

# Semicontinuous Emulsion Polymerization of Styrene–Butyl Acrylate–Methacrylic Acid with High Solid Content

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**ABSTRACT:** High-solid-content (>60 wt %) lattices of styrene (St), butyl acrylate (BA), methacrylic acid (MMA), and *N*-hydroxymethacrylic amide (NMA) were prepared through semicontinuous emulsion polymerization. In order to obtain high-solid-content lattices with low viscosity, the intermediate emulsion (IE) of the two-stage pathway had to have viscosity kept low, and so the amount of surfactant for the second stage was about 5–6 wt %. The relationships between IE viscosity and coagulum formation and between surfactant concentration and viscosity are discussed in this article. Particle size and particle size distribution (PSD) were investigated and are also discussed. Lattices through the two-stage pathway were found to have a bimodal PSD and good mechanical and chemical stability. However, lattices through the one-stage pathway had a narrow PSD and low mechanical and chemical stability. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2352–2356, 2001

**Key words:** high solid content; latex; particle size distribution; semicontinuous polymerization; two-stage pathway

## INTRODUCTION

Because of such properties as low levels of volatile organic compounds, quick drying velocity, and good film forming, high-solid-content lattices have recently received extensive attention. Most reports about them have been on patents; very little research has focused on basic theory. However, some interesting progress has been reported. López and Asua<sup>1</sup> found that for batch terpolymerization, through the miniemulsion process coagulum-free 60 wt % solid-content lattices had a broader particle size distribution with a low viscosity. Masa et al.<sup>2</sup> studied bimodal PSD and found it could decrease viscosity of lattices. They

investigated the effect of the type and amount of surfactant on overall polymerization features and final product properties. Ruckenstein and Park<sup>3</sup> prepared a latex with a large volume fraction of the dispersed phase and a small volume fraction of the continuous phase. Zezza and Talmo<sup>4</sup> discussed viscosity reduction via monomer selection in solvent-borne high-solid-content styrene–acrylic coating resins. Unzué and Asua<sup>5</sup> studied the effect of operation variables on the feasibility of obtaining a 65 wt % solid-content latex with a low amount of coagulum and found that the feed-flow rate had no effect on the amount of coagulum formed and that mixed surfactant system could decrease the amount of coagulum formed. Ruckenstein and Sun<sup>6</sup> used a two-step concentrated emulsion polymerization pathway in order to ensure stability of the concentrated emulsion. Chu et al.<sup>7,9</sup> studied bimodal and trimodal PSD copo-

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**Table I Recipes Used for IE of Two-Stage Pathway**

Run	Solid Content (wt %)	Surfactant	
		Ionic (DSB) (wt %)	Nonionic (CA897 + OP - 10) (wt %)
A1	50	0.65	2.1
A2	50	0.65	1.62
A3	50	0.70	2.1
A4	50	0.70	1.62

lymerization of poly(St-BA-MAA) lattices and found that when the weight fraction of the large particles was around 80%, low viscosity and coagulum-free lattices were obtained through secondary nucleation with minimum viscosity.

In the current study we took on two semicontinuous polymerizations: the two-step and the one-step pathways. The purpose of this work was to obtain high-solid-content lattices with low viscosity through semicontinuous polymerization and to investigate the effect of these surfactants on particle size, PSD, and other properties.

## EXPERIMENTAL

### Materials

Technical-grade monomers were used. Styrene (St), butyl acrylate (BA), and methyl methacrylate (MAA), (Dongfang Chem Co., Ltd., China) contained 10–20 ppm butylcatechol as inhibitor. Self-prepared *N*-hydroxymethacrylic amide (NMA) was a 50% water solution. APS (ammonium persulfate; Shanghai, China), CO-436 (ammonium salt of sulfated nonylphenoxy ethanol, Rhone-Poulenc Co., Ltd., France), CA-897 [70%, poly(oxyethylene octylphenyl ether); Rhone-Poulenc Co., Ltd., France], disulfide bridges (40%, disodium salt of sulfonic alkyldiphenylate, Rhone-Poulenc Co., Ltd., France) and OP-10 [poly(oxyethylene nonylphenyl ether)] were also used. Deionized water was used throughout the work.

