

Electrolyte Effect on the Particle Characteristics Prepared by Soap-Free Emulsion Polymerization

Seungtak Han, Kangseok Lee, Sang Eun Shim, Prakash J. Saikia, and Soonja Choe*

Department of Chemical Engineering, Inha University, Incheon 402-751, Korea

Inwoo Cheong

Department of Applied Chemistry, Kyungpook National University, Daegu 702-701, Korea

Received January 10, 2007; Revised April 17, 2007

Abstract: Monodisperse micron-sized polystyrene (PS) spheres were successfully obtained using a single stage soap-free emulsion method in aqueous media mixed with ethanol (co-solvent) containing NaCl as the electrolyte. The optimum conditions for preparing the monodisperse PS microspheres, using soap-free emulsion polymerization in a water/ethanol mixture with an electrolyte, were studied. The presence of the co-solvent and electrolyte controlled the particle dispersion stability during the polymerization. The microspheres formed using PS, with a weight-average diameter of 2.6 μm , coefficient of variation of 5.3% and zeta potential of -15.1 eV, were successfully obtained in the presence of 0.1 wt% NaCl, 10 wt% monomer, 0.1 wt% initiator and 95/5 (g/g) of a water/ethanol mixture reacted at 70 °C for 24 h.

Keywords: soap-free, emulsion polymerization, styrene, electrolyte.

Introduction

The development of new techniques for producing micron-sized polymer particles has long been interested in industries because of its important applications in wide areas including toners, instrument calibration standards, column packing materials for chromatography, microelectronics materials, and supporting materials for biomedical and biochemical analysis.¹⁻⁵ Typical methods that recently adopted for preparing micron-sized monodisperse polymer particles are non-aqueous dispersion polymerization,^{6,7} seeded growth technique,⁸ and two-step swelling techniques.^{1,9} However, these methods face problems such as broad particle size distributions, difficulty in size control, use of hazardous solvents, or multi-step polymerization.¹⁰ To overcome these difficulties, it was proposed a single stage polymerization technique, which is based on soap-free emulsion polymerization.¹¹ In this technique, the aggregation and dispersion stability of polymer particles in the course of the reaction is controlled by the addition of ionic surfactants to the reaction system. The final size distribution of polymer particles that are formed in the soap-free emulsion polymerization depends strongly on the electrostatic potential of the particle surface.¹²⁻¹⁴ During the course of reaction, the surface potential

can be altered by the addition of ionic surfactants and type of electrolytes.

In the synthesis of micron-sized polymer particles via emulsion polymerization, several attempts have been made. Homola *et al.* prepared polystyrene microspheres of diameter 1.6 μm with the mixture of methanol/water as a reaction medium in the presence of an electrolyte using the soap-free emulsion polymerization.¹⁵ Gu *et al.* reported that polystyrene spheres were prepared in the range of 2-2.5 μm of diameter with 20-30% deviation by adding the cationic surfactant such as cetyltrimethyl-ammonium bromide at the very early stage of emulsion polymerization.^{16,17} The polystyrene particles of 1.65 μm diameter was prepared by employing the seeded growth technique in various alcohols/water medium by Zhang *et al.*, but no information of the uniformity was reported.¹⁸ To prepare polystyrene microspheres of approximately 2 μm diameter, a modified soap-free emulsion polymerization technique was developed.¹⁹ But in this technique a long polymerization period is required due to the successive monomer feeding even though the swelling step was omitted.

One of the ways in preparing micron-sized polymer particles in the soap-free emulsion polymerization is the use of an electrolyte reported by Liein, Kuist and Stannett working with vinyl acetate.²⁰ While Goodwin, Ottewill *et al.*²¹ reported that the ionic strength affected the particle size and

*Corresponding Author. E-mail: sjchoe@inha.ac.kr

colloid stability of polystyrene in the soap-free emulsion polymerization. However, these methods were generally used only to prepare nano-sized particles with the control of complex pH.

In this study, to prepare the micron-sized PS particles using the conventional soap-free emulsion polymerization technique, an electrolyte, NaCl and a co-solvent, ethanol, was utilized. The effects of different ratio of the medium mixture, concentration of the monomer, initiator and electrolyte, and the type of the electrolyte on the polymerization characteristics in terms of the conversion, polymerization rate, particle size and its distribution, coefficient of variation, and the zeta potential were investigated.

Experimental

Materials. Styrene (99%, Junsei, Japan) was purified using an inhibitor removal column (Aldrich, USA) and stored at -5°C prior to use. Potassium persulfate (KPS, Junsei, Japan) was used as an initiator without further purification. Alkali chloride (NaCl) purchased from Samchun Chemical, Korea, was used as an electrolyte agent. Ethanol (99%; Samchun Chemical, Korea) and double-distilled deionized water were used as polymerization media.

Characterizations. The weight-average diameter (D_w) and the coefficient of variation (C_v) of the particle diameter were defined using the following equations by counting at least 100 individual particles from SEM microphotographs.

$$D_w = \frac{\sum_{i=1}^n n_i D_i^2}{\sum_{i=1}^n n_i D_i}, \quad (1)$$

$$C_v = \frac{(\sum (d_i - (\sum n_i d_i / \sum n_i))^2 / \sum n_i)^{1/2}}{(\sum n_i d_i / \sum n_i)} \times 100, \quad (2)$$

where n_i is the number of particles having d_i .

Particle size distribution (LS230[®], Beckman Coulter, USA) measured the principle of laser diffraction. A Hitachi SEM (Scanning Electron Microscopy) S-4300 was used to investigate the shape and size of the synthesized polystyrene (PS). Zeta-potential (Malvern Zetasizer 4) was used to measure the charge of the particle surface.

