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Polymerization of vinyl acetate in ternary microemulsions stabilized with hexadecyltrimethylammonium bromide

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Summary

The polymerization of vinyl acetate (VA) in three component o/w microemulsions stabilized with the cationic surfactant, CTAB, is presented. Initiation is achieved thermally with a water soluble initiator (V-50). Stable latex containing small particles (ca. 35 nm) with molecular weights (M_w) of around 4 x 10^5 are obtained. Analysis of the molecular weight distribution suggests that chain transfer to monomer (and *not* to polymer, which is the typical termination mechanism in emulsion polymerization, specially at high conversions) is the dominant mechanism of termination.

Introduction

Polymerization in microemulsion media has been widely studied in recent years.(1-3) The feasibility of preparing stable microlattices with polymer particles of high molecular weight by this method has been well demonstrated.(4-12) Styrene and methyl methacrylate (MMA) are the monomers that have been studied in more detail, particularly in three-component microemulsions.(6-9) Microemulsion polymerization of more polar monomers, such as vinyl acetate (VA), have been scarcely examined. Recently, Donescu et al. (13,14) reported the polymerization in cosolubilized systems and their kinetics results differ from the typical behavior of microemulsion polymerization. Hence, polymerization of VA in microemulsion media needs to be clarified and understood.

This work reports the one-phase o/w microemulsion regions at 25 and 60°C of water, VA and cetyltrimethylammonium bromide (CTAB), and the polymerization of VA in these microemulsions initiated with the water-soluble initiator, 2,2′-azobis(2-amidinopropane) dihydrochloride or V-50.

Experimental

CTAB (99% from Aldrich) was recristallized from a 50/50 (v/v) mixture of acetone and ethanol. V-50 (Wako Chem.) was recristallized from methanol. VA (Aldrich) was distilled at 30°C under reduced pressure and argon atmosphere, stored at 4°C in dark vials, and used within 30 hours after distillation. For phase diagrams determinations, VA containing 50 ppm of hydroquinone (Aldrich) was used to avoid polymerization. Water was distilled and deionized.

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One-phase regions at 25 and 60°C were determined visually by titrating aqueous solutions of CTAB with VA. Samples were examined through cross polarizers to assure they were not birefringent. Electrical conductivity of microemulsions was measured at 60°C and 1000 Hz with an Orion 101 conductimeter.

A 100 mL glass reactor with magnetic stirring was used to polymerize at 60°C a microemulsion containing 4 wt% VA and a S/W ratio of 5/95 (w/w) with various concentrations of V-50. Prior to polymerization, VA and the aqueous solution of CTAB and V-50 were degassed. Conversion was followed by gravimetry. Particle size was measured with a Malvern 4700 light scattering (QLS) apparatus. Average molecular weights and molecular weight distributions were measured with a LC30 Perkin Elmer gel permeation chromatograph (GPC) equipped with a refractive index detector and a Dawn multiangle light scattering detector from Wyatt Technology.

Results and Discussion

One-phase microemulsion regions at 25 and 60°C are depicted in Figure 1. Samples are transparent and exhibit low viscosities at surfactant concentrations up to 20 wt%. For higher CTAB concentrations, microemulsions are transparent and non-birefringent but highly viscous. Since there is no practical interest in polymerizing microemulsions with such high surfactant content, upper phase boundaries were not determined. The one phase region increases with increasing temperature probably because of the amphiphilic character of VA. Similar behavior has been observed with relatively water-soluble monomers, such as MMA and tetrahydrofurfuryl methacrylate. (8,15)

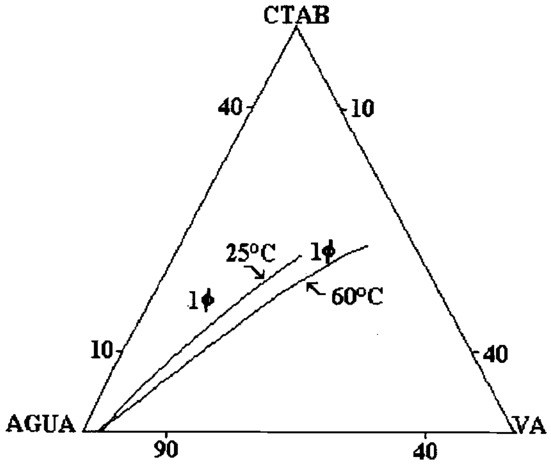

Figure 1. Partial phase diagrams of mixtures of CTAB, water and VA showing the one-phase microemulsion regions at 25 and 60°C.