### Preparation Process

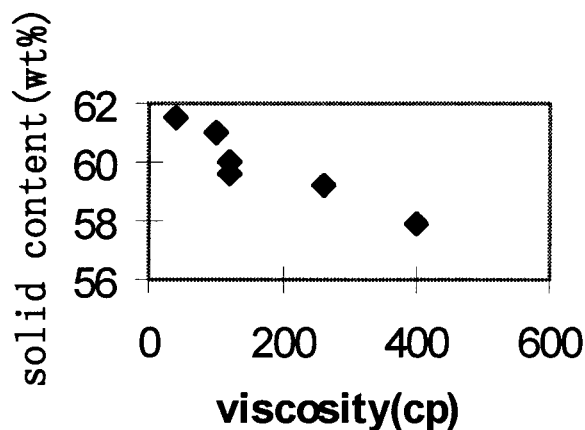
All the experiments were carried out in a 0.5-L glass reactor. The experiments were divided into two series of polymerizations. The first series of polymerizations was carried out through a two-stage pathway, the first step stage of which pre-

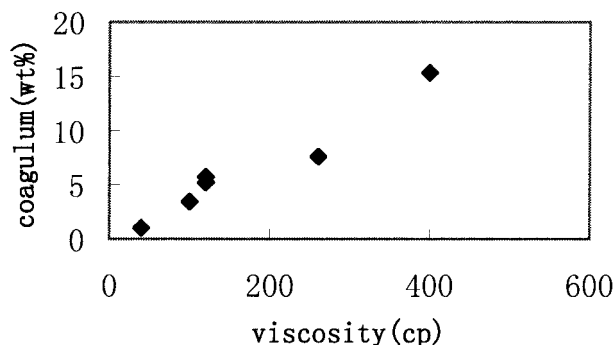
**Table II Recipes Used for Second-Stage Lattices of Two-Stage Pathway**

Run	Solid Content (wt %)	Surfactant	
		Ionic (CA436) (wt %)	Nonionic (CA897 + OP - 10) (wt %)
B1	61.8	2.15	4.73
B2	61.5	2.15	5.05
B3	61.7	2.64	4.2
B4	62.3	2.64	5.7

pared an intermediate emulsion (IE). In the preparation of the IE, the monomer, initiator, surfactant, and water were mixed as a seed, which was heated to 70°C and maintained at that temperature for 1.5 h, then heated to 80°C. Then the feed, composed of two streams, was started. One stream was a preemulsion of the monomer, surfactant, and water; the other was an aqueous solution of the initiator. The flow rates of the two feeds were adjusted to finish in 5 h simultaneously; then the polymerization continued for another 2 h.

After the IE was prepared, the second stage began. Latex was used as seed for further polymerization, and some additional surfactant and initiator were added, then heated to 80°C. A preemulsion that included the monomer, surfactant, and water was fed into the reactor. At the same time, for 3 h an aqueous solution of the initiator was also fed in. The polymerization then continued for another 2 h. As can be seen in Tables I and II, during the preparation of the IE, the ratio of the monomers was St:BA:MAA:NMA

**Figure 1** Effect of viscosity of IE on solid content of the second stage.

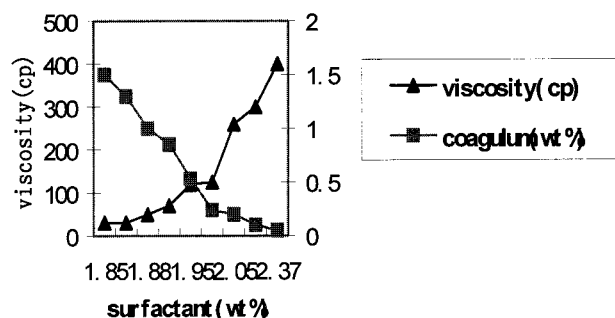


**Figure 2** Effect of viscosity of IE coagulum of the second stage.

= 196.5:96:3:4.5. The ratio of the monomers in the second stage was St:BA:MAA:NMA = 65:32:3:0.

The second series of experiments was carried out through a semicontinuous one-stage pathway. The polymerization was similar to the IE of the two-stage pathway; however, the feed was different. In Run C1–C2 one feed was composed only of monomer; the other was an aqueous solution of the initiator. In Run C3–C4 one feed was also an aqueous solution of the initiator, but the other was a preemulsion. The reactor was heated to 80°C for 6 h and the reaction then continued for another 2 h.