Results and Discussion

Effect of the Reaction Medium. Table I shows the reaction recipes employed in this experiment, representing the variables, which are the medium ratio, the concentration of the initiator, electrolyte, and monomer. The experimental results and discussion will be employed in term of the variables.

The first variables are the reaction medium (expt. 1) in

Table I. Recipe Used in the Soap-free Emulsion Polymerization Using NaCl

SL. No.	Monomer	Electrolyte	Initiator	Medium	
	Styrene (g)	NaCl (g)	KPS (g)	Water (g)	Ethanol (g)
Medium ratio (expt. 1)	10	0.1	0.1	100	0
				95	5
				90	10
				80	20
Initiator Concentration (expt. 2)	10	0.1	0.05	95	5
			0.1		
			0.2		
			0.3		
Electrolyte Concentration (expt. 3)	10	0.05	0.1	95	5
		0.1			
		0.2			
		0.3			
Monomer Concentration (expt. 4)	5	0.1	0.1	95	5
	10				
	15				
	20				

Table I. Figure 1 shows the SEM images of the PS particles prepared by soap-free emulsion polymerization using various medium ratios of water to ethanol from (a) 100 : 0, (b) 95 : 5, (c) 90 : 10, to (d) 80 : 20 at 70°C . In this experiment, monomer content is fixed at 10 wt% relative to the medium, and NaCl and KPS contents are fixed at 1 wt% refer to monomer. As seen in Figure 1(a), when the medium ratio is 100 : 0, which means the soap-free emulsion polymerization, the particle size is $1 \mu\text{m}$ with narrow size distribution. On the other hand, the substitution of 5 g of ethanol in the water medium produces fairly large particles with narrow size distribution since the presence of small amount of ethanol could facilitate the nucleation of oligomer and particle adsorption. When more (10 and 20 g) ethanol is substituted in Figures 1(c) and 1(d), respectively, the particle size distribution becomes broad with bimodal type. In particular, the surface of the large particles becomes rough representing the poor stability in Figure 1(c) and significant coagulation of the primary particles is observed at the higher content of ethanol due to the reduced electrostatic repulsive energy in Figure 1(d). The substitution of ethanol with fixed ratio in the water medium reduces the negative charge of sulfate for the particle surface to form stable and spherical particles. However, when the ethanol content is too large, the particle size distribution turns to bimodal, where the larger particle size increases to 3 and $4 \mu\text{m}$, but the small particles become

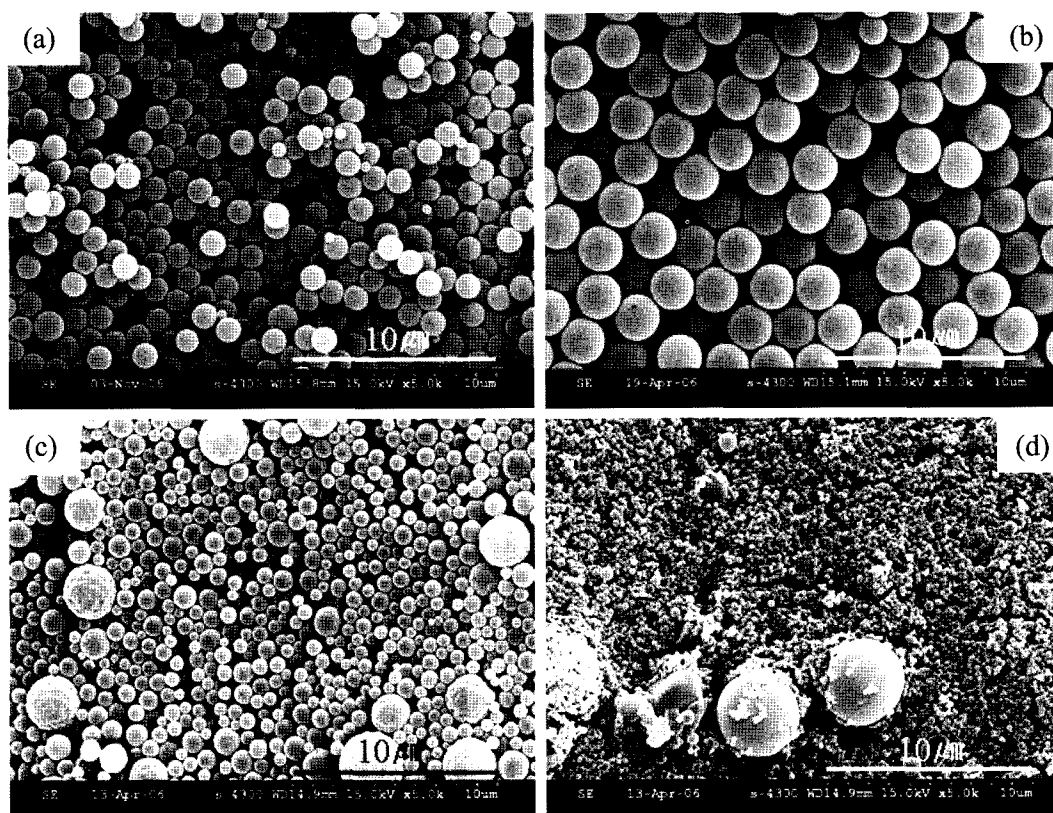


Figure 1. SEM photographs of PS microspheres prepared by soap-free emulsion polymerization in 0.1 g of KPS and NaCl at 70°C for 24 h in various water : ethanol ratios of (a) 100 : 0, (b) 95 : 5, (c) 90 : 10, and (d) 80 : 20.

