

# Preparation and Properties of Polystyrene-g-Poly(butyl acrylate) Copolymer Emulsions with Ultrasonic Radiation. I. Preparation Technology and Coagulum Ratio

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**ABSTRACT:** A stable emulsion of polystyrene-g-poly(butyl acrylate) was prepared via the following steps: (1) foam polystyrene waste was dissolved in butyl acrylate; (2) the solution was added to an aqueous solution of sodium dodecyl sulfate, ammonium persulfate, and sodium hydrogen bicarbonate; and (3) the mixture was emulsified and graft-copolymerized by ultrasonic radiation and agitation. Then, the effects of various factors, such as the strength and time of the ultrasonic radiation, the type and dosage of the emulsi-

fier, the concentrations of the initiator and butyl acrylate, the quantity of acrylic acid, and the reaction temperature, on the coagulum ratio were investigated and analyzed. As a result, a suitable technology for reducing the amount of coagulum could be proposed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1405–1409, 2005

**Key words:** emulsion polymerization; foams; graft copolymers; polystyrene; radiation; waste

## INTRODUCTION

Polystyrene (PSt) is one of three standard plastics [polyolefins, poly(vinyl chloride), and PSt], and the foam products of PSt can be applied in many fields, such as the packaging of electrical equipment, apparatus, instruments, and foods, thermal insulation materials for buildings and cold storage, and disposable dinner service. Unfortunately, PSt does not degrade naturally, and this leads to millions of tons of white pollution, that is, waste foam PSt, annually. The recycling or utilization of polymer waste saves raw materials and protects the environment, to which much attention has been directed recently. We have used foam PSt waste to prepare a polystyrene-g-poly(butyl acrylate) (PSt-g-PBA) emulsion, which is widely used as a coating and adhesive, via the ultrasonic graft copolymerization of PSt and butyl acrylate (BA).

Early work involving ultrasonic radiation emulsion polymerization was proposed by Ostroski and Stanbaugh,<sup>1</sup> and its intense power for emulsification, dispersion, and decomposition has attracted much attention.<sup>2</sup> Stoffer and Sitten<sup>3</sup> investigated the ultrasonic polymerization of methyl methacrylate (MMA) with a special nonpolymeric initiator and gave the corresponding reaction mechanism. Chou and coworkers<sup>4,5</sup> reported the ultrasonic polymerization of MMA without an initiator, and Biggs and Grieser<sup>6</sup> and Liao et

al.<sup>6,7</sup> investigated the ultrasonic copolymerization of styrene, BA, and MMA. More recently, Zhang et al.<sup>8</sup> reported the microemulsion polymerization of MMA by ultrasonic radiation. To the best of our knowledge, no investigation involving the emulsion graft copolymerization of foam PSt and BA by ultrasonic radiation has been reported.

It is very difficult to conduct an emulsion graft copolymerization of PSt with a molecular mass over  $2 \times 10^5$  in the absence of a solvent. The key points are the preparation of a stable polymer emulsion and the reduction of the coagulum ratio (CR) to a negligible extent. This article examines a recipe and technology for graft copolymerization and the influence of various factors on CR. It also proposes an approach and technology for reducing CR.

## EXPERIMENTAL

### Materials

Foam PSt waste was rinsed and aired before use. BA and acrylic acid (AA) monomers (commercial grades; Beijing Dongfang Chemical Co., Beijing, China) were filtered through inhibitor removal columns before use. *N*-Hydroxymethyl acrylamide (HMA; 98%; Fine Chemical Co. of Hubei University, Wuhan, China), ammonium persulfate (APS) and sodium hydrogen bisulfite (Tianjin Reagent Manufacturer No. 6, Tianjin, China), and octyl phenyl polyoxyethylene ether (OP-10) and sodium dodecyl sulfate (SDS; Beijing Qiuxian Chemical Manufacturer, Beijing, China), were all used as received. Water was deionized.

