

Synthesis of Polystyrene Nanoparticles with Monodisperse Size Distribution and Positive Surface Charge Using Metal Stearates

Mi Sun Kim, Seok Ki Kim, and Jun Young Lee*

Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea

Seung Hyun Cho and Ki-Hoon Lee

Polymer Technology Institute, Sungkyunkwan University, Suwon 440-746, Korea

Junkyung Kim and Sang-Soo Lee

Polymer Hybrids Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

Received November 9, 2007; Revised January 11, 2008

Abstract: Polystyrene (PS) nanospheres with a monodisperse size distribution, positive surface charge and high molecular weight were successfully synthesized using various types of metal stearates in an aqueous NaOH medium. The diameter of the PS nanospheres was controlled from 80 to 450 nm by changing the type of metal stearate. It was also found that controlling the NaOH concentration in solution was important for producing monodisperse PS nanoparticles. The nanospheres prepared with zinc stearate possessed a positive surface charge of 60 to 80 mV, confirming that PS particles were functionalized with metal stearates. It is believed that the metal stearates provide PS particles with not only colloidal stability but also a positive surface charge.

Keywords: emulsion polymerization, metal stearate, monodisperse nanoparticle, polystyrene, positive surface charge.

Introduction

Polymeric nanoparticles dispersed in poor solvents, called polymer latexes, enjoy great popularity in academia and industry.¹⁻³ Especially, polymer colloidal particles with the surface charges offer interesting prospects in various applications. Surface-charged polymer particles with diameters of less than 1 μm are of special interest in diagnostic applications of biotechnology or in electrophoretic display applications.⁴⁻¹⁰

Aqueous polystyrene (PS) latexes are usually prepared by the typical emulsion or emulsifier-free emulsion polymerization,¹¹⁻¹³ where stabilization of the emulsion can be obtained by electrostatic or steric force. Either diffusion of monomer molecules into the growing polymer particle (Ostwald ripening) or coalescence may result in destabilization and failure of emulsion. Coalescence of latexes can be avoided by use of excess amount of emulsifier, while the diffusional instability of the emulsion can be greatly reduced by addition of a small quantity of a highly monomer-soluble and water-insoluble agent. It is noted that the improved stability results from additional build-up of an osmotic pressure.^{14,15} How-

ever, in the emulsion polymerization, complete removal of the emulsifier adsorbed on polymer particles is quite difficult, which may be significant disadvantage in many applications such as electronic devices.

Polymer composites including metal stearates are known to be useful in preparing polymer resin with excellent heat resistance or improved moldability.¹⁶⁻¹⁸ Several carboxylic groups in metal stearates can form the coordination bonding with a core metal atom. The metal stearates are compatible with the styrene monomer through stearate group and are expected to increase surface energy of the PS particles. Therefore, metal stearates may act as the additive to form a stable emulsion and at the same time provide positive surface charge to the particles.

In this study, we report an emulsion polymerization method using various kinds of metal stearates to obtain monodisperse PS nanospheres with positive surface charge, which may be applied for the electrophoretic display. We investigated the effects of the polymerization conditions on the various properties of the resulting PS particles.

Experimental

Materials. Inhibitor in styrene monomer (CiCa) was removed

*Corresponding Author. E-mail: jylee7@skku.edu

by passing the monomer through an alumina-charged column (Aldrich) and then styrene was distilled under reduced pressure. Potassium persulfate (KPS, Aldrich) as an initiator and the metal (Zn, Al, Mg, Ca, Ba) stearates as the additives were used as received. Deionized water was used as a polymerization medium.

Polymerization Procedure. Polymerization of PS particles with the metal stearates was carried out by following the typical procedure. Mixture of a metal stearate and 20 g of styrene (0.96 M) was added to 200 mL of NaOH aqueous solution with moderate stirring, resulting in milky emulsion. In order to investigate the effects of the polymerization conditions on the properties of the resulting PS particles, various polymerization parameters such as kind of metal stearate, concentration (0.15, 0.25, 0.5, and 0.8 mM) of the metal stearate and the concentration of NaOH solution (0, 0.01, 0.1, 0.2, and 0.4 N) were changed.