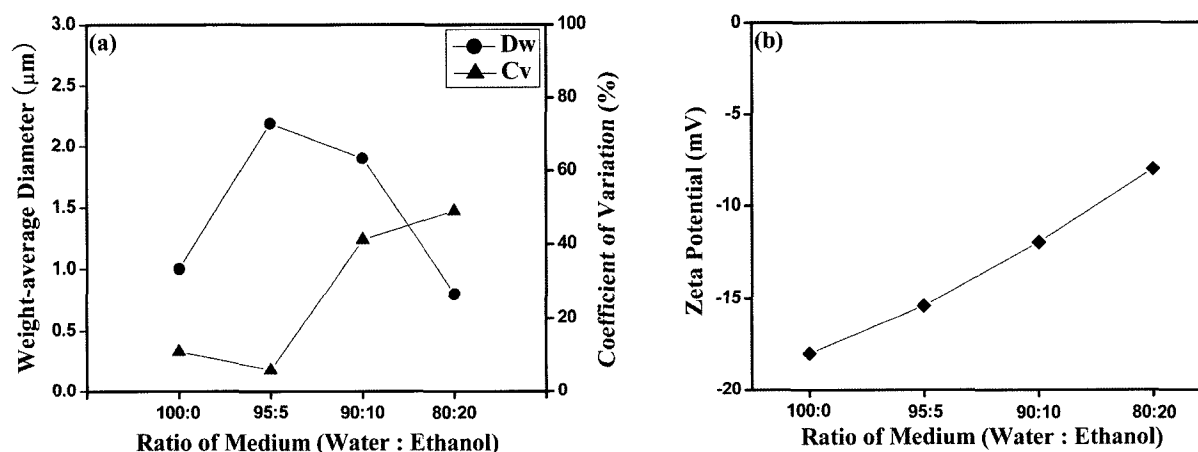


Figure 2. (a) Weight-average diameter and coefficient of variation and (b) zeta potential of the synthesized PS particles obtained in 0.1 g of KPS and NaCl at 70°C for 24 h at various ratios of the medium (water : ethanol).

to 500 and 300 nm in Figures 1(c) and 1(d), respectively.

The weight-average particle size, coefficient of variation and the zeta potential of PS particles synthesized at various ratios of the medium in water to ethanol at 70°C for 24 h are plotted in Figure 2. The weight-average diameter of PS in Figure 2(a) increased from 1.0 to 2.19 μm for the medium ratio from 0 to 5 wt% ethanol, respectively, and then the

diameter decreased to 1.90 and 0.79 μm for 10 and 20 wt% of ethanol in the water medium, respectively. The coefficient of variation was 11.1 and 5.8, when 0 and 5% of ethanol were added, respectively, but dramatically increased to 40.2 and 48.9 for 10 and 20% ethanol, respectively. The presence of ethanol could facilitate the nucleation of oligomer and particle adsorption due to the reduced electrostatic repul-

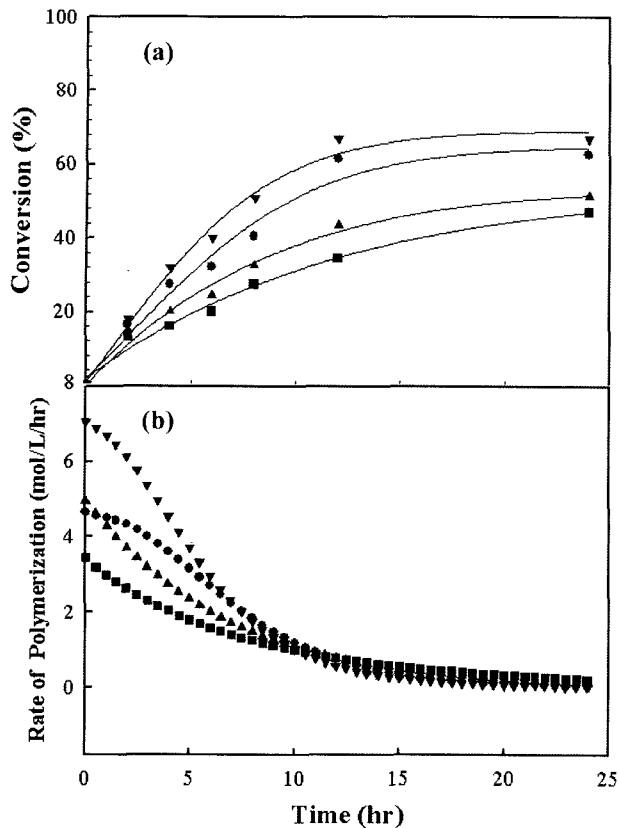


Figure 3. (a) Conversion and (b) rate of polymerization as functions of time of PS prepared in 0.1 g of KPS and NaCl at 70°C for 24 h at various water : ethanol ratios of (\blacktriangledown) 100 : 0, (\bullet) 95 : 5, (\blacktriangle) 90 : 10, and (\blacksquare) 80 : 20.

sion energy.^{22,23} The zeta potential of the synthesized PS particles linearly increased from -8.2 to -18.1 mV with the water content from 80 to 100% as seen in Figure 2(b), respectively.

In general, solubility parameter of the reaction medium influences the particle size. A linear relationship between the particle size and solubility parameters of the dispersing media was reported in dispersion polymerization.²⁴ The increase in particle size was attributed to the retardation during the nucleation due to increased solubility of the oligomers in the dispersing media. However, the addition of ethanol possesses the similar effects on the chemical composition of growing oligoradicals.

