

Formation of Highly Monodispersed Emulsifier-Free Cationic Poly(methylstyrene) Latex Particles

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ABSTRACT: Highly monodispersed emulsifier-free poly(methylstyrene) (PMS) latex particles were prepared via an emulsifier-free emulsion polymerization in the presence of 2,2'-azobis-(2-amidineopropane) dihydrochloride (V-50) as an initiator. A combination of kinetics and molecular weight distribution studies revealed that the polymerization followed the micellization nucleation mechanism. Results showed that an appropriate initiator concentration was necessary to obtain monodisperse and stable latex particles. Conversion of methylstyrene was found to increase significantly with increasing initiator concentrations. However, the size of PMS latex particles decreased with both the increase of initiator concentration and the reaction temperature at a constant ionic strength. The particle size was increased as the ionic strength of the aqueous phase increased, yet the variation of ionic strength had little effect on the particle size distribution. SEM micrographs showed that an agitation rate of 350 rpm or higher was required in order to produce highly monodispersed poly(methylstyrene) latex particles. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 2069–2074, 1999

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INTRODUCTION

The emulsifier-free emulsion polymerization of hydrophobic monomers has received much attention because it has both practical and academic interest.^{1,2} Besides its obvious advantage of having no added surfactant for applications in adhesive, coating, calibration standards, and supports for biomolecules, this technique allows us to prepare highly monodispersed polymer particles with well-defined surface properties, which are often used as model systems to study coagulation, flocculation, and rheology of colloids.^{3,4} Data from emulsifier-free polymerization are also useful for

testing new kinetic theories and models of particle nucleation in emulsion polymerization.⁵

Emulsifier-free emulsion polymerization was first reported by Kotera et al.,⁶ who demonstrated the possibility of conducting the emulsion polymerization of styrene in the absence of emulsifier. The formation of stable latex particles was explained by a homogeneous nucleation mechanism.^{7,8} Song and Poehlein⁹ have also suggested a two-stage model of particle formation for the emulsifier-free emulsion polymerization of styrene. The most studied emulsifier-free system is styrene/persulfate/water. Goodwin et al.^{10,11} described the effect of initiator type and its concentration, ionic strength, and reaction temperature as well as monomer concentration on the particle size and surface charge density. Rudin et al.¹² also reported conditions for the synthesis of

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Table I. Initial Composition of the Reaction Mixture in the Emulsifier-Free Polymerization of Methylstyrene at 70°C and an Agitation Rate of 350 rpm

Reaction Condition	Amount (g)	Concentration (<i>M</i>)
Deionized water	285	—
V-50 (initiator)	0.109–1.722	4.23×10^{-3} – 2.23×10^{-2}
Methylstyrene	15.0	0.424
Sodium chloride	0.05–0.50	3.0×10^{-3} – 3.0×10^{-2}

monodisperse emulsifier-free polystyrene particles of different sizes. Besides the anionic polystyrene particles, Goodwin et al.^{10,13} also reported a detailed experimental procedure for synthesizing cationic polystyrene latexes in an emulsifier-free system.

Recently, we have successfully prepared both anionic and cationic poly(methylstyrene) (PMS) latex particles containing aldehyde and carboxylic acid groups on the particle surface, via a copper-catalyzed oxidation in the presence of surfactant.^{14–16} Our continuing studies on the surface functionalization of poly(methylstyrene) latexes have prompted us to prepare emulsifier-free functional poly(methylstyrene) latex particles for biological applications. We, therefore, need to synthesize monodisperse emulsifier-free cationic poly(methylstyrene) particles prior to the surface functionalization. Although experimental procedures and the mechanism of the emulsifier-free emulsion polymerization of styrene have been well established, there are no instances in the literature concerning the synthesis of monodisperse emulsifier-free cationic poly(methylstyrene) particles. The aim of this article is to report conditions for the synthesis of these particles, as well as to describe the effect of initiator concentration, ionic strength, agitation speed, and reaction temperature on the rate of polymerization and the particle size. The similarities and differences between the emulsifier-free emulsion polymerization of styrene and methylstyrene are also compared.

EXPERIMENTAL

Materials

3(4)-Methylstyrene (60:40 *m*-:*p*-methylstyrene) from Aldrich Chemical Co. was freed from phenolic inhibitor by washing three times with a 10% sodium hydroxide solution, and then deionized

water until the pH of the monomer dropped to 7. It was further purified by vacuum distillation. Freshly deionized and distilled water was used as a dispersion medium. Initiator, 2,2'-azobis(2-amidinopropane) dihydrochloride (V-50) from Wako Chemicals and other chemicals were all used without further purification.

