

Aqueous Phase Polymerization of Vinyl Acetate: Effects of the Surfactant Concentration on the Kinetics, Molar Masses and Particle Formation

Martínez-Gutiérrez, H.^{1,3}, Ovando-Medina V.M.², Cortez G.Y.¹, Peralta R.D.¹

¹ Centro de Investigación en Química Aplicada (CIQA), Blvd. Enrique Reyna 140, Saltillo, Coah., México 25100.

² Departamento de Ingeniería Química, Coordinación Académica Región Altiplano – Universidad Autónoma de San Luis Potosí, Carretera a Cedral KM 5+600, San José de las Trojes, Matehuala, SLP, México 78700.

³ Instituto Potosino de Investigación Científica y Tecnológica, Camino a la Presa San José 2055, San Luis Potosí, S.L.P., México 78216.

e-mail: rene@ciqa.mx

1. Abstract

Vinyl acetate was polymerized in concentrations below its water saturation value (batch regime, 60 °C) using low concentrations of sodium dodecyl sulfate ([SDS], below and above the critical micelle concentration) initiated with potassium persulfate. The effects of [SDS] on kinetics, particle formation and molecular weight were studied. Particle diameter ($18.7 \leq D_p \leq 277\text{nm}$) and weight average molecular weight ($1 \times 10^5 \leq M_w \leq 8.7 \times 10^5 \text{ Da}$) decrease as [SDS] increases. High reaction rates (R_p) were observed in all reactions. When no SDS was added, lower R_p occurred at the onset of the reaction. R_p was inversely proportional to the surfactant concentration.

2. Introduction

Monomers like vinyl acetate with relatively high water solubility can be polymerized in absence of any added surfactants using a water soluble ionic initiator such as potassium persulfate [1]. Stabilization of latex polymer particles can be possible due to the *in situ* surfactant formation by the oligomers formed in the aqueous phase which contains a charged hydrophilic group derived from the initiator. In surfactant free polymerizations, the number of particles would be proportional to the number of chains initiated in solution (which grow to the critical size and then precipitate) with a possible reduction in this number due to radical combinations or capture by a particle before homogeneous particle formation occurs. The present work reports the VAc polymerization using surfactant concentrations below and above the critical micelle concentration (CMC) and VAc concentrations below the water saturation value.

3. Experimental conditions

Tri-distilled grade water was employed. Tetrahydrofurane (THF) used as mobile phase for molar mass determinations was HPLC-grade. All reactants (purity > 99%) were purchased from Aldrich. VAc was distilled under reduced pressure, kept under refrigeration, protected against light and used within a week. SDS and potassium persulfate (KPS) were used as received. The CMC of SDS in water was measured by conductimetry in presence of vinyl acetate (0.0137 g/cm^3 of water) and potassium sulfate ($8.8 \times 10^{-5} \text{ g/cm}^3$ of water) at 60°C ; the concentration of the VAc was the same to that used in the reaction mixtures and that of potassium sulfate was the molar equivalent to that of the KPS used as initiator.

The polymerizations were carried out in duplicate at atmospheric pressure and 60°C in a 1 L glass jacketed reactor with three inlets equipped with a reflux condenser. The compositions of polymerized mixtures are given in Table 1. The reaction mixture was stirred mechanically at 330 rpm. At the beginning, water, SDS and KPS (2 wt.-% with respect to the VAc) were charged to the reactor; the solution temperature was increased to 60°C and then was bubbled with argon of ultrahigh purity for an hour to eliminate oxygen. Then, the batch polymerization was started with a one-shot addition of oxygen-free VAc. The stream of argon was maintained into the reaction mixture during the whole polymerization process. Conversions were calculated by gravimetry. Particle size was determined by quasi-elastic light scattering with a Nano S90 (Malvern) apparatus at 25°C .

Table 1 Formulations used in polymerizations.

Run	VAc (g)	SDS (g)	KPS (g)	Water (g)
A	14.20	0.0	0.30	1035.0
B	14.20	0.766 (2.57 mmol/L)	0.30	1035.0
C	14.20	1.530 (5.13 mmol/L)	0.30	1035.0
D	14.20	3.30 (11.0 mmol/L)	0.30	1035.0

Average molar masses of polymers (dissolved in THF) were determined in a Hewlett-Packard series 1100 gel permeation chromatograph apparatus equipped with a refractive index detector and three PL Gel serial columns (Pore sizes 103, 105 and 106 \AA). The GPC was

calibrated with narrow polystyrene standards (Polymer Laboratories) using Mark – Houwink PVAc parameters taken from the literature ($\alpha = 0.708$ and $K = 15.6 \times 10^{-3}$) [2].