The conversion and rate of polymerization of the PS particles upon various medium ratio at 70°C for 24 h is plotted in Figures 3(a) and 3(b), respectively. The maximum conversion was 66 and 62% for 0 and 5% of ethanol for 12 h, respectively, then leveled off. Thus, the conversion of the PS particles increased with the water concentration in the medium mixture and the rate of polymerization shows the maximum when no ethanol is evolved. From the previous results shown in Figures 1 and 2, the best medium ratio for obtaining micron-sized monodisperse PS particles is 95 : 5

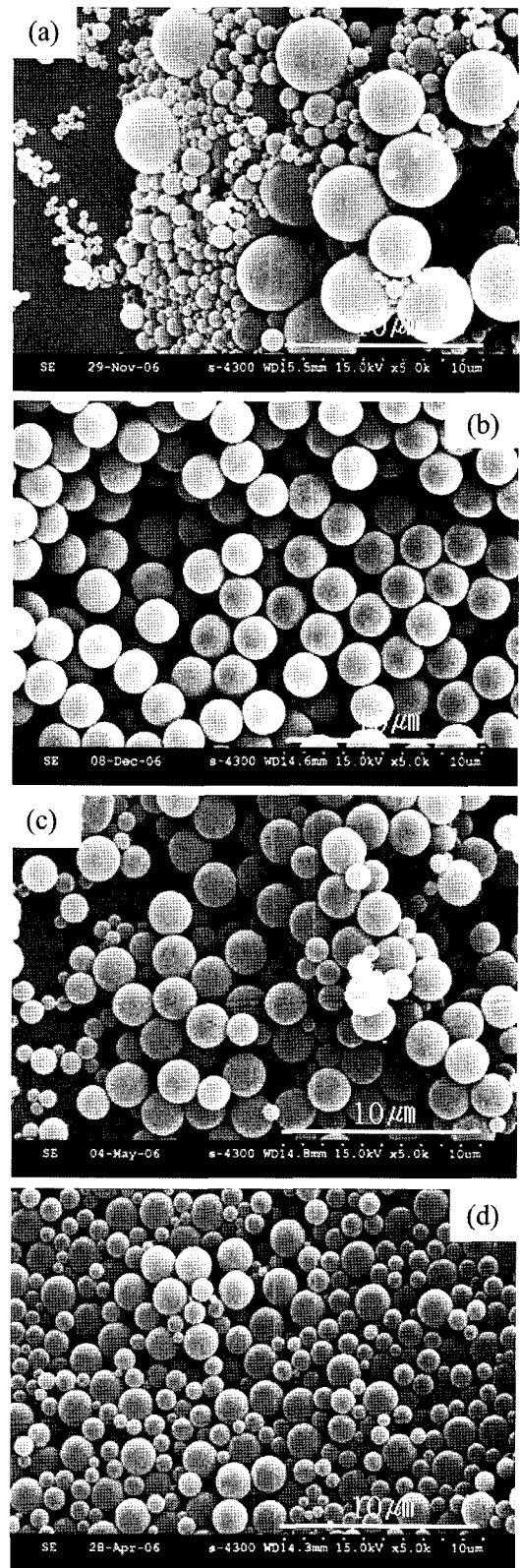


Figure 4. SEM photographs of PS microspheres prepared by soap-free emulsion polymerization in 95 : 5 of water to ethanol ratio and 0.1 g NaCl at 70°C for 24 h at various concentrations of initiator (a) 0.05 g, (b) 0.1 g, (c) 0.2 g, and (d) 0.3 g.

(water : ethanol).

Effect of the Initiator Concentration. Expt. 2 in Table I represents the recipe for the variance of the initiator concentration. The concentration of monomer and electrolyte was 10 wt% relative to the medium and 0.1 wt% to the monomer, respectively, and the water to ethanol ratio in the medium was 95 : 5. Figure 4 shows the SEM images of the PS particles prepared by soap-free emulsion polymerization at various initiator (KPS) concentrations of (a) 0.05, (b) 0.1, (c) 0.2, to (d) 0.3 g at 70 °C for 24 h. As seen in this figure, the weight-average diameter decreased with the initiator concentration with poor distribution. In general, when initiator concentration increased, the initial number of oligomers increased due to the increased sulfate ion in the reaction, and then a large number of micelles were formed. Since the fixed amount of monomer is added in the system, the number of particles increased and resulted in the reduced particle size in the soap-free emulsion polymerization simultaneously.

The weight-average particle size, coefficient of variation

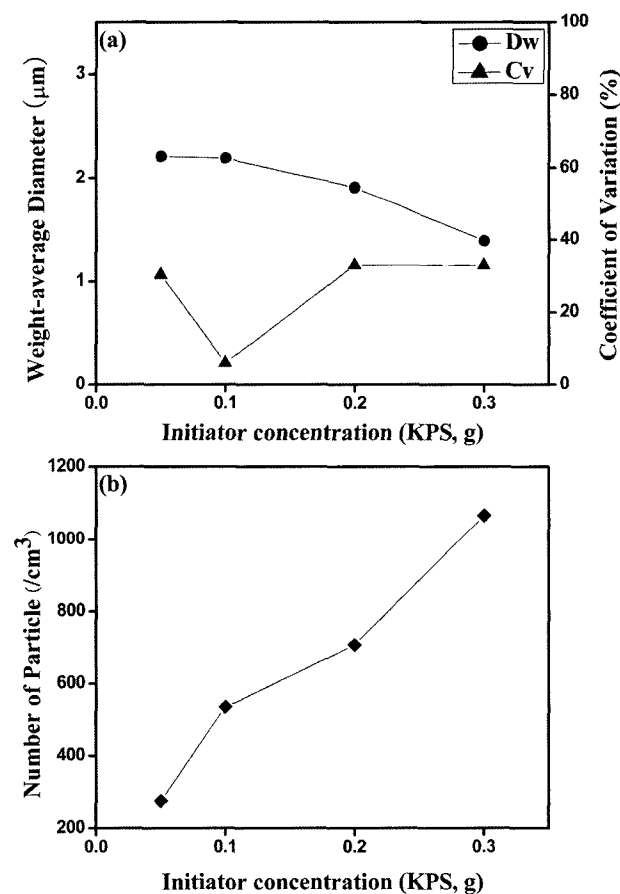


Figure 5. (a) Weight-average diameter and coefficient of variation and (b) Number of PS particles of the synthesized PS particle obtained in 95 : 5 of water to ethanol ratio and 0.1 g NaCl at 70 °C for 24 h using the various concentrations of initiator (KPS).