Synthesis of Emulsifier-Free Poly(methylstyrene) Latex Particles

A 500-mL round-bottomed three-necked flask, equipped with a mechanical stirrer and a condenser, was immersed in a thermostatic water bath. A prescribed amount of deionized water was charged to the vessel, and stirred for 20 min under nitrogen at 70°C. Freshly distilled 3(4)-methylstyrene (15 g) was then added to the reaction vessel, and stirring was continued for 15 min prior to the addition of 2,2'-azobis-(2-amidinopropane) dihydrochloride (V-50) dissolved in 5 mL of deionized water. A slow nitrogen purge was maintained throughout the polymerization, and the reaction was stopped after 24 h. A typical recipe is given in Table I. The conversion of methylstyrene to poly(methylstyrene) was determined using a gravimetric method; that is, a small amount of the reaction mixture was withdrawn from the reaction vessel at different reaction times, and the polymerization of the sample was stopped by adding hydroquinone aqueous solution (0.5 g/L). The sample was first dried in air at room temperature, then under vacuum at 40°C to a constant weight.

Characterization

Molar mass and distributions of PMS were determined by Gel Permeation Chromatography (GPC, Waters model 201) with a differential refractometer detector at 30°C. Tetrahydrofuran was used as the elute, and the elution rate was 1 mL/min.

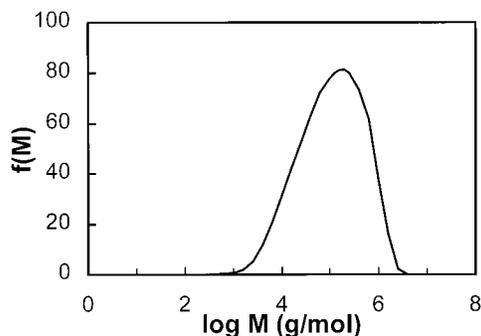


Figure 1. Typical GPC molar mass distribution of poly(methylstyrene) using V-50 as the initiator.

The GPC columns were calibrated with polystyrene standards and the apparent molar masses were calculated with Water's Direct Access version 4.1 software. Particle size and distribution were determined by a Coulter LS-230 Particle Size Analyzer. Scanning Electron Microscopy (SEM) photomicrographs were obtained on a Stereoscan 440, Leica instrument. A drop of diluted latex dispersion was spread onto a glass surface and dried in a dust-free environment at room temperature. The dried specimen was then coated under vacuum with a thin layer of gold to a depth of c.a. 5 Å.

Dialysis of Poly(methylstyrene) Latexes

Poly(methylstyrene) latexes (20 mL, 5% solid content) were placed into a dialysis tube (Model Spectra / pore 4, MWCO 12,000–14,000), and immersed in 1 L of deionized water at 25°C. The dialysis procedure was monitored by the conductivity meter (Model ES-14, Horiba).

RESULTS AND DISCUSSION

Figure 1 shows a GPC analysis of the poly(methylstyrene) particles. A single and broad peak with a low molar mass tail is observed, which is comparable to the styrene / $K_2S_2O_8$ / water system.⁷ Three possible nucleation mechanisms for the emulsifier-free emulsion polymerization have been previously proposed: homogeneous nucleation; micellization nucleation; and coagulation nucleation.^{17,18} The solubility of monomer in water is a key factor governing the reaction mechanism. For example, for sparing water-soluble monomers such as styrene, the micellization nucleation mechanism was proposed by Goodall et

al.⁷ The electron micrograph showed the formation of tiny micelle-like particles in the early stage of polymerization. The GPC results also indicated that particles, formed in the early stage of polymerization, contained a large amount of styrene oligomers (MW ca. 1000). It was suggested that these oligomers were surface active and their micellization provided sites for further polymerization, resulting in a high molar mass of polymer chains. Because methylstyrene exhibits reactivity being analogous to that of styrene, it is reasonable to anticipate that the polymerization of methylstyrene is comparable to styrene, which follows the micellization nucleation mechanism. Our GPC analysis of the poly(methylstyrene) indicated that low molar mass methylstyrene oligomers were formed during the polymerization, which might be due to the termination between the relatively stable methylstyrene oligomeric radicals. This result strongly suggested that the emulsifier-free emulsion polymerization of methylstyrene also proceeded through a micellization nucleation mechanism, similar to styrene.

