Emulsion Polymerization of Styrene with Ionic Comonomer in the Presence of Methanol

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Synopsis

Soap-free emulsion polymerization of styrene with sodium vinylbenzyl sulfonate (NaVBS) was studied in the presence of water–methanol mixtures. In the presence of both methanol and NaVBS, the particle size and uniformity increased with methanol content. Increasing the concentration of NaVBS decreased the particle size. Initiator and electrolyte level had similar effects on particle size as in recipes prepared in aqueous medium.

INTRODUCTION

In the past few years, emulsion polymerization techniques have been used to prepare monodisperse latices to be used as model colloidal dispersions in various studies.[1-4] Each technique has its own advantages and its own drawbacks. In emulsifier-containing methods, complete removal of emulsifiers is quite often difficult and can destabilize the latex.[1,5,6] Latices prepared by conventional emulsifier-free recipes tend to have low solids contents, slow conversion rates, and small surface charge densities.[7] Most of these problems can be alleviated by incorporating a small amount of ionic comonomer;[8] however, the use of high concentrations of ionic comonomer may contaminate the system by polyelectrolyte produced *in situ*.[9]

The solubility of styrene and thus the conversion rate can be increased by using a suitable cosolvent. Methanol is attractive for this purpose, because of its miscibility with both water and styrene, and its lack of solvency for the polymer. Emulsifier-free polymerization of styrene in the presence of methanol was first reported by McCracken and Datyner.[10] Homola and Inoue[11] reported a preliminary study on the effect of methanol as cosolvent in emulsifier-free polymerization of styrene. Labib[12] also mentioned the use of water–methanol mixture in copolymerization of sodium styrene sulfonate with styrene.

In this article, we report the effect of methanol on the copolymerization of small amounts of sodium vinylbenzyl sulfonate (NaVBS) with styrene. This study includes the effects of methanol on latex particle size and uniformity, at different concentrations of ionic comonomer, persulfate initiator, and added electrolyte.

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EXPERIMENTAL

Materials. All water used was doubly distilled from all-Pyrex apparatus. Styrene (Eastman) was freshly distilled under reduced pressure. Reagent-grade methanol and analytical-grade potassium persulfate were used as received. Sodium vinylbenzyl sulfonate was prepared by reacting sodium sulfite with vinylbenzyl chloride as previously reported.[13]

Latex Preparation. Emulsion polymerizations were carried out in 2- or 4-liter Pyrex flasks equipped with Teflon-blade stirrer, condenser, and nitrogen inlet. To exclude oxygen, purified nitrogen gas was passed through the reagents before and during the course of polymerization. The polymerizations were conducted at 65°C using potassium persulfate as initiator.
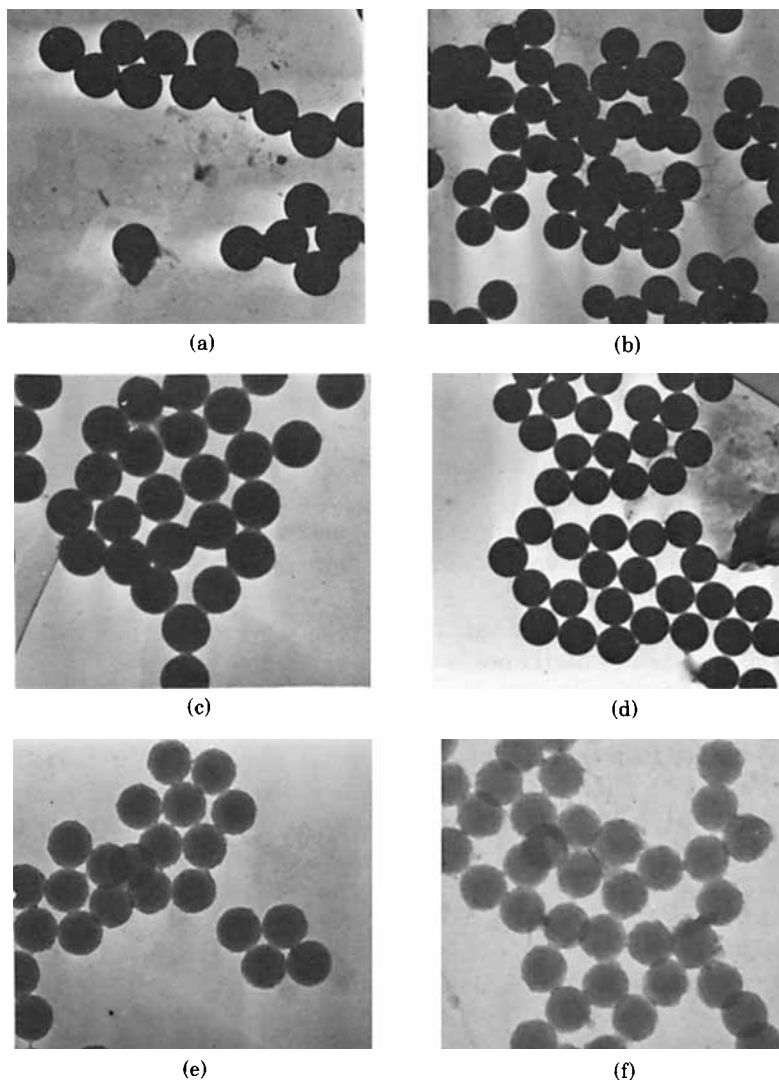