and particle numbers of PS particles synthesized using the various concentrations of initiator are plotted in Figure 5. The weight-average particle diameter analyzed in Figure 5(a) is 2.21, 2.19, 1.91 and 1.39 μm for 0.05, 0.1, 0.2 and 0.3 g of KPS, respectively, which decreases with the KPS content. The coefficient of variation of the particles is 30.4, 5.8, 34.0 and 32.7 for 0.05, 0.1, 0.2 and 0.3 g of KPS, respectively, thus, 0.1 g of KPS gives the best size distribution in this system. Figure 5(b) represents that the number of particles linearly increased with the initiator concentration. The particle numbers are 250, 530, 670 and 1,080 for the system with 0.05, 0.1, 0.2 and 0.3 g of KPS, respectively. When the initiator concentration increased, the initial number of oligomers increased due to the increased sulfate ion in the reaction medium and then large number of micelles was formed.

The conversion and rate of polymerization of 10 wt% styrene relative to medium and 95 : 5 of water to ethanol ratio upon the initiator concentration at 70 °C for 24 h are plotted as a function of reaction time in Figure 6. The conversion (Figure 6(a)) increased with the reaction time and initiator concentration. In addition, the conversion increased up to 12 h and then leveled off. However, when 0.05 g of KPS is

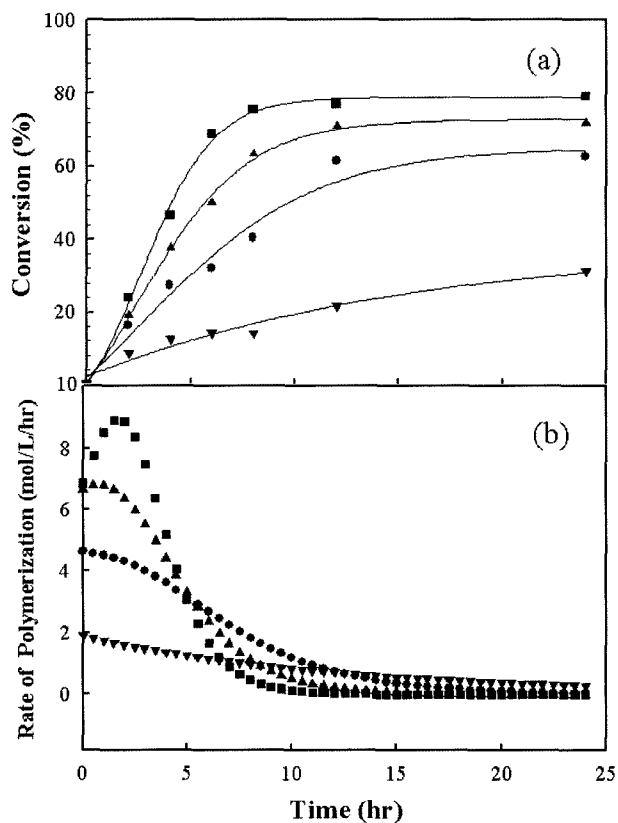


Figure 6. (a) conversion and (b) rate of polymerization as functions of time of PS prepared in 95 : 5 of water to ethanol ratio and 0.1 g NaCl at 70 °C for 24 h using various initiator concentrations of (▼) 0.05 g, (●) 0.1 g, (▲) 0.2 g, and (■) 0.3 g.

used, the conversion is extremely low, which is 30%, this may arise from the insufficient initiator concentration to form reactive oligomeric radicals and thus the reaction occurs very slowly. Regarding the rate of polymerization in Figure 6(b), the initial polymerization rate increased with increased initiator concentration. When 0.05 g of KPS is used, the initial rate of polymerization is very low due to the big hindrance of the electrolyte (NaCl) and thereby the reaction time takes long. On the other hand, when 0.1 g of KPS is used, the initial rate of the polymerization is also not so high due to the same hindrance of the electrolyte (NaCl) as seen in Figure 6(b), but the later rate of the polymerization gradually decreased. As a consequence, the particle size increased in monodisperse form due to the formation of micelles and diffusion of monomer into the micelles. However, when 0.2 and 0.3 g of KPS were used, the initial rate of the polymerization rapidly increased due to less hindrance of the electrolyte upon the increased reactive radicals, and the later rate of polymerization also rapidly decreased. Thus, the different profile of the rate of polymerization between 0.1 and 0.3 g of KPS induces the difference in particle size and its distribution. In addition, initiator concentration is one of the important factors to eliminate the hindrance of the electrolyte.

Effect of the Electrolyte Concentration. Expt. 3 in Table I represents the recipe for the variance of the electrolyte concentration. Figure 7 shows the SEM photographs of PS particles prepared in various concentrations of NaCl at 70°C for 24 h. The particle size distribution is narrow with 0.1 g of NaCl, but broad with 0.05, 0.2 and 0.3 g of NaCl.