Polymerization was initiated by adding 0.73 mM aqueous solution of KPS to the monomer emulsion at 70 °C under nitrogen atmosphere. Polymerization was carried out for 6 h and terminated by quenching the solution to 0 °C. The PS particles were repeatedly washed with water and methanol and finally collected by centrifugation. The particles were then dried by a freeze-dryer for one day.

Characterization. Electrophoretic light scattering (ELS, Otsuka ELS-8000) at high field strength was used to measure particle size, its distribution and zeta potential of PS particles suspended in a dielectric medium. Transmission electron microscopy (TEM, Philips CM 30T) and scanning electron microscopy (SEM, Hitachi S-2500C) with energy dispersive X-ray elemental analyzer (EDX) were used to investigate the micro-structure and to confirm existence of metal atom on PS particles. Molecular weight and its distribution of PS particles were determined by the gel permeation chromatograph (Young Lin, GPC 9200) with a wide dynamic range of RI750F detector, where THF was used as an eluting solvent.

Results and Discussion

Table I shows the mean diameters and standard deviations of PS particles measured by ELS. It was confirmed that emulsion polymerization of styrene using metal stearates could produce monodisperse PS nanoparticles with positive surface charge. However, PS polymerized without any metal stearate showed much larger particle size and broader size distribution than PS prepared with metal stearate. It is believed that the hydrophobic nature of the stearate group increased osmotic pressure in the droplets, giving rise to emulsion stability against Ostwald ripening. It is also believed that the increased osmotic pressure prevented the monomer molecules from diffusing out of monomer micelle, eventually resulting in monodisperse PS nanoparticles.

Amount of the metal stearate showed little effect on the size and its distribution of the particle as listed in Table I. The size of PS particles prepared using zinc stearate showed little change with the amount of zinc stearate from 0.15 up to 0.8 mM. It must be also noted that the standard deviation did not show any significant change with the amount of zinc stearate.

However, the kind of metal stearate significantly affected the particle size as shown in Table I. Zinc and aluminum stearates yielded PS particles with the diameter of about 80 nm, while barium, calcium or magnesium stearates produced PS particles with much larger diameter ranging from 170 to 450 nm. The size of PS nanospheres and their distribution examined by ELS were confirmed by TEM. As shown in Figure 1, the particle sizes of PS particles prepared with zinc and magnesium stearates were about 75 and 185 nm, respectively, which are almost same as the sizes obtained by ELS.

It was found that concentration of NaOH solution is one of the key factors to yield great effect on the diameter and its distribution of PS particles. When PS was prepared without NaOH solution, particle size and deviation were

Table I. Mean Diameter and Its Standard Deviation of PS Particles Prepared Under Various Conditions

Metal Stearate	Electronegativity of Metal Atom	NaOH Concentration (N)	Mean Diameter (nm)	Standard Deviation (nm)
Without Metal Stearate	-	0.1	480	90
Ba (0.25 mM)	0.89	0.1	395	53
Ca (0.25 mM)	1.0	0.1	450	67
Mg (0.25 mM)	1.31	0.1	170	29
Al (0.25 mM)	1.61	0.1	80	18
Zn (0.15 mM)	1.65	without NaOH	950	360
Zn (0.15 mM)	1.65	0.1	77	18
Zn (0.25 mM)	1.65	0.1	78	17
Zn (0.50 mM)	1.65	0.1	80	18
Zn (0.80 mM)	1.65	0.1	75	20

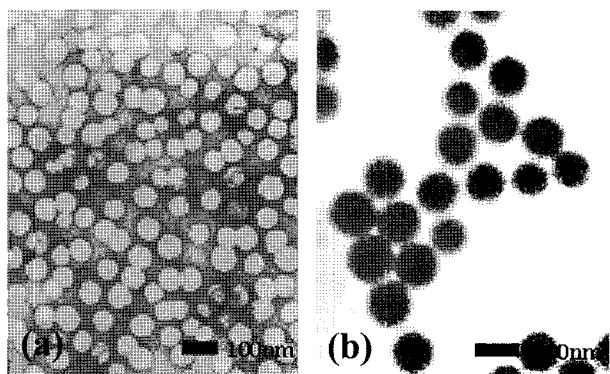


Figure 1. TEM images of PS particles prepared using (a) 0.25 mM zinc stearate and (b) 0.25 mM magnesium stearate.