Samples were withdrawn during the process, and the polymerization was stopped with hydroquinone. The overall conversion was determined gravimetrically. The viscosity of the final lattices was measured with a Brookfield viscometer using spindle N0.1 at 12 rpm, NO<sub>3</sub> at 30 rpm and 25°C. The salt tolerance of the lattices was measured by the amount of coagulum formed. The diameter of the particles was checked by transmission electron microscopy (TEM).



**Figure 3** Effect of surfactant on viscosity of IE and coagulum of the second stage.

**Table III** Particle Size of IE-A1

Run	A1	A2	A3	A4
Particle size	370	365	358	367

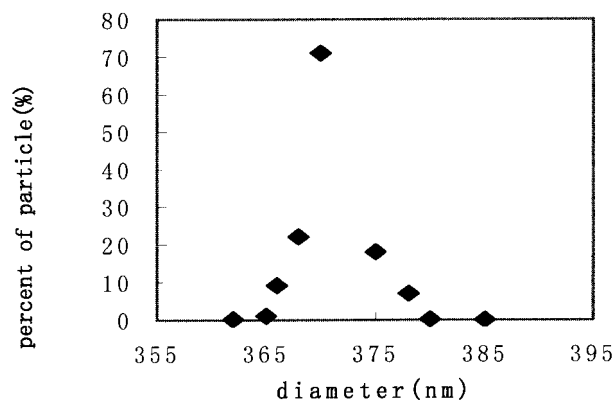
## RESULTS AND DISCUSSION

### Two-Stage Pathway

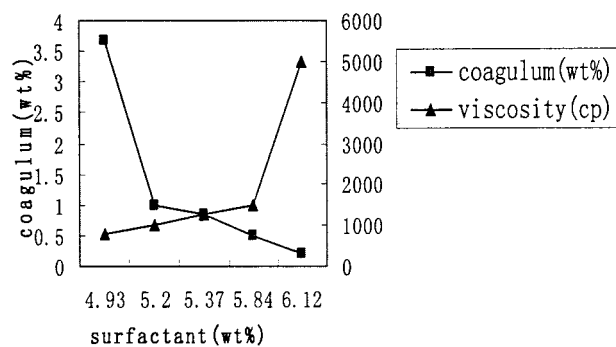
#### Intermediate Emulsion

Obtaining high-solid-content lattices with low viscosity requires either multimodal particle size distribution of the lattices or a decrease of the thickness of the particle-surface water-composed layer. The two-stage and one-stage pathways are based on this principle. In the two-stage polymerization, the intermediate emulsion (IE) must have the following characteristics: to decrease viscosity and to increase the particle size as much as possible. Based on the theory of the solid structural stack, the maxim stack volume fraction must be obtained through various particle sizes and the IE must have a large particle size with low viscosity. One the other hand, the new particle produced from the second stage is very small. So the lattices particles have a multimodal particle size distribution.

As seen in Figure 1, when the viscosity of IE is 400 cp, the second-stage solid content is even lower than 58 wt %. The coagulum of the second-stage lattices is greater than 15 wt %. Figure 2 shows the effect of the viscosity of the IE on the coagulum of the second-stage lattices. The coagulum increases when the viscosity of IE increases. The viscosity increase of the IE results from the surfactant increase of the IE. Thus, the second



**Figure 4** Particle size distribution of IE.



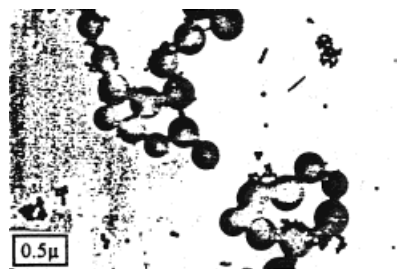
**Figure 5** Effect of surfactant of the second stage on coagulum and viscosity.

stage monomers are more difficult to disperse, which may result in more flocculation of particles. In order to prepare coagulum-free high-solid-content lattices, the IE should be lower than 40 cp. Figure 3 presents the effect of the surfactant of the IE on the viscosity of the IE and the coagulum of the second stage. When the amount of surfactant is 1.90–2.00 wt %, the viscosity and coagulum are accepted.