Electrical conductivity of one-phase microemulsions measured at different S/W ratios is shown in Figure 2. Conductivity of all samples is quite high (> 4 mS/cm), which indicates that the structure may be water-continuous. Also, and in contrast with the behavior observed with styrene and other monomers, (9.12) conductivity increases upon increasing VA content. This apparently anomalous behavior has also been reported for MMA microemulsions (8) and it has been attributed to the partial hydrolysis of MMA. VA (16) also hydrolyzes in water to produce acetic acid, which dissociates to increase the conductivity. This effect must be important enough to overcome the decrease in conductivity produced by micellar growth upon incorporation of monomer.

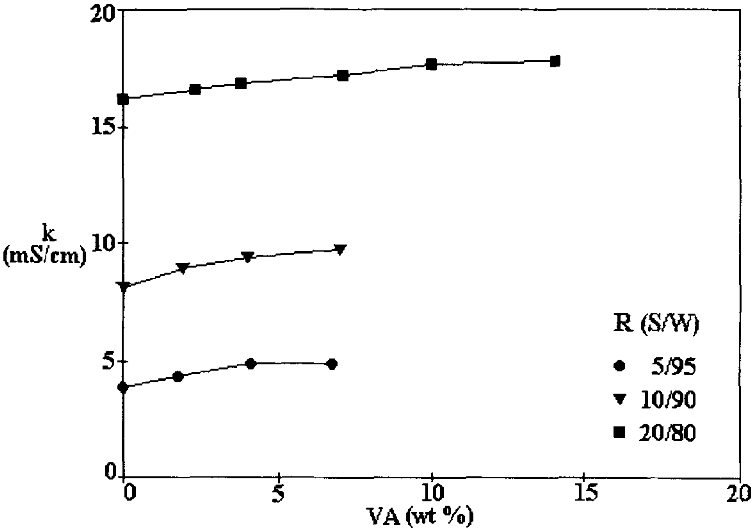

Figure 2. Electrical conductivity at 60°C of microemulsions made at various S/W weight ratios versus VA concentrations.

Figure 3 shows conversion versus reaction time as function of V-50 concentration. Reactions are fast and the polymerization rates increase with increasing initiator concentration because of the increasing flux of free radicals, which should result in a higher probability of homogeneous nucleation of the relatively water-soluble VA. The maximum in reaction rate follows a dependence on initiator concentration of the form: $Rp_{max} \alpha [V\text{-}50]^{0.7}$. It is noteworthy that O'Donell et al.(17) and Dunn and Taylor(18) reported a dependence on initiator concentration with an exponent of 0.7 and 0.64, respectively, for the emulsion polymerization of VA.

Upon reaction, the initially transparent microemulsions become bluish (at the onset of nucleation) and increasingly turbid as the reaction proceeds because of particle growth and the increase in refractive index difference between dispersed particles and the aqueous medium. Plots of reaction rate as a function of conversion (inset in Fig. 3) show the two typical intervals of microemulsion polymerization(3): The rate first increases because of fast particle nucleation, and then it decreases steadily as the monomer within the reacting particles is being consumed. This fact do not contravene the continuous particle nucleation mechanism, which has been proposed for microemulsions polymerization.(19,20) In fact, the large amount of surfactant present in microemulsion polymerization allows the nucleation and stabilization of new particles thorough the reaction.(21) Maximum reaction rates appear at the same conversion (ca. 18%) for all V-50 concentrations. They range from 0.031 to 0.097 mol/L-min and are higher than those reported for the polymerization of styrene/water/DTAB(9) and MMA/water/DTAB(8) microemulsions initiated with V-50. This is mainly because the propagation rate constant of polar monomers is higher than those of nonpolar monomers.(22)