Figure 2 shows the time dependence of the conversion of methylstyrene with different amounts of initiator. The percentage of conversion increased with the increase of initiator concentration, and 88% conversion was achieved when methylstyrene to V-50 ratio was 20:1 ($[V-50] = 2.23 \times 10^{-2} M$). This ratio was much higher than the styrene to V-50 ratio reported by Goodwin,¹³ of which only 300:1 was required. This remarkable difference between the emulsifier-free emulsion polymerization of styrene and methylstyrene may be attributed to the fact that methylstyrene has lower activation energy (13.4 kcal/mol) than styrene (17.6 kcal/mol),¹⁹ as a re-

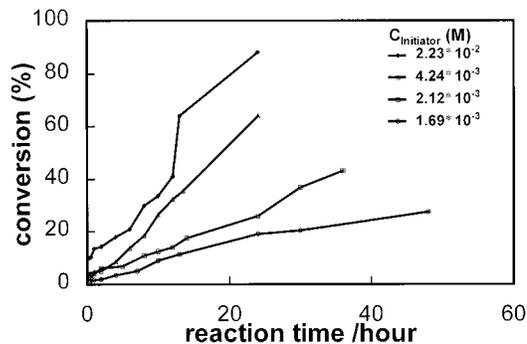


Figure 2. Reaction kinetics for different initiator concentrations with a constant ionic strength of $2.6 \times 10^{-2} M$. Details of the reaction conditions are listed in Table I.

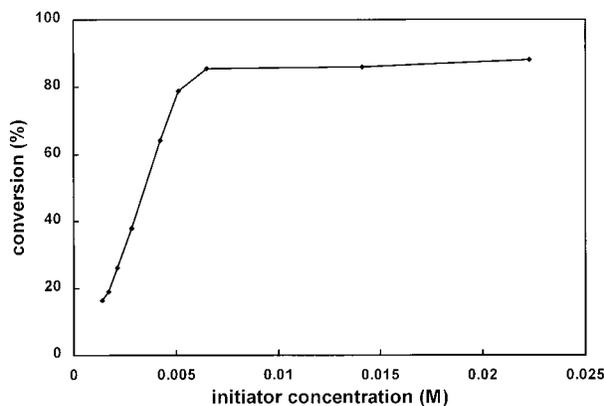


Figure 3. Dependence of the final conversion on the initiator concentration. Details of the reaction conditions are listed in Table I. All conversions were determined after 24 h reaction.

sult of a more stable benzylic radical. Thus, a higher number of methylstyrene radicals are generated during the initiation stage of the polymerization. On the other hand, the propagation rate constant of methylstyrene [$220/(\text{mol} \cdot \text{s})$] is lower than styrene [$300/(\text{mol} \cdot \text{s})$] due to its higher radical stability.¹⁹ The rate of polymerization is, therefore, slower. A combination of these two factors may result in a higher degree of terminations between the monomer radicals, monomer and low molar mass oligomeric radicals in an early stage. This hypothesis was confirmed by a dialysis study of the PMS latexes. A sharp increase in the specific conductance of deionized water outside the dialysis tube during dialysis was observed. The electrolytes dialyzed out from the emulsion were low molar mass substances, which did not contribute to the nucleation and polymerization reactions. In other words, a large amount of initiator was wasted during the initiation stage of the polymerization.

To obtain optimal initiator concentration for the complete conversion of methylstyrene, the dependence of final conversion of methylstyrene on initiator concentration was systematically studied by using various initiator concentrations, as shown in Figure 3. It was found that increasing initiator concentrations up to $8.92 \times 10^{-3} \text{ M}$ resulted in a significant increase of conversion, while a further increase of initiator concentrations only had a slight effect. Therefore, an initiator concentration of $8.92 \times 10^{-3} \text{ M}$ was used for subsequent studies in order to achieve quantitative conversion.