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 1. Effect of NaVBS on the uniformity of final latex particles in the presence of 22% (v/v) methanol. Recipe (in moles/l.): [styrene] = 1.18; $[K_2S_2O_8]$ = 2.15 × 10^{-3}; [NaVBS] × 10^3: (a) 0; (b) 0.9; (c) 2.6; (d) 5.3; (e) 8.1; (f) 10.5.
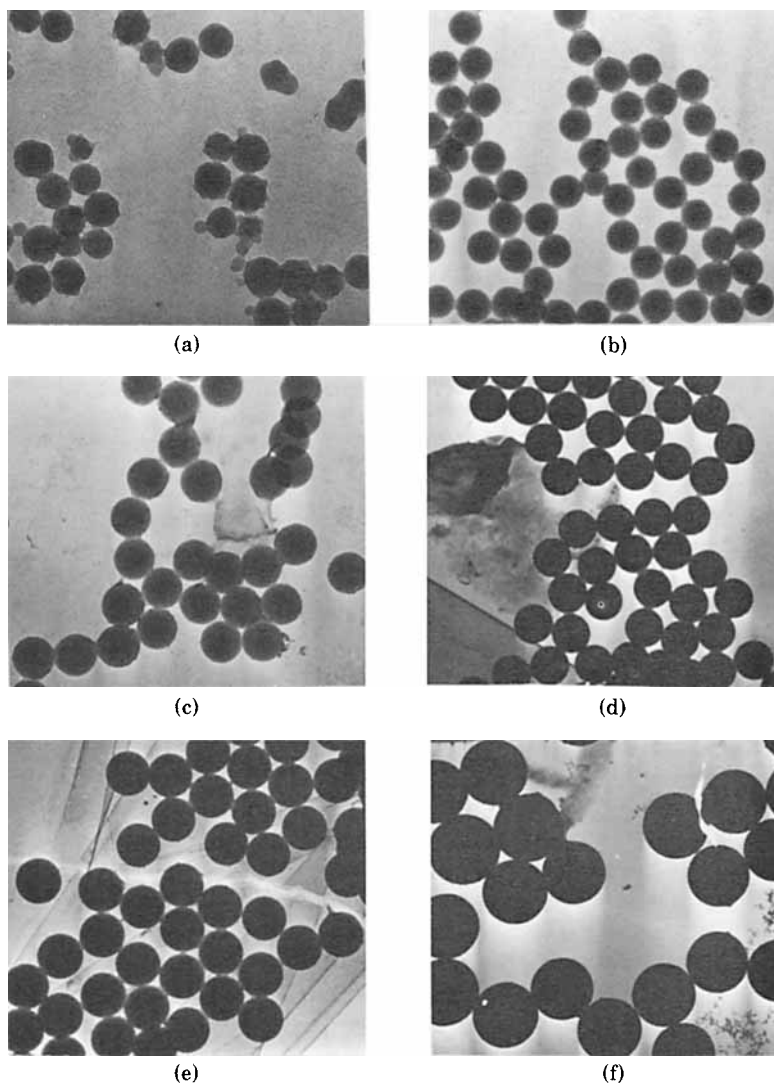
(a)