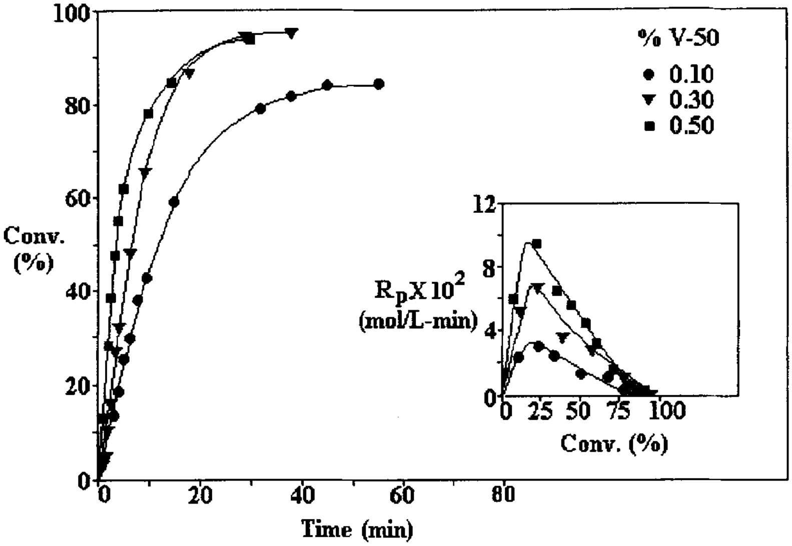

Figure 3. Conversion versus time as a function of V-50 concentration for the microemulsion polymerization of vinyl acetate. Inset: Polymerization rate versus conversion for data shown in Figure.

Table 1 reports particle size and average molecular weights at different conversions obtained with various V-50 concentrations. Particle size increases slightly with conversion but final particle size appears to be independent of initiator concentration. Molecular weight is also independent of initiator concentration. Moreover, and in contrast with emulsion polymerization, both M_n and M_w remain constant throughout the reaction and the polydispersity ratio (PD) is small (< 3).

In emulsion polymerization of VA, the molecular weight is independent of the number and size distribution of polymer particles and of initiator and emulsifier level.(24,25)) However, M_n increases with conversion because terminal double-bond polymerization reactions, and M_w increases due to chain transfer reactions to polymer. These two types of reactions lead to branched polymers. At high conversions, because the high concentration of polymer chains within the particles, M_w grows faster leading to highly branched polymer structures and to large polydispersity ratios (PD > 20).

Information about the chain-stopping mechanisms can be obtained by examining the molecular weight distribution (MWD). For the case where chain transfer reactions are mainly to monomer in a zero-one free radical compartmentalized polymerization, the number molecular weight distribution, P(M), is given by:(26)

$$P(M) = \exp\left(-k_{tr,M} M / k_p M_o\right)$$

where $k_{tr,M}$ and k_p are the rate constants for chain transfer to monomer and for propagation, respectively, M is the molecular weight variable and M_o is the monomer molecular weight.

Figure 4 shows plots of log P(M) vs. M as a function of V-50 concentration. All the plots are linear and have the same slope regardless of the concentration of initiator, in agreement with the equation shown above, suggesting that chain transfer to monomer (and *not* chain transfer to polymer) is the dominant termination mechanism under these conditions. The slope of these plots gives a value of $k_{tr,M}/k_p$ of 3.3 x 10^{-4}, which is similar to the value reported in the literature (1.5 to 2.8 x 10^{-4}) for VA at 60°C.[(22)]

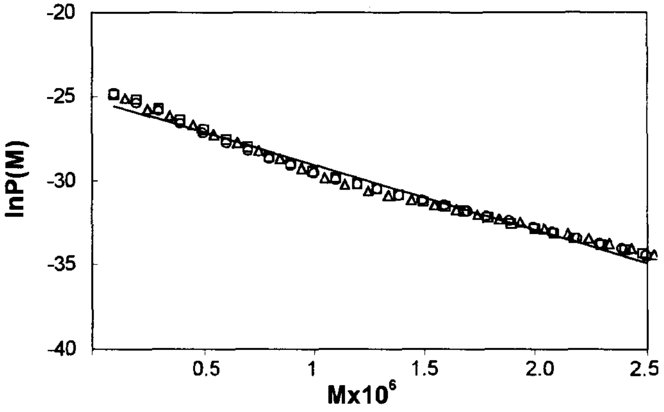

Figure 4. Instantaneous molecular weight distribution, P(M), as a function of molecular weight for the polymerization of VA in CTAB microemulsions initiated at 60°C with various V-50 concentrations (in w/w of monomer): (O) 0.1, (Δ) 0.3 and (□) 0.5.

At this time it is not clear why microemulsion polymerization of VA does not yield highly branched polymers at high conversions. Further work is required to measure the degree of branching of the polymers produced by this process.

Conclusions

The polymerization of VA in three-component microemulsions shows similar characteristics to those reported in the literature with less water-soluble monomers: only two reaction-rate stages are observed with a maximum occurring at low conversions. At the end of the reaction, stable microlatex containing small particles (ca. 35 nm) of relatively high molecular weights are obtained. Chain transfer to monomer appears to be the dominant mechanism of termination.

