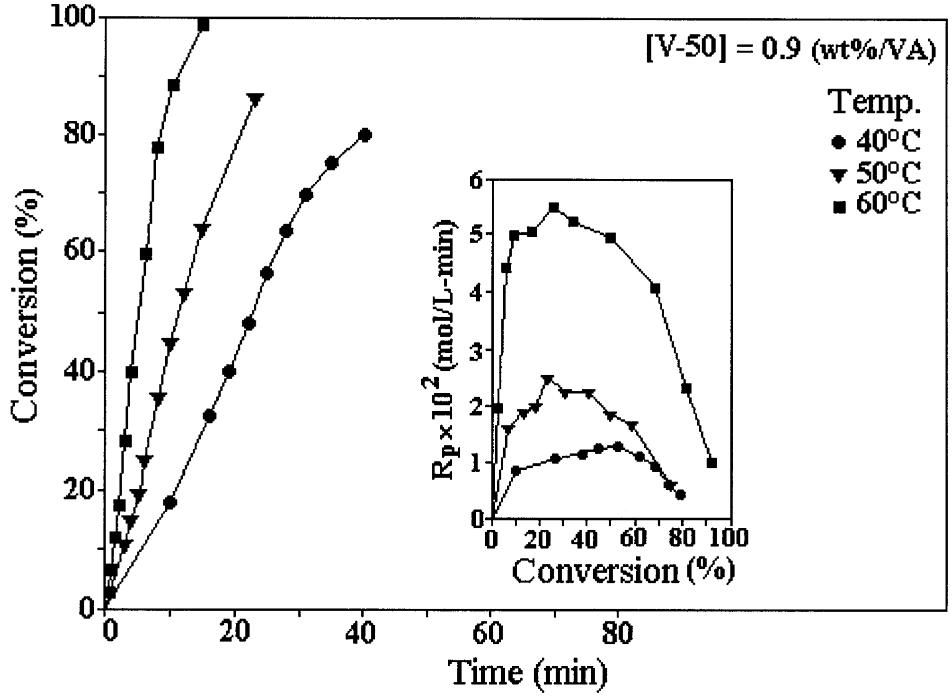

Figure 2. Conversion versus time as a function of temperature for the microemulsion polymerization of VA. Inset: Polymerization rate versus conversion for data shown in figure.

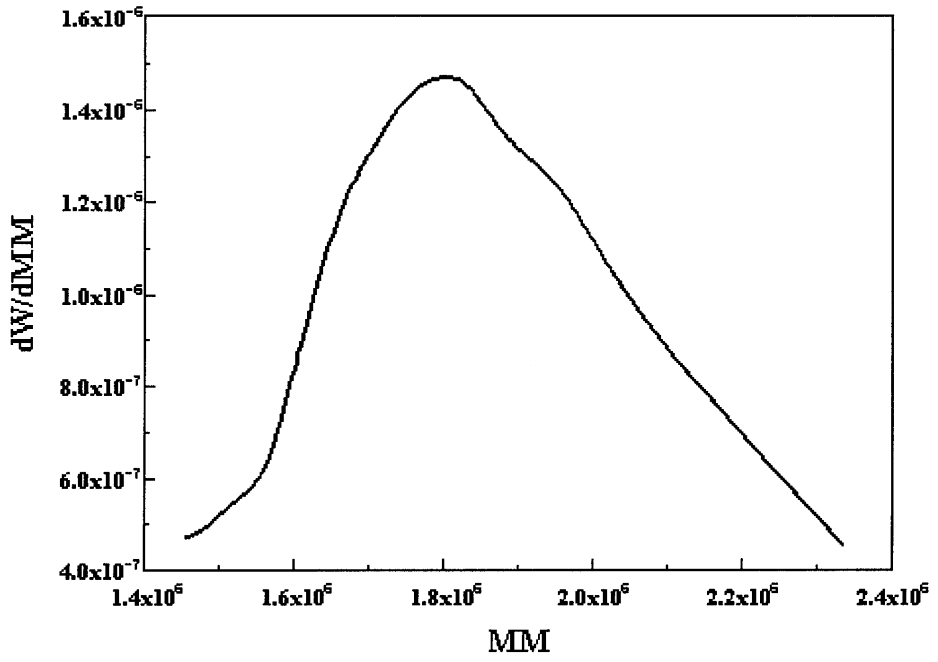

Figure 3. Molar mass distribution of PVA obtained at final conversion in microemulsion polymerization at 60°C, using 4.0 wt% VA and 0.90 wt% V-50 with respect to monomer.

Table 2. Average molar masses as a function of temperature at final conversions for the microemulsion polymerization of VA.

T (°C)	[V-50] (wt %/VA)	$\overline{M}_n \times 10^{-3}$ (g/mol)
60	0.9	2,011
50	0.9	1,490
40	0.9	1,239

Conclusions

The polymerization of vinyl acetate in o/w microemulsions stabilized with a mixture of the cationic surfactants, DTAB and DDAB in a weight ratio of 3, exhibits the typical features of microemulsion polymerization, i.e., fast reaction rates, two polymerization rate intervals and the production of stable latexes. However, because of coagulation, particles are bigger than expected for microemulsion polymerization. Average molar masses are substantially smaller than those reported for emulsion polymerization.

Acknowledgment

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