The weight-average diameter and the coefficient of variation are plotted in Figure 8(a) as a function of the NaCl concentration. The weight-average particle sizes are 0.725, 2.19, 1.56, and 1.34 μm and the coefficient of variation is 28.3, 5.8, 27.8 and 34.6 for 0.05, 0.1, 0.2 and 0.3 g of NaCl, respectively. Thus, the suitable amount of electrolyte affects the particle size and its distribution. The zeta potential of the PS particles obtained from various concentrations of NaCl strongly supports the above results in Figure 8(b). The higher the NaCl concentration, the lower the zeta potential value was observed, which meant that the sodium ion (positive charge) diffused on the negatively charged particle surface resulting in the decrease in negative charge with the NaCl concentration. Thus, sufficiently large concentration of electrolyte will destabilize electrostatically stabilized lattices and cause them to coagulate or coalesce. It is also possible to study the effects of electrolyte additions over a range of concentrations below the critical coagulation concentration of latex.²⁶

Regarding on the conversion of styrene to PS as a function of time at various concentrations of NaCl, the higher the NaCl concentration, the lower the conversion was observed with time. This can be explained in the following way: the chloride radical reacts with water to result in

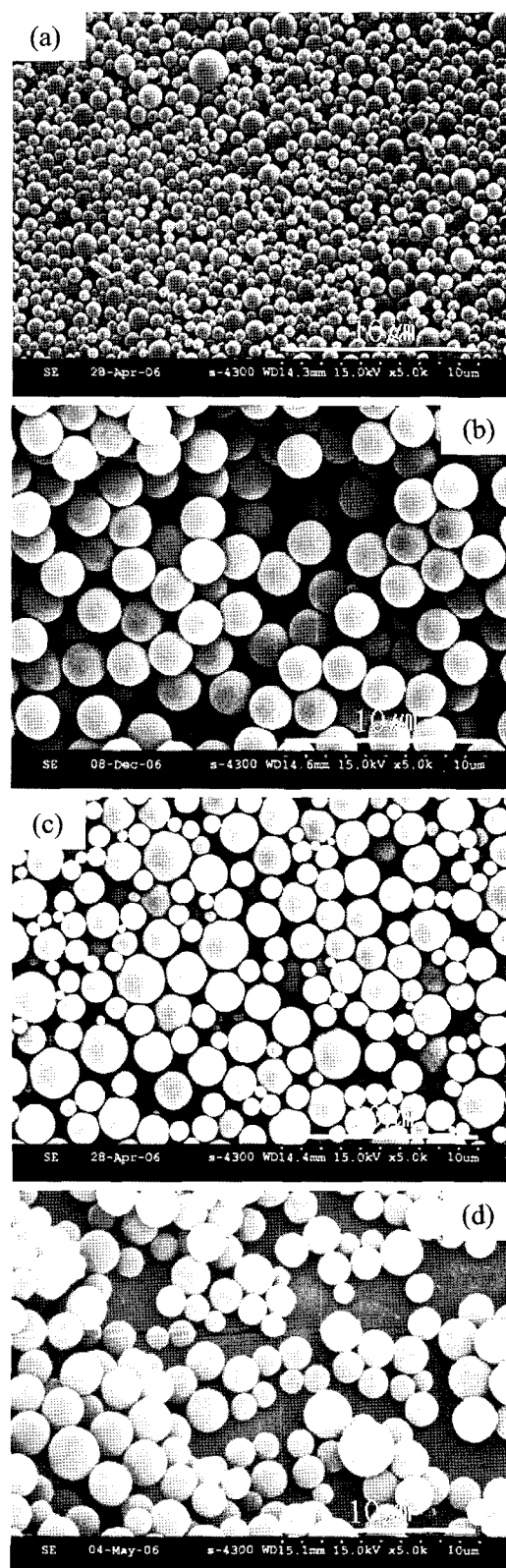
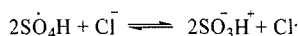
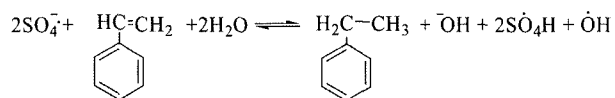
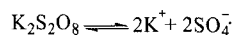


Figure 7. SEM photographs of PS microspheres prepared by soap-free emulsion polymerization in 95 : 5 of water to ethanol ratio and 0.1 g of KPS at 70°C for 24 h with various concentrations of NaCl (a) 0.05 g, (b) 0.1 g, (c) 0.2 g, and (d) 0.3 g.

hydroxyl radicals, which are responsible for the hydroxyl groups to be found in the polymers obtained. In addition, since the life time of the hydroxyl radical is shorter than that of the bisulphate radical, the total number of radical decreases resulting in decreasing the initial rate of polymerization.²⁵ Thus, by the following principle, the conversion will decrease as long as the higher concentration of Cl^- .



Effects on the Monomer Concentration. Expt. 4 in Table I represents the recipe for the variance of the mono-

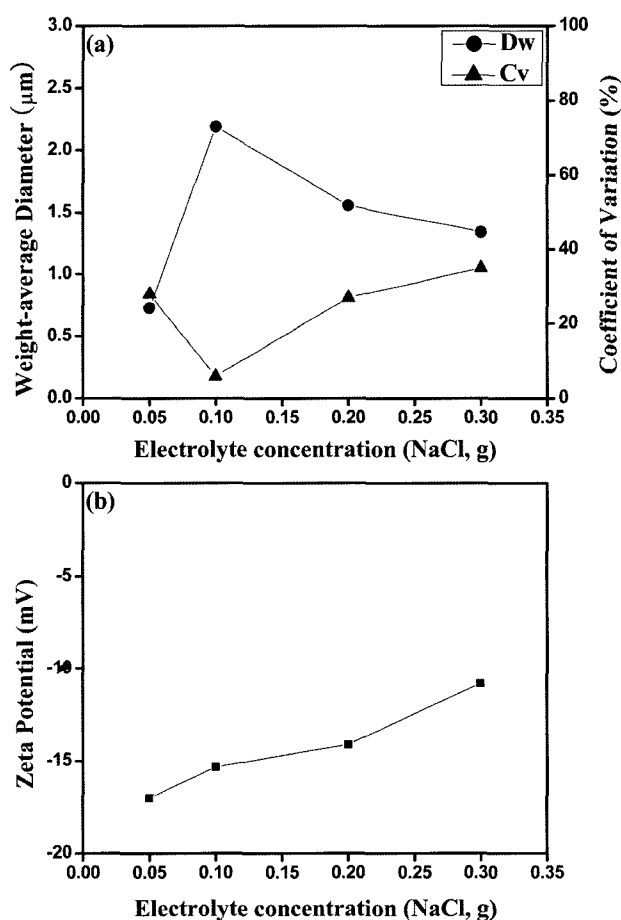


Figure 8. (a) Weight-average diameter and coefficient of variation and (b) zeta potential of the synthesized PS particles obtained in 95 : 5 of water to ethanol ratio and 0.1 g of KPS at 70 °C for 24 h with various NaCl concentrations.