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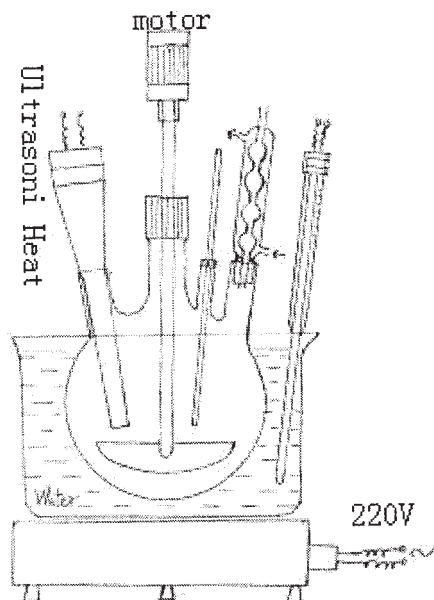


Figure 1 Ultrasonic emulsion polymerization installation.

### Apparatus and preparation of the graft copolymer emulsion

The polymerizations were carried out in a 250-mL, four-necked flask equipped with a reflux condenser, a stirrer, an ultrasonic horn (JTC-2, Jilin Tonghua Ultrasonic Equipment Co., Jilin, China), and a thermometer, as shown in Figure 1. The temperature was controlled with a thermostated water bath. After PSt was dissolved in BA in the reactor, the temperature was raised according to the protocol shown in Table I. Then, OP-10, AA, HMA, SDS, water, NaHSO<sub>3</sub>, and APS were fed into the reactor one by one. When the blue fluorescence appeared, the ultrasound power was turned off. The temperature was kept at 80°C until the polymerization rate reached 99% under agitation, and then the products were cooled to room temperature and discharged.

### Measurement of CR

The amount of coagulum that formed during the reaction was measured via the filtration of the emulsion through a 120-mesh filter at the ambient temperature

TABLE I  
Typical Recipes for the Preparation of PSt-g-BA Copolymer Emulsions

PSt (g)	17	APS	0.15
BA (g)	40	NaHSO <sub>3</sub>	0.08
AA (g)	0.5	Water	140
HMA (g)	0.5	Ultrasonic intensity (%)	80
SDS (g)	0.5	Ultrasonic time (min)	10
OP-10 (g)	1.5	Temperature (°C)	70 ± 2

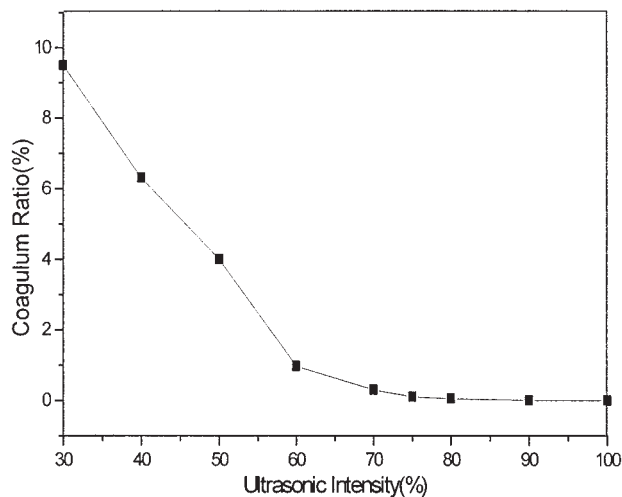


Figure 2 Effects of the ultrasonic intensity on CR.

to avoid film formation. Then, the coagulum in the filter, as well as that on the stirrer and reactor, was collected carefully. The coagulum was rinsed with deionized water and dried in an oven at 105°C for 1 night. CR was calculated as follows:

$$\text{CR} (\%) = G_2 / (G_1 - G_0) \times 100 \quad (1)$$

where  $G_1$  is the mass of the emulsion,  $G_2$  is the mass of the dried coagulum, and  $G_0$  is the mass of the volatile materials in the emulsion.

### Determination of the polymerization rate

During the polymerization, samples (ca. 1 g) were withdrawn with a syringe at appropriate intervals and poured into a small, weighed aluminum foil dish containing a small amount of an aqueous solution of hydroquinone to prevent further polymerization. The remaining monomer and water were removed via the drying of the samples to a constant weight in a vacuum oven at 50°C. The dried polymers were weighed to calculate the general monomer conversions. The calculation was based on a simple mass-balance equation.

## RESULTS AND DISCUSSION

### Effects of the acoustic intensity on CR

A series of polymerizations were carried out with different acoustic intensities (30–100%), and Figure 2 shows the influence of the acoustic intensity on CR. CR decreased as the acoustic intensity increased, and when the intensity exceeded 70%, CR approached 0. The high CR at a low acoustic intensity could be ascribed to the low dispersion and emulsification efficiency.