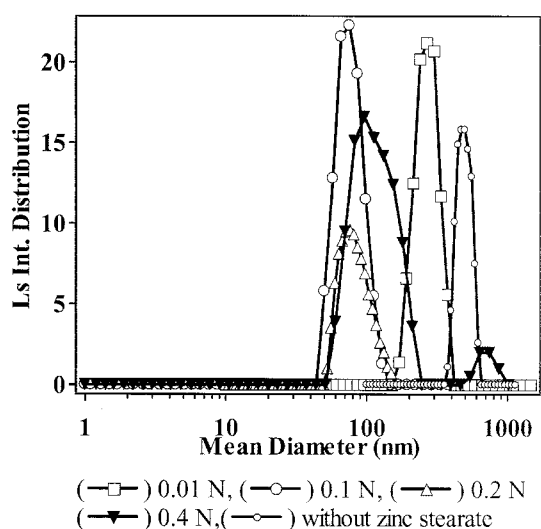


Figure 2. Size distribution of PS particle prepared using various concentrations of NaOH solution.

950 and 360 nm, respectively as shown in Table I. These values are much greater than those prepared with NaOH solution, indicating formation of large and non-uniform PS particles. Figure 2 shows the particle size distribution curves of the PS particles prepared using various NaOH concentrations at a fixed zinc stearate concentration (0.25 mM). As shown in Figure 2, the diameter of PS particles prepared with 0.01 N NaOH solution was about 300 nm, while the diameter of PS particle prepared using 0.1 N NaOH solution significantly decreased to about 80 nm with quite monodisperse distribution.

However, when concentration of NaOH solution was 0.2 N, the particle size increased a little and the size distribution became broader. The size distribution became even bimodal distribution at 0.4 N NaOH. We consider the PS particles with the diameter less than 100 nm and narrow size distribution could be obtained when zinc stearate was used at an optimum NaOH concentration. NaOH may play a role as an electrostatic stabilizer as illustrated in Figure 3, improving stability of

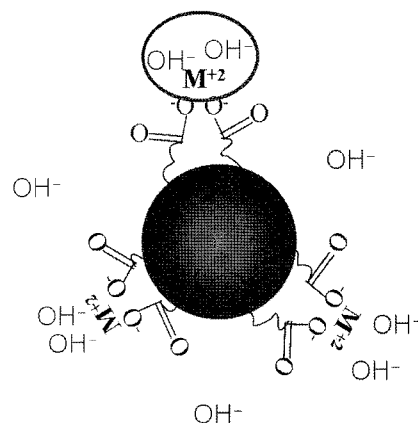


Figure 3. Schematic diagram of stable emulsion droplet formation.

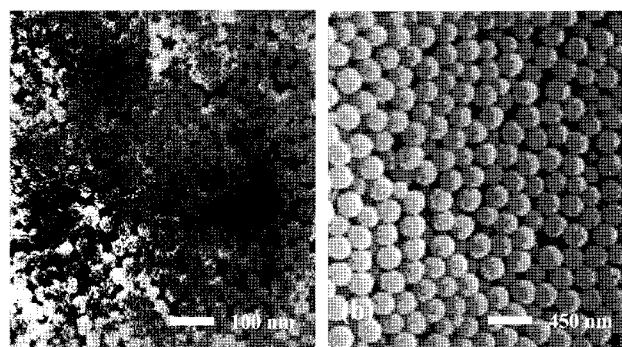


Figure 4. SEM images of freeze-dried PS nanospheres prepared using (a) 0.25 mM zinc stearate and (b) 0.25 mM magnesium stearate.

monomer emulsion droplet. To verify the stability of PS nanospheres in dry condition, SEM measurement was performed for extensively washed and freeze-dried specimens. As shown in Figure 4, monodisperse particles without aggregation and collapse can be observed, implying the PS nanospheres synthesized by metal stearates are highly stable.