(b)

(c)

(d)

(e)

(f)

Fig. 2. Effect of methanol content on the uniformity of final latex particles. Recipe (in moles/l.): [styrene] = 1.18; [$K_2S_2O_8$] = 2.5×10^{-3}; [NaVBS] = 5.3×10^{-3}, % methanol (v/v): (a) 0; (b) 7.7; (c) 17; (d) 22; (e) 43; (f) 60.

Kinetic study. This was conducted on a large-scale recipe; small samples (~5 ml for the first 90 min, then 10 ml) were taken from the reaction vessel to determine percentage conversion, particle size distribution, and number of particles per milliliter. Hydroquinone was used to short-stop the polymerization.

Microscopy. A JEOL-100 electron microscope was used for transmission electron microscopy.[14] The latex samples with uniformity ratio $U \leq 1.01$ were considered monodisperse.*

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*$U = \overline{D}_w / \overline{D}_n$; where $\overline{D}_w = [(\Sigma_i N_i D_i^6)/(\Sigma_i N_i D_i^3)]^{1/3}$ and $\overline{D}_n = (\Sigma_i N_i D_i)/(\Sigma_i N_i)$.
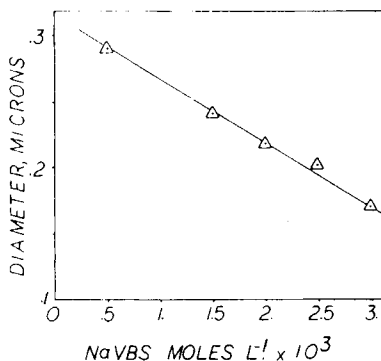
Fig. 3. Effect of concentration of sodium vinylbenzyl sulfonate on particle diameter. Recipe (in moles/l.): [styrene] = 0.96; [$K_2S_2O_8$] = 1.53 × 10^{-3}; ionic strength = 1.76 × 10^{-2}.

RESULTS

A series of polymerizations were conducted to investigate the effect of experimental parameters on the size and uniformity of final latex particles. The mechanism of particle formation in a water–methanol mixture was studied as a function of the concentrations of methanol and sodium vinylbenzyl sulfonate.

The effects of methanol and ionic comonomer on the final particle size and uniformity are shown in Figures 1 to 4. The presence of methanol greatly improved both monodispersity and smoothness of the particle surface. Particle size decreased with concentration of NaVBS in the absence of methanol (Fig. 3). The presence of methanol decreased particle diameter in the absence of NaVBS (Fig. 4). However, particle size was more sensitive to variation in NaVBS than to methanol content.

In the system containing both methanol and NaVBS, their effects on particle size and uniformity were studied by keeping one variable constant while varying the other. The purpose of this study was to develop a method for preparing monodisperse particles possessing smooth surface and high charge density. When ionic comonomers were present, the particle diameter increased with concentration of methanol, as shown in Figure 5. Up to 40 vol %, the increase in diameter was linear and had a shallow slope. The slope increased sharply beyond 40% methanol. Increasing the concentration of NaVBS at constant
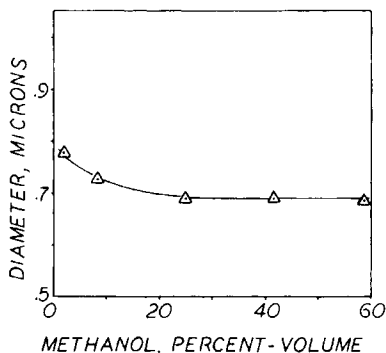