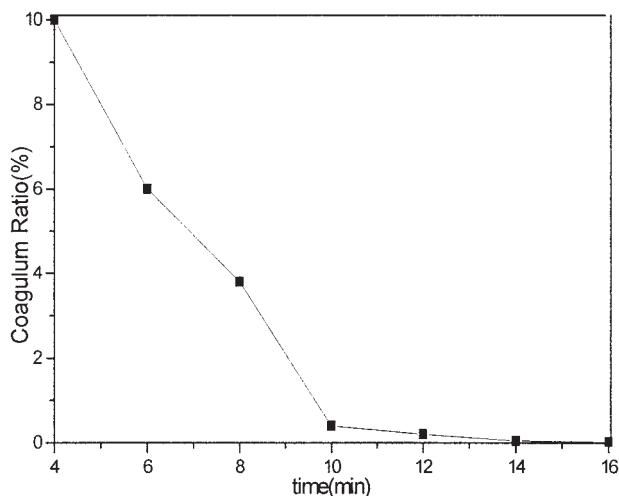


Figure 3 Effects of the acoustic irradiation time on CR.

### Effects of the acoustic irradiation time on CR

A series of polymerizations were carried out according to the given recipe with variations in the acoustic irradiation time. Figure 3 shows that, at a certain acoustic intensity, the longer the acoustic irradiation time was, the lower CR was. In addition, after 12 min, CR was negligible. As a result, for the reduction of CR, enough time was essential, as well as enough intensity. When the irradiation time was not long enough to disperse PSt into small colloidal particles, the large PSt particles that formed were prone to aggregation over the course of the reaction.

### Effects of the emulsifier type and concentration

Several polymerizations were carried out with different types and concentrations of emulsifiers, and the results are shown in Figure 4. CR was greater than

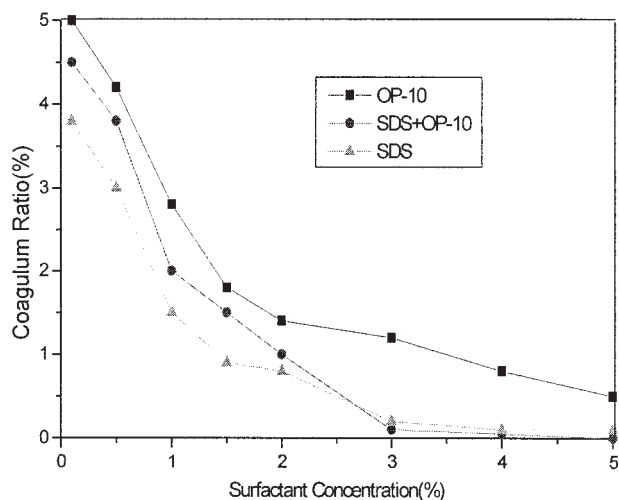


Figure 4 Effects of the emulsifier concentration on CR.

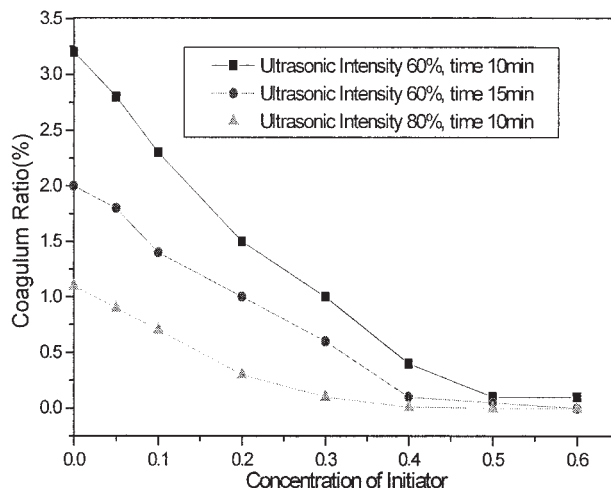


Figure 5 Effects of the initiator concentration on CR.

50% in the absence of an emulsifier (this is not depicted in Fig. 4); CR decreased to 5 and 4% when the concentration of the emulsifier was 0.2 or 0.5 wt % with respect to the monomers. Moreover, when the concentration was 3 wt %, CR was less than 0.5%.