When $(\text{conversion})^{2/3}$ was plotted against the reaction time for the emulsifier-free emulsion po-

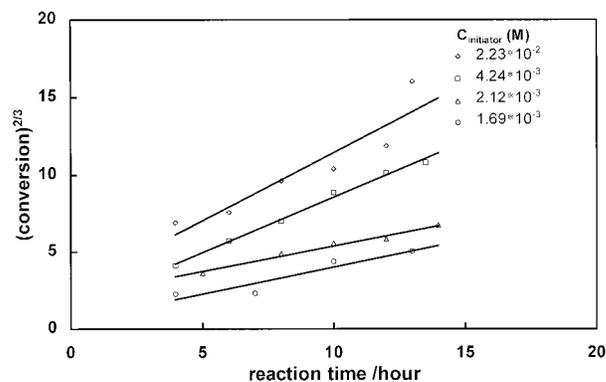


Figure 4. Plots of $(\text{conversion})^{2/3}$ vs. t , where t is reaction time, and the ionic strength is $2.6 \times 10^{-2} \text{ M}$.

lymerization of methylstyrene, a linear relationship was observed, as shown in Figure 4. The linear range can be extended to about 50% conversion. This relationship is similar to the styrene/KPS/water system reported by Chen et al.²⁰ They suggested that the linear relationship between $(\text{conversion})^{2/3}$ and time implied that polymerization might occur mainly in the shell of the particle during the particle propagation stage.

Figure 5 shows the initiator concentration dependence of the particle size of PMS latexes, where the initial ionic strength was maintained at $2.6 \times 10^{-2} \text{ M}$ by the addition of appropriate amounts of inert sodium chloride. It was noted that the particle size of PMS latexes decreased considerably with the increase of initiator concentration. As the initiator concentration increased, number of ionic groups involved in the stabilization of latexes increased, resulting in the formation of smaller particles. By comparing the results

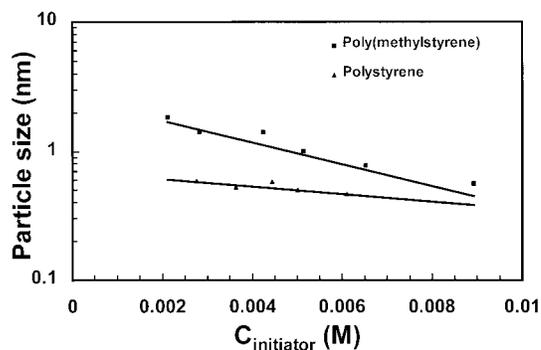


Figure 5. Dependence of final size of latex particles on initiator concentration, where \blacklozenge is for poly(methylstyrene) at ionic strength $2.6 \times 10^{-2} \text{ M}$, and \blacktriangle is for polystyrene at ionic strength $1.8 \times 10^{-2} \text{ M}$. Polystyrene data is taken from ref. 13.

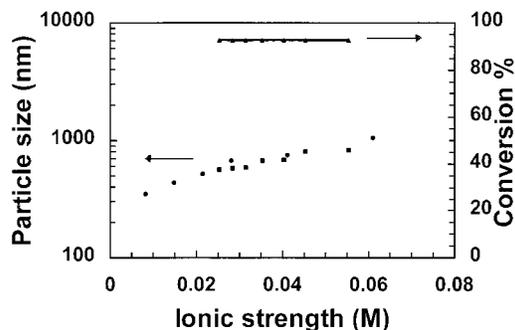


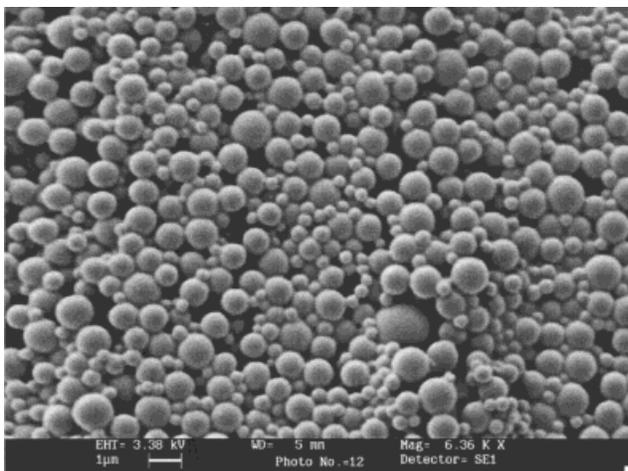
Figure 6. Dependence of the final size of PMS and PS latex particles on ionic strength, where the squares (■) are data of poly(methylstyrene) at a constant initiator concentration ($8.4 \times 10^{-3} M$), and the circles (●) are polystyrene data taken from ref. 13 at a constant initiator concentration ($2.76 \times 10^{-3} M$). Triangles (▲) plot is for the conversion of final PMS latex vs. ionic strength.