Fig. 4. Effect of methanol content on particle diameter. Recipe (in moles/l.): [styrene] = 1.28; [$K_2S_2O_8$] = 2.33 × 10^{-3}; ionic strength = 1.48 × 10^{-2}.
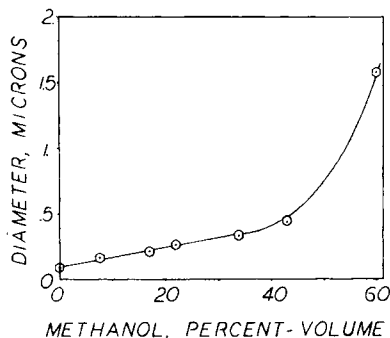
Fig. 5. Effect of methanol content on particle diameter in the presence of ionic comonomer. Recipe (in moles/l.): [styrene] = 1.18; $[K_2S_2O_8]$ = 2.15 × 10^{-3}; [NaVBS] = 5.27 × 10^{-3}.

amount of methanol (22% v/v) decreased the particle diameter (Fig. 6). At low concentration of NaVBS (<2 × $10^{-3}M$), the particle size decreased sharply, followed by a slow, linear decrease with increasing NaVBS concentration. The effect of low concentration of NaVBS (<4 × $10^{-3}M$) on particle size was comparable to similar recipes without methanol. Latex particles prepared in water at higher concentrations of NaVBS (>5 × $10^{-3}M$) were polydisperse, with diameters below 0.1 μ. Use of methanol as a cosolvent greatly improved particle uniformity. However, as shown in Figure 6, larger amounts of NaVBS have lesser effect; increasing the concentration fivefold decreased particle diameter by only 30% (0.3–0.2 μ).

The effect of persulfate concentration on particle diameter was studied at constant concentrations of styrene, NaVBS, methanol, and ionic strength. The result is shown in Figure 7. As anticipated, the particle size decreased with the amount of persulfate. The decrease in particle diameter was comparable to that in aqueous medium under similar experimental conditions. At higher concentration of persulfate, the particle size increased because of increased ionic strength.

The variation in particle size with increased electrolyte level, keeping other variables constant, is shown in Figure 8. The increase in particle size was similar to that reported for emulsifier-free recipes.

The effect of methanol on the nature and concentration of final particle surface charge is shown in Table I. Here, the lack of dependence of weakly titratable acid suggests that, in the presence of styrene and methanol, all sulfate ion radicals are captured by styrene monomer.
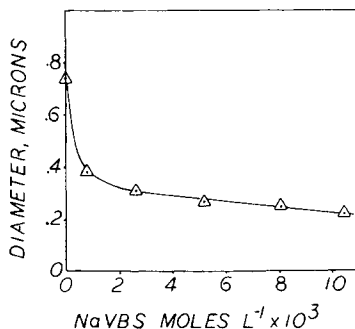

Fig. 6. Variation of particle diameter with sodium vinylbenzyl sulfonate concentration. Recipe (in moles/l.): [styrene] = 1.18; $[K_2S_2O_8]$ = 2.15 × 10^{-3}; methanol (v/v) = 22%.
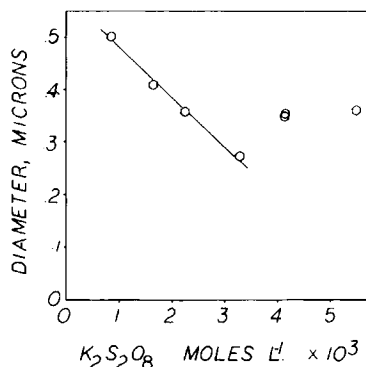
Fig. 7. Effect of persulfate initiator on particle diameter. Recipe (in moles/l.): [styrene] = 1.18; [NaVBS] = 3.52 × 10⁻³; ionic strength = 2.79 × 10⁻²; methanol (v/v) = 22%.