As for the type of emulsifier, CR was lowest when only SDS was used as the emulsifier, and CR was highest when only OP-10 was used. Using sheer SDS led to a lot of foam. As a result, a compound emulsifier, 1:3 SDS/OP-10, was used, and the total concentration was 3 wt % with respect to the monomers.

### Effects of the initiator concentration

With the APS concentration varied from 0 to 0.6 wt % with respect to the monomers, several experiments were conducted, with the molar ratio of APS to NaHSO<sub>3</sub> fixed at 3:2; Figure 5 shows the evolution of CR. Two scenarios exist: when the concentration of APS was less than 0.5%, CR decreased as the concentration increased; but if the concentration was greater than 0.5%, the ratio increased a little as the APS concentration increased. On the other hand, at the same initiator concentration, CR decreased as the ultrasonic intensity and acoustic irradiation time increased according to the results in Figures 2 and 3.

When APS decomposed, some generated fragments of —SO<sub>4</sub> and —SO<sub>3</sub>H stabilized the polymer colloid particles because of the increased charge density and hydrophilicity on their surface. Therefore, CR directly decreased. On the other hand, as the concentration increased, the ion fragment increased the ion intensity of the emulsion. When the ion intensity exceeded a critical value, the latex became instable. In addition, polymerization could take place without an initiator (not shown in Fig. 5). This demonstrated that ultrasonic radiation could initiate the free-radical polymerization to some extent.

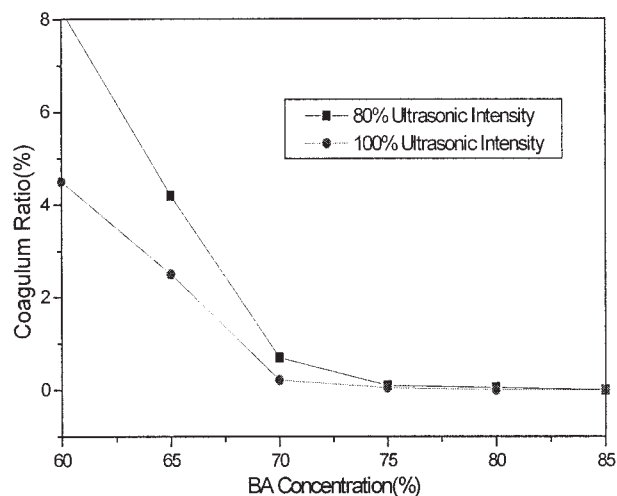


Figure 6 Effects of the BA concentration on CR.

### Effects of the quantity of BA

One of the functions of BA was to dissolve PSt into a solution. The more BA there was, the lower the viscosity was of the PSt solution, and the smaller the monomer-swollen PSt particles were that were generated during the ultrasonic dispersion; this could lead to a larger total surface area. Under such conditions, particles more easily seized the free radicals over the course of polymerization, and a stable emulsion with little coagulum could be obtained, as shown in Figure 6. Changing the concentration of BA in the PSt solution from 50 to 80%, we found that when the concentration was 50%, CR was over 15% (not shown in Fig. 6); CR was 0.7% when the concentration was 70%; and it was negligible when the concentration was greater than 75%.

### Effects of the acoustic temperature

Figure 7 reveals that CR decreased sharply as the temperature rose, although there was a slight increase in CR when the temperature was greater than 85°C. There were two kinds of influences of temperature in these experiments. First, because it was an exponential function of the temperature, the viscosity of the polymer solution or melt was significantly influenced by the changing temperature. As a result, raising the temperature of the ultrasonic emulsification was an effective approach for reducing the viscosity in these emulsions. Second, a high temperature induced a high polymerization rate for two reasons: ultrasonic irradiation at a high temperature more easily generated free radical, and the decomposition rate of the initiator increased. In fact, for a certain particle, it was more stable after polymerization than before. However, an extra-high temperature led to a high rate of initiator decomposition and reduced the efficiency of the initi-