Table III shows the particle size of the IE, and Figure 4 shows the particle size distribution (PSD) of A-1. The particle size of the IE is very large, and the PSD is composed solely of single large particles.

### Second-Stage Polymerization

Figure 5 presents the effect of the surfactant of the second stage on coagulum. As long as the amount of surfactant is greater than 5 wt % but less than 6 wt %, the coagulum is very low. But if the amount of surfactant is greater than 6 wt %, the viscosity is very high. For instance, with 6.12 wt % surfactant, the viscosity is 5000 cp. The feed of the second-stage surfactant is used to introduce the second polymer particles. The concentration of surfactant must be below the critical micelle concentration in order to avoid the first polymer



**Figure 6** TEM micrograph of second-stage latex B4.

**Table IV** Mechanical Stability

Run	B1	B2	B3	B4	C1	C2	C3	C4
Coagulum (wt %)	1.5	0.9	0.1	0.02	15	20.8	1.3	1.03

particles adsorbing the additional surfactant in the increase, resulting in greatly increased viscosity.

Based on the above, we think the 5–6 wt % surfactant of the second stage is feasible. Figure 6 shows the TEM micrographs of the second-stage lattices. It can be clearly seen that the lattices have a bimodal PSD that is composed of a few large particles and a great many small ones. Table IV gives the mechanical stability and Table V the chemical stability of the lattices. Those with a high solid content and low viscosity have good mechanical and chemical stability (as can be seen in B3 and B4). Lattices with a high-viscosity agglomerate have a low stability. These characteristics can be attributed to low heat dispersion with high viscosity.

### One-Stage Pathway

The results of the one-stage polymerization lattices are shown in Table VI. The lattices with preemulsion feed (C3 and C4) have a lower coagulum than those with monomer feed (C1 and C2). This behavior can be explained by the droplets of monomers in C1 and C2 absorbing surfactants from particles, which then cause the aggregation of lattices particles and form coagulum. The viscosity of lattices is often high (>1500 cp), which

**Table V** Chemical Stability

Run	Coagulum (wt %)					
	NaCl		CaCl <sub>2</sub>		A <sub>12</sub> (SO <sub>4</sub> ) <sub>3</sub>	
	0.1M	1.0M	0.1M	1.0M	0.1M	1.0M
B1	0.2	1.1	0.25	1.21	0.32	1.7
B2	0.15	1.0	0.20	0.97	0.25	1.3
B3	0.04	0.1	0.07	0.2	0.05	0.42
B4	0.02	0.04	0.03	0.05	0.02	0.03
C1	10.3	20.7	10	32	13	37.6
C2	12	18	10	26.5	7.8	23.4
C3	0.6	2.4	0.7	3.25	0.45	2.43
C4	1.0	1.56	0.21	1.2	0.36	2.1

**Table VI Results of One-Stage Pathway**

Run	Surfactant (wt %)	Coagulum (wt %)	Solid Content (wt %)	Viscosity (cp)
C1 (without preemulsion)	2.2	18.9	62.9	2080
C2 (without preemulsion)	3.7	10	66.3	5000
C3 (preemulsion)	1.68	0.9	64	1550
C4 (preemulsion)	2.5	0.5	63.2	3000

causes low mechanical and chemical stability. As seen Tables IV–VI, the coagulum of the one-stage pathway is on the average greater than that of the two-stage lattices, although the solid content of the one-step lattices is very high. It is possible that the lattices have a narrower PSD than that of the two-stage lattices.

## CONCLUSIONS

The possibility of obtaining high-solid-content lattices with low viscosity through semicontinuous polymerization was investigated. In the two-stage polymerization the amount of surfactant of the IE was about 1.90–2.00 wt % and the viscosity of the IE was lower than 100 cp, all of which made possible second-stage lattices with a high solid content and low coagulum. It was found that when the amount of surfactant of the second stage was about 5–6 wt %, the lattices had a low viscosity and were coagulum free. The two-stage polymerization lattices had a typical bimodal par-

ticle size distribution, which is more stable than the one-stage polymerized lattices. One-stage lattices usually have a high viscosity and high coagulum, with low mechanical and chemical stability, which is attributable to a narrow PSD.

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