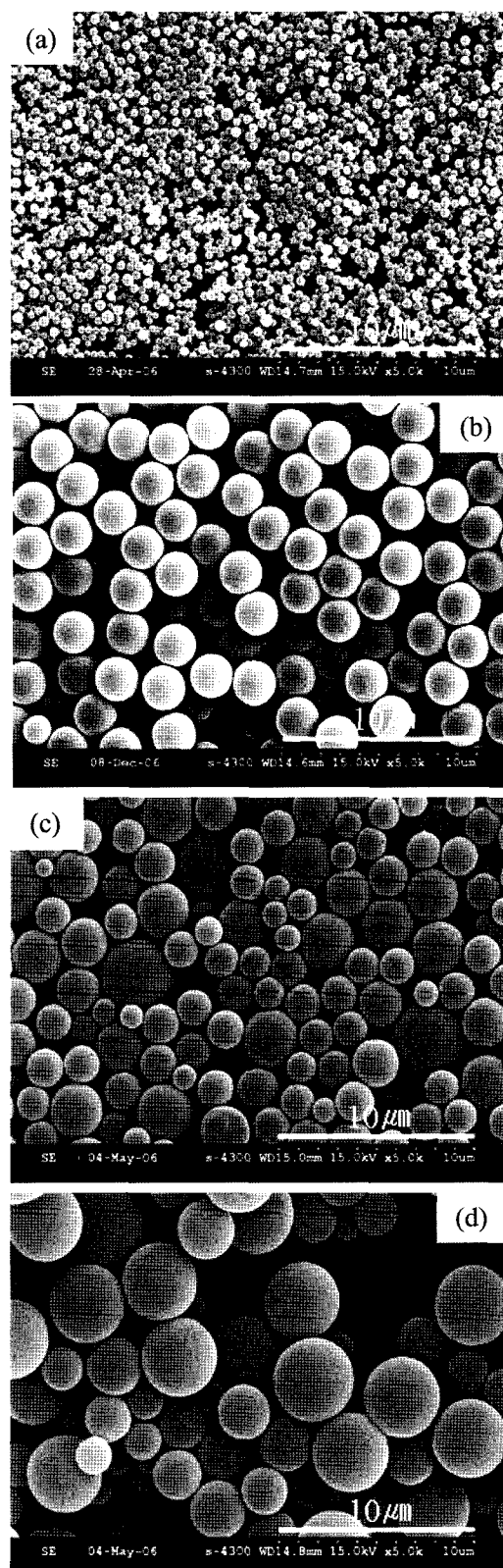


Figure 9. SEM photographs of PS microspheres prepared by soap-free emulsion polymerization in 95 : 5 of water to ethanol ratio and 0.1 g of KPS and NaCl with various monomer concentrations at 70 °C for 24 h. (a) 5 g, (b) 10 g, (c) 15 g, and (d) 20 g.

mer concentration. Figure 9 shows the SEM images of PS particles prepared at 70 °C for 24 h with various concentrations of monomer; (a) 5, (b) 10, (c) 15 and (d) 20 g, respectively. In Figure 9(a), the particle sizes are all submicron, whereas, the rest of the particles are all micron-sized as seen in Figures 9(b)-9(d). The increase in the diameter along with the monomer concentration obeys the trend observed in emulsion polymerization.

The weight-average diameter and coefficient of variation are plotted in Figure 10(a). As the monomer concentration increased, the weight-average particle size increased from 0.74, 2.19, 2.24, to 3.15 μm for 5, 10, 15 and 20 g of monomer, respectively, due to the increased monomer diffusion into the micelles. The coefficient of variation is 27.4, 5.8, 26.6 and 25.8 for 5, 10, 15 and 20 g of styrene monomer, respectively. This implies that the coefficient of variation represents no monomer concentration dependent relationship except with 10 g of monomer showing the best size distribution. Figure 10(b) also shows no monomer concentration dependent on the zeta potential of the synthesized PS

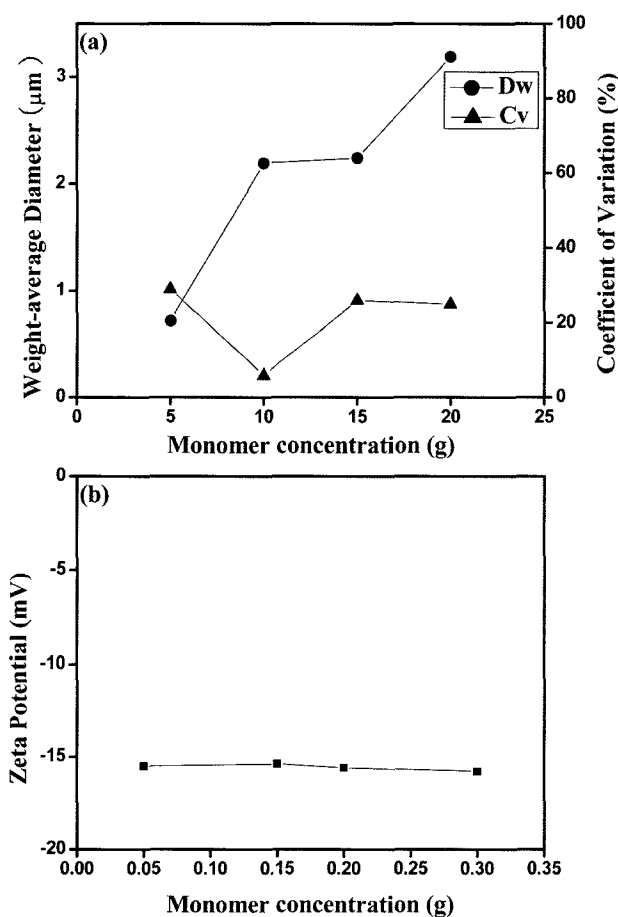


Figure 10. (a) Weight-average diameter and coefficient of variation and (b) zeta potential of the synthesized PS particle obtained in 95 : 5 of water to ethanol ratio and 0.1 g of KPS and NaCl at 70 °C for 24 h with the various concentrations of monomer.