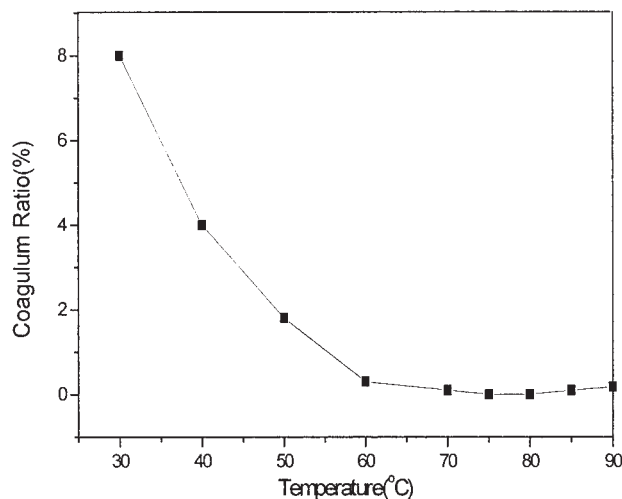


Figure 7 Effects of the temperature on CR.

ator. Therefore, in a certain range, raising the temperature was advantageous for the reduction of CR.

### Effects of the amount of AA

The effects of the amount of AA on CR can be seen in Figure 8. When the concentration exceeded 2 wt % of the total mass of PSt and BA, CR increased with the concentration; on the contrary, when the concentration was less than 2 wt %, CR decreased as the concentration increased. It is probable that a small quantity of AA could stabilize the polymer colloid particles because of its protecting colloidal action. An excessive amount of AA, however, augmented the acidity and viscosity of the emulsion and diminished the emulsification efficiency. This reduced the stability of the emulsion and increased CR. In addition, the impact of HMA was the same as that of AA to some extent.

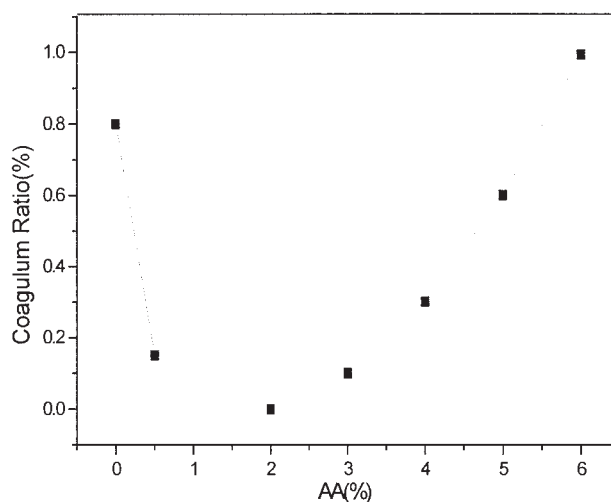
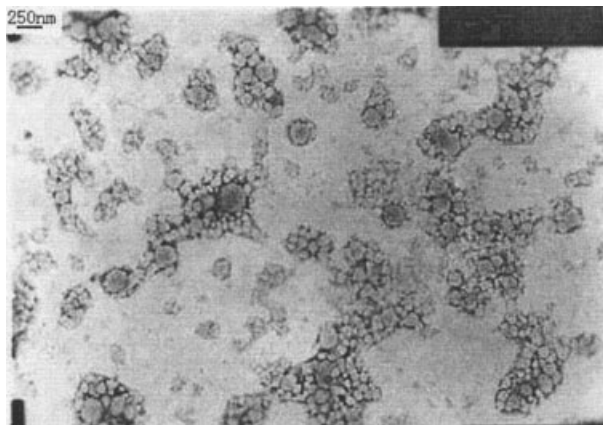


Figure 8 Effects of the AA concentration on CR.



**Figure 9** Transmission electron micrograph (JEM-100SX) of a latex sample prepared with the recipe in Table I. Phosphotungstic acid was used as a marker to allow us to detect the small particles in the film (observed at room temperature).

#### Particle size and particle size distribution (PSD)

As shown in Figure 9, the particle size of the latex ranged from 25 to 250 nm, and the PSD was obviously polydisperse. This indicated, to some extent, that the nucleation loci of this kind of emulsion polymerization were the drops of monomers.<sup>9</sup> The polydispersity of the monomer drops led to the polydispersity of the polymer colloid particles.

#### CONCLUSIONS

A systematic study of the synthesis of a stable PSt-g-BA emulsion with a low CR by ultrasonic radiation has been presented in this article. It has been demonstrated that a high acoustic intensity, a long acoustic irradiation time, and a high temperature are advantageous for reducing CR. In addition, the type and concentration of the emulsifier, the amount of the initiator, BA, and AA significantly affect CR. Furthermore, the PSD of the latex is polydisperse, and the particle size ranges from 25 to 250 nm.

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