of the styrene/V-50/water system under similar conditions as reported by Goodwin,¹³ it is found that the particle size of the polystyrene is less influenced by the initiator concentration than poly(methylstyrene). The particle size of the polystyrene latexes is also smaller than PMS at the same initiator concentration. These effects may be due to a lower initiation efficiency of methylstyrene system because of its significant termination at the initiation stage of the polymerization. Finally, it was observed that when the initiator

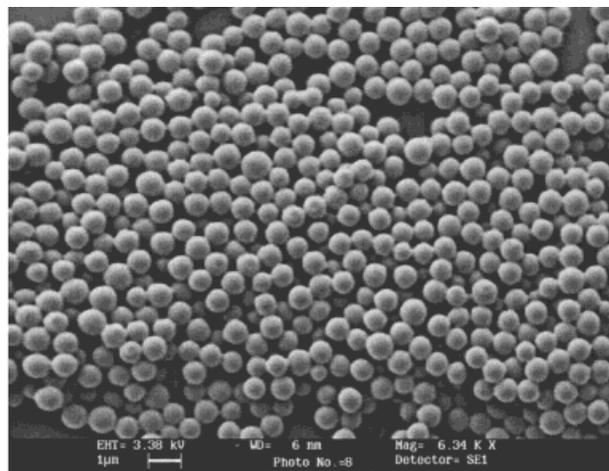
concentration was less than $2.1 \times 10^{-3} M$, the resulting particles were unstable in the dispersion. This instability may be attributed to the incomplete polymerization of methylstyrene, because less than 45% conversion was achieved.

Figure 6 shows the dependence of particle size on ionic strength, where the squares are data of methylstyrene at a constant initiator concentration ($8.4 \times 10^{-3} M$), and the circles are styrene data that are taken from Goodwin's work¹³ at a constant initiator concentration ($2.76 \times 10^{-3} M$), respectively. It was noted that poly(methylstyrene) and polystyrene had the same dependence of particle size on the ionic strength, which was the particle size increased with the increase of ionic strength. In addition, the ionic strength had little effect on the particle size distribution, which was demonstrated by the SEM photomicrographs. Similarly, it was found to have almost not effect on the overall reaction conversion, as shown in Figure 6.

As well as examining the effects of initiator concentration and ionic strength on the particle size, the agitation speed was found to have a remarkable influence on the particle size distribution. Figure 7(a) illustrated that a low agitation speed, for example, < 250 rpm, gave a bimodal particle size distribution, while a speed of 350 rpm resulted in nearly monodisperse latex particles [Fig. 7(b)]. Therefore, all of the polymeriza-



(a)



(b)

Figure 7. SEM photographs of the PMS latexes prepared using different agitation rates: (a) 250 rpm, and (b) 350 rpm. Details of the reaction conditions are listed in Table I.

Table II. Reaction Temperature Dependence of the Final Monomer Conversion and Particle Size

Latex	Temperature (°C)	Particle Diameter (nm)
T1	60	683
T2	70	562
T3	80	476

tions reported here were carried out at an agitation speed of 350 rpm.

Table II summarizes the temperature dependence of particle size, where the ionic strength, monomer, and initiator concentrations were kept constant. It shows that the latex particle size decreases as the temperature increases. This interesting effect may be due to the fact that, at a higher reaction temperature, the propagation rate of methylstyrene may considerably increase, reducing the radical termination and enhancing the initiation efficiency. As a result, more ionic groups are involved in the stabilization of the particles, giving a smaller particle size.

CONCLUSIONS

Our results demonstrate that the emulsifier-free emulsion polymerization of methylstyrene followed the micellization nucleation mechanism, giving highly monodispersed latex particles. In comparison with the styrene system, a bigger particle size and a lower conversion were found for the emulsifier-free emulsion polymerization of methylstyrene under the same initiator concentration. This effect might be attributed to the presence of the methyl group, which could stabilize the benzylic radical. The particle size was found to decrease with the increase of initiator concentration and reaction temperature. The conversion of methylstyrene increased remarkably with the increase in initiator concentration. On the other hand, the increase of the ionic strength of the aqueous phase led to the formation of bigger particles, but had little effect on particle size distribution and conversion. Finally, an appropri-

ate agitation speed rate (above 350 rpm in our study) was a necessity for the preparation of highly monodispersed poly(methylstyrene) latex particles.

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