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Table 1. Weight average molecular weights and particle sizes at various conversions for the microemulsion polymerization of VA at different initiator concentrations.

[V-50] (wt %)	Conversion (%)	$\overline{M}_w X 10^{-3}$ (Dalton)	$\overline{M}_w / \overline{M}_n$	D_p (nm)
0.1	29.9	367	2.6	----
0.1	62.4	----	----	35.2
0.1	83.8	382	2.3	35.4
0.3	65.8	----	----	32.2
0.3	95.2	429	2.3	36.9
0.5	56.4	----	----	29.3
0.5	93.7	418	1.8	36.3

References

1) F. Candau in *Polymerization in Organized Media*, Chap. 4, C.M. Paleos, Ed., Gordon Breach Sci. Pub., Philadelphia, Pa., 1992.
2) F. Candau in *Encyclopedia of Polymer Science and Engineering*, Vol. 9, H.F. Mark, N.M. Bikales, C.G. Overberger and G. Menges (Eds), John Wiley, New York, 1987.
3) J.E. Puig in *The Polymeric Materials Encyclopedia*, J.C. Salamone, Ed., CRC Press, Boca Raton, 1996, Vol. 4.
4) F. Candau, Y.S. Leong and R.M. Fitch, J. Polym. Sci. Polym. Chem. Ed. **23**, 193 (1985).
5) J.S. Guo, M. El-Aasser and J.W. Vanderhoff, J. Polym. Sci. Polym. Chem. Ed. **27**, 691 (1989).
6) V.H. Pérez-Luna, J.E. Puig, V.M. Castaño, B.E. Rodríguez, A.K. Murthy and E.W. Kaler, Langmuir **6**, 1040 (1990).
7) L.M. Gan, C.H. Chew and I. Lye, Makromol. Chem. **193**, 1249 (1992).
8) L.A. Rodríguez-Guadarrama, E. Mendizábal, J.E. Puig and E.W. Kaler, J. Appl. Polym. Sci. **48**, 775 (1993).
9) J.E. Puig, V.H. Pérez-Luna, M. Pérez-González, E.R. Macías, B.E. Rodríguez and E.W. Kaler, Colloid Polym. Sci. **270**, 1 (1993).
10) C. Wu, Macromolecules **27**, 298 (1994).
11) M. Antonietti, R. Basten and S. Lohmann, Macromol. Chem. Phys. **196**, 441 (1995).
12) J.I. Escalante-Vásquez, L.A. Rodríguez-Guadarrama, R.G. López, E. Mendizábal, J.E. Puig and I. Katime, J. Appl. Polym. Sci. (in press).
13) D. Donescu, D.F. Anghel, M. Balcan and K. Gosa, Materiale Plastice **25**, 125 (1988).
14) D. Donescu, D.F. Anghel, K. Gosa and M. Balcan, Die Angew. Makromol. Chem. **188**, 1 (1991).
15) A.P. Full, J.E. Puig, L.U. Gron, E.W. Kaler, J.R. Minter, T.H. Mourey and J. Texter, Macromol. **25**, 5157 (1992).

16) *Kirk Othmer Encyclophedia of Chemical Technology*; Vol. 23, pg. 819, John Wiley & Sons, New York, 1981.
17) J.T. O'Donell, R.B. Mesrobian and A.E. Woodward, J. Polym. Sci. **28**, 171 (1958).
18) A.S. Dunn and P.A. Taylor, Makromol. Chem. **83**, 207 (1965).
19) J.S. Guo, E.D. Sudol, J.W. Vanderhoff and M.S. El-Aasser, J. Polym. Sci. Polym. Chem. Ed. **30**, 691 (1992).
20) F. Bléger, A.K. Murthy, F. Pla and E.W. Kaler, Mocromol. **27**, 2559 (1994).
21) A.P. Full, E.W. Kaler, J. Arellano and J.E. Puig, Macromol. **29**, (1996).
22) G. Odian in *Principles of Polymerization*, Chap. 3 and 4, 3rd. Ed., John Wiley & Sons, New York, 1991.
23) E.A. Zaragoza, Tesis de Maestría, Universidad Autónoma de Coahuila, México, 1995.
24) N. Friis, D. Goosney, J.D. Wright and A.E. Hamielec, J. Appl. Polym. Sci. **18**, 1247 (1974).
25) N. Friis and A.E. Hamielec, J. Appl. Polym. Sci. **19**, 97 (1975).
26) R.G. Gilbert, *Emulsion Polymerization*, Academic Press, New York, 1995.