particles. This result indicates that the surface charge of the particles evolved with electrolyte is not affected by the monomer concentration, but by the concentration of initiator, electrolyte, and medium constituents.

Conclusions

In this study, we reported a novel synthetic route to prepare monodisperse micron-sized PS particles in the soap-free emulsion polymerization in the presence of small amount of ethanol and electrolyte. The effect of the polymerization parameters such as the medium ratio, concentrations of initiator, monomer, and electrolyte were studied, and the conversion and rate of polymerizations were evaluated. The best medium ratio for the monodisperse and large particles is 95 : 5 of water to ethanol and this medium ratio gives the particle size of 2.19 μm at 70 °C for 24 h. However, the highest zeta potential is obtained when 100% water was used. The optimum concentration of the initiator is one of the important factors to eliminate the hindrance of the electrolyte. It was observed that the PS particle size and stability were greatly affected by the concentrations of co-solvent, initiator, electrolyte and monomer. The zeta potential of the particle surface is also affected by the medium and the concentrations of initiator and electrolyte, but not affected by the monomer concentration. Thus, the optimum conditions for the monodisperse micron-sized PS particles in the soap-free polymerization are the water to ethanol ratio to be 95 : 5, 10 wt% of styrene refers to the medium, 0.1 wt% of KPS and electrolyte refer to monomer, using NaCl. From this recipe, the obtained weight average diameter (D_w) of PS is of 2.19 μm , the coefficient of variation (C_v) is 5.8, and the zeta potential is 15.1 mV.

Acknowledgement. The authors thank to the financial support of the KOSEF (R01-2005-000-10367-0) during the year of 2005~2007.

References

- (1) J. Ugelstad, *J. Polym. Sci., Polym. Symp.*, **72**, 225 (1985).
- (2) K. O. Christopher, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 103 (1985).
- (3) K. P. Lok and C. K. Ober, *Can. J. Chem.*, **63**, 209 (1985).
- (4) J. G. Park, J. W. Kim, S. G. Oh, and K. D. Suh, *J. Appl. Polym. Sci.*, **87**, 420 (2003).
- (5) T. Isao, Y. Yutaka, N. Atsuo, and G. Yasushi, US Patent, 5,001,542 (1991).
- (6) Y. Almong, S. Reich, and M. Levy, *Br. Polym. J.*, **14**, 131 (1982).
- (7) C. K. Ober, K. P. Lok, and M. L. Hair, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 103 (1985).
- (8) M. Okubo, M. Shiozaki, M. Tsujihiro, and Y. Tsukada, *Colloid Polym. Sci.*, **269**, 222 (1991).
- (9) J. Ugelstad, K. H. Kaggerud, F. K. Hansen, and A. Berge,

- Makromol. Chem.*, **180**, 737 (1979).
- (10) S. Gu and M. Konno, *J. Chem. Eng. Japan*, **30**, 742 (1997).
- (11) J. H. Kim, M. Chainey, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Chem., Ed.*, **30**, 171 (1992).
- (12) T. D. S. Grant, G. A. Vandezande, and A. Rudin, *Eur. Polym. J.*, **30**, 179 (1994).
- (13) M. Konno, Y. Terunuma, and S. Saito, *J. Chem. Eng. Japan*, **24**, 429 (1991).
- (14) Z. Song and G. W. Poehlein, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 2359 (1990).
- (15) A. M. Homola, M. Inoue, and A. A. Robertson, *J. Appl. Polym. Sci.*, **19**, 3077 (1975).
- (16) S. Gu, T. Mogi, and K. Konno, *J. Colloid Interf. Sci.*, **207**, 113 (1998).
- (17) S. Gu, T. Mogi, and K. Konno, *Colloid Surf. A*, **153**, 209 (1999).
- (18) J. Zhang, Z. Chen, Z. Wang, W. Zhang, and N. Ming, *Mater. Lett.*, **57**, 4466 (2003).
- (19) S. E. Shim, Y. J. Cha, J. M. Byun, and S. Choe, *J. Appl. Polym. Sci.*, **71**, 2259 (1999).
- (20) A. Klein, C. H. Kuist, and V. T. J. Stannett, *Polym. Sci., Polym. Chem. Ed.*, **11**, 2111 (1978).
- (21) J. W. Goodwin, R. H. Ottewill, R. Pelton, G. Vianello, and D. E. Bates, *Br. Polym. J.*, **10**, 137 (1978).
- (22) A. M. Homola, M. Inoue, and A. A. Robertson, *J. Appl. Polym. Sci.*, **19**, 3077 (1975).
- (23) Z. Liu and H. Xiao, *Polymer*, **41**, 7023 (2003).
- (24) K. P. Lok and C. K. Ober, *Can. J. Chem.*, **63**, 209 (1985).
- (25) A. B. Moustafa and A. Abdel-hakim, *J. Appl. Polym. Sci.*, **66**, 711 (1997).
- (26) A. S. Dunn and Z. F. M. Said, *Polymer*, **23**, 1172 (1982).