KINETIC STUDY

Conversion Rates

Typical conversion rate curves are shown in Figure 9. The conversion curves at different methanol and ionic comonomer contents showed three distinct stages: induction period, linear growth period, and an accelerated monomer-starved growth period. Addition of either methanol or ionic comonomer further in-
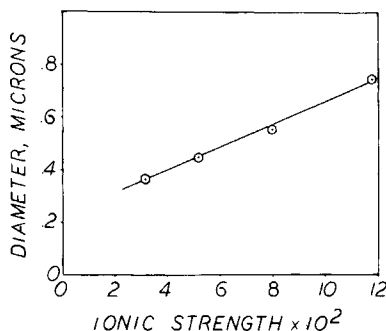

Fig. 8. Effect of added electrolyte (NaCl) on latex diameter. Recipe (in moles/l.): [styrene] = 1.18; [K$_2$S$_2$O$_8$] = 2.15 × 10⁻³; [NaVBS] = 3.52 × 10⁻³; methanol (v/v) = 22%.

TABLE I
Effect of Methanol Content on Particle Size and Surface Charge of Latex in the Absence of Ionic Comonomer

Latex code	Methanol, % (v/v)	$\overline{D}, \mu$	Surface charge, μC cm^{2a}		
			SA	WA	SA + WA[b]
M2	4.2	0.788	5.09	1.24	6.33
M3	8.4	0.728			
M4	25.1	0.691	5.06	1.18	6.24
M5	41.9	0.694	6.50	1.65	8.15
M7	58.7	0.688	6.4	0.97	7.37

[a] Latex samples steam stripped for 2 hr at 80–90°C, ion exchanged, and then centrifuged once and redispersed before titration. Recipe: [styrene] = 1.28 mole/l., [K$_2$S$_2$O$_8$] = 2.33 × 10⁻³ mole/l. Ionic strength = 1.47 × 10⁻² mole/l.
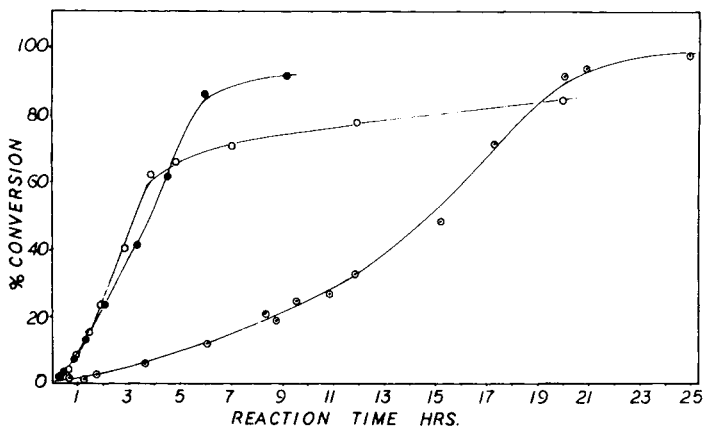
[b] SA = Strong acid; WA = weak acid (carboxyl?).

Fig. 9. Effect of NaVBS and methanol contents on conversion rate. Recipe (in moles/l.): [styrene] = 1.18; [K$_2$S$_2$O$_8$] = 2.15 × 10^{-3}; (⊙) [NaVBS] = 0, methanol (v/v) = 7.7%; (O) [NaVBS] = 2.8 × 10^{-3}, methanol (v/v) = 7.7%; (●) [NaVBS] = 3.8 × 10^{-3}, methanol (v/v) = 19%.

creased the conversion rate. However, at low methanol content, the conversion rate was more sensitive to the concentration of ionic comonomer than to the variation in methanol content.