4. Results and discussion

Figure 1(a) shows conversion vs. time as a function of surfactant concentration. High final conversions were obtained, except for the reaction where the surfactant concentration was 11 mmol/L. Figure 1(b) shows the polymerization rates as a function of conversion, where it can be seen that when the surfactant concentration used is above the CMC, two polymerization periods are observed, which is typical of microemulsion polymerization where particle formation throughout the reaction has been reported [3]. Nevertheless, the three classical emulsion polymerization rate periods are observed when the surfactant concentration used is below the CMC. For surfactant concentrations below the CMC, there are not micelles and the particles are formed by the contribution of surfactant, surface active oligomers derived from initiator and the VAc present in the reaction medium, which acts as co-surfactant.

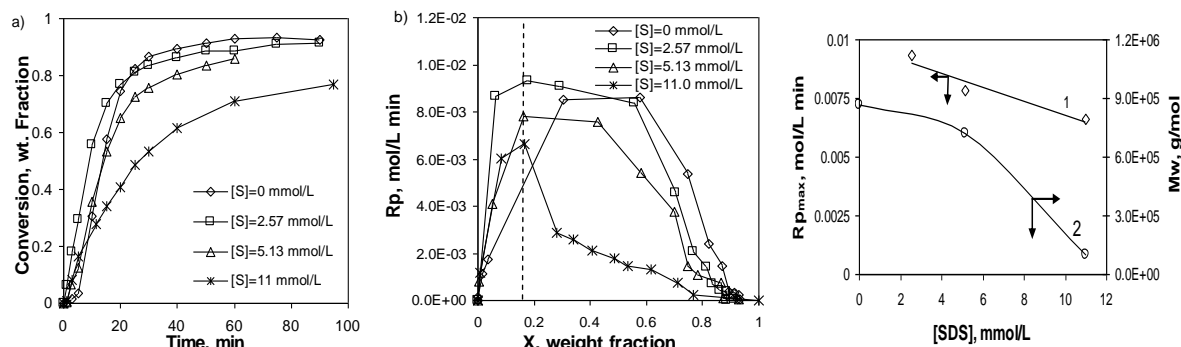


Figure 1. (a) Conversion vs. Time, (b) polymerization rate and (c) maximum polymerization rate and Mw vs. SDS concentration for batch aqueous polymerization of vinyl acetate at 60 °C for different surfactant concentration.

Figure 1(c) shows the maximum polymerization rate (R_{pmax}) and the weight average molecular weight (M_w) of the final polymers as a function of the SDS concentration. It can be seen (curve 1) that R_{pmax} decreases by increasing the surfactant concentration. This behavior has been reported by Donescu et al. [4] who attributed this behavior to strong transfer of the growing radical to SDS to generate low reactivity radicals that decrease the reaction rate. In our work, the

molar masses of the final polymers decrease with the increase of SDS concentration (Figure 1(c), curve 2). As will be discussed, this behavior of molecular weight with surfactant concentration is related to desorption of radicals from the polymer particles to the aqueous phase.

Table 2 shows the average number of radicals per particle obtained at different conversions using different surfactant concentration. The high values of \bar{n} when $[\text{SDS}] = 0.0$ are normally observed when all radicals produced in the aqueous phase are captured by the polymer particles, no radicals diffuse out, and particles are big enough to contain more than one radical at a time. In contrast, the low values of \bar{n} indicate that radicals can diffuse out of the particles quite readily, which is reasonable for radicals of low molecular weight. In our results, when no surfactant was used, particle diameters between 59 and 270 nm were observed through the reaction. For this reason, the probability that various radicals coexist within a particle increases for this particle size range. Additional details will be given in the presentation.

Table 2. Average number of radicals per particles (\bar{n}) obtained at different conversions as a function of surfactant concentration.

[SDS] = 0.0 mmol/L		[SDS] = 2.57 mmol /L		[SDS] = 5.13 mmol /L		[SDS] = 11.0 mmol /L	
X	\bar{n}	X	\bar{n}	X	\bar{n}	X	\bar{n}
0.037	0.718	0.179	0.023	0.050	0.0068	0.532	0.0002
0.577	3.240	0.558	0.027	0.427	0.0072	0.616	0.0002
0.822	2.073	0.768	0.013	0.700	0.0064	0.711	0.0001
0.892	0.533	0.862	0.005	0.874	0.0005	0.767	0.0001
0.932	0.078	0.914	0.001	0.927	0.0064		

5. References

1. Nomura M, Sasaki S, Harada M, Eguchi W. J. Appl. Polym. Sci. 1978, 22(x):1043-1060.
2. R. Jovanovic, M. A. Dube J. Appl. Polym. Sci. 2001, 82, 2958.
3. Gómez-Cisneros M, López RG, Peralta RD, Cesteros LC, Katime I, Mendizábal E, Puig JE. Polymer 2002; 43:2993-2999.
4. Donescu D, Anghel D, Gosa C, Balcan M. Die Angewandte Makromol. Chem. 1991; 188:1-10.