Particle Nucleation and Growth

The mechanisms proposed for emulsion polymerization of styrene using water as medium and persulfate as initiator are based on limited solubility of monomer and of oligomeric radicals. Consequently, the use of a cosolvent that increases the solubility of both styrene and oligomeric radicals could have a significant effect on the growth and stability of latex particles. The shapes of particle growth curves (Figs. 10 and 11) obtained in this study were typical of those of emulsifier-free aqueous emulsion polymerizations of styrene.[7,15,16] Both in presence and in absence of ionic comonomer, the number of particles per unit
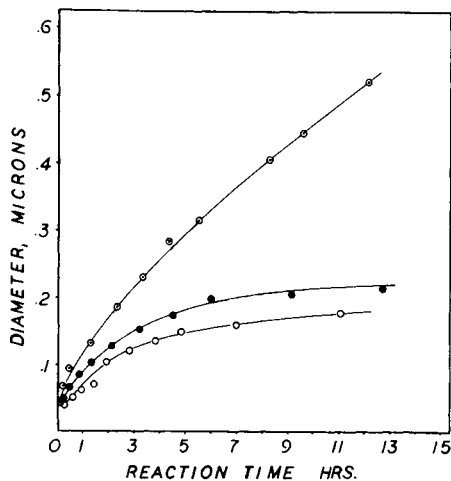

Fig. 10. Effect of NaVBS and methanol content on particle diameter. Same samples as in Fig. 9.
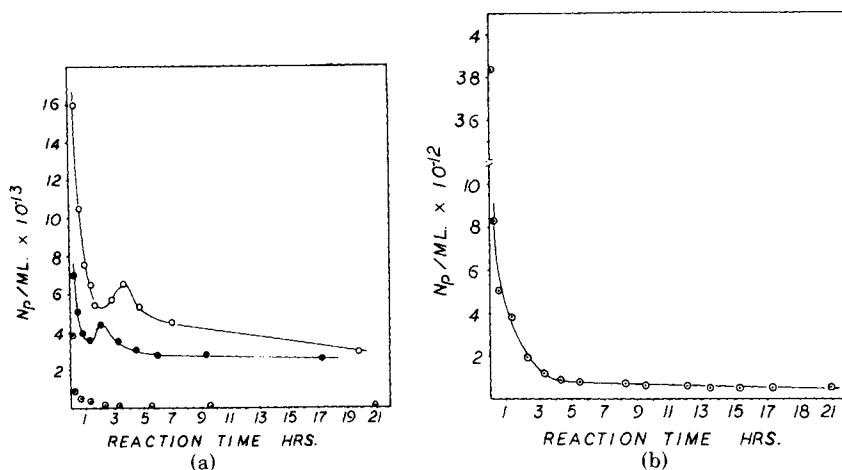
Fig. 11. (a) Effect of NaVBS and methanol on the average particle number density. Same recipe as in Fig. 9. (b) Data for % methanol replotted on expanded scale.

volume [Fig. 11(a)] fell during the nucleation stage. The number of particles present at early stages was larger in the presence of ionic comonomer and decreased with increase in the amount of methanol. In the system containing no ionic comonomer, the initial number was smaller and fell more rapidly.

DISCUSSION

The presence of methanol can affect polymerization by modifying physical properties of the continuous phase and by catalyzing the decomposition of persulfate initiator through chain transfer. As suggested by McCracken[10] and by Homola et al.,[11] the presence of methanol increases the solubility of styrene and of growing oligomeric radicals. It may also modify the hydrophobic–hydrophilic interaction between polymer chains.

In polymerizations without ionic comonomer, increasing methanol concentration would decrease the dielectric constant of the medium and increase the decomposition rate of persulfate by chain transfer. At lower concentrations of methanol, strong-acid endgroups will still ionize, and the lower dielectric constant of the medium would result in stronger repulsion between endgroups, thereby stabilizing smaller primary particles. However, as the concentration of methanol is increased, fewer end groups would ionize. In order to account for the observed decrease in particle size with methanol level, it appears necessary to postulate stabilization of particles by surfactants generated *in situ*.

The decrease in particle size with increasing concentration of NaVBS, in the presence or absence of methanol, is attributable to electrostatic stabilization of primary particles by sulfonic acid end groups. In the presence of ionic comonomer, the particle size increases with methanol content. This phenomenon may be explained by the increased solubility of styrene, so that it competes more effectively in the copolymerization. The resulting randomized copolymer could reach larger size before precipitation.

Advantages of the incorporation of methanol as cosolvent are high charge densities and low level of removable polyelectrolyte in the final latex, as shown by conductometric titration of centrifuged latex. In addition, larger particle sizes can be achieved than in aqueous medium.

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