The weight average molecular weight of PS nanospheres prepared using zinc stearate was 800,000–1,000,000 g/mol, which is in the same range of the molecular weight of PS prepared by a typical emulsion polymerization. We also confirmed from the zeta potential measurement that the PS particles prepared in this study possessed the positive surface charge ranging from 60 to 80 mV in non-polar medium. We confirmed the existence of zinc atom including PS nanospheres from an elemental analysis. The zinc content in PS nanospheres showed increase with increase of the amount of zinc stearate up to 0.8 mM.

Conclusions

We successfully synthesized monodisperse PS nanospheres with the positive surface charge and high molecular weight using various kinds of metal stearates in NaOH aqueous

medium. The diameter of PS nanospheres was in the range of 80 to 450 nm depending on the kind of metal stearate used. It was also found that existence of NaOH was extraordinarily important to produce monodisperse PS nanoparticles. The nanospheres prepared with metal stearates possessed positive surface charge of 60 to 80 mV. It is believed that the metal stearates provide the PS particles with not only colloidal stability but a positive surface charge.

Acknowledgements. This work was supported by the Korea Research Foundation Grant No. KRF-2006-005-J04603.

References

- (1) A. Kondo and H. Fukuda, *Colloid Surface A*, **153**, 435 (1999).
- (2) R. M. Renault, P. Denjean, and R. B. Pansu, *Sensor Actuat. B*, **59**, 108 (1999).
- (3) M. O. M. Edwards, T. Gruszecki, H. Pettersson, G. Thuraiingham, and A. Hagfeldt, *Electrochem. Commun.*, **4**, 963 (2002).
- (4) S. Y. Lin, C. S. Chern, T. J. Hsu, C. T. Hsu, and I. Capek, *Polymer*, **42**, 1481 (2001).
- (5) G. Tuin, J. H. J. E. Senders, and H. N. Stein, *J. Colloid Interf. Sci.*, **176**, 522 (1996).
- (6) H. Lee, S. Yu, K. Jeong, and Y. Kim, *Macromol. Res.*, **15**, 547 (2007).
- (7) I. Chen, J. Mort, M. A. Machonkin, J. R. Larson, and F. Bon-signore, *J. Appl. Phys.*, **80**, 6796 (1996).
- (8) C. E. Reese, C. D. Guerrero, J. M. Weissman, K. Lee, and S. A. Asher, *J. Colloid Interf. Sci.*, **232**, 76 (2000).
- (9) Z. W. Wang, G. Z. Li, D. R. Guan, X. Z. Yi, and A. J. Lou, *J. Colloid Interf. Sci.*, **246**, 302 (2002).
- (10) J. Jang, J. Ha, and S. Kim, *Macromol. Res.*, **15**, 154 (2007).
- (11) S. S. Madaeni and M. Ghanbarian, *Polym. Int.*, **49**, 1356 (2000).
- (12) S.-J. Fang, F. Fujimoto, S. Kondo, and H. Kawaguchi, *Colloidal Polymer Science*, **278**, 864 (2000).
- (13) J. Blaakmeer and G. J. Fleer, *Colloids and Surfaces*, **36**, 439 (1989).
- (14) K. Landfester, *Macromol. Rapid Commun.*, **22**, 896 (2001).
- (15) K. Landfester, N. Bechthold, F. Tiarks, and M. Anronietti, *Macromolecules*, **32**, 5222 (1999).
- (16) S. Toda, A. Sakai, and Y. Kojima, *Spectrochim. Acta.*, **27^a**, 581 (1971).
- (17) T. Ishioka, K. Maeda, I. Watanabe, S. Kawauchi, and M. Harada, *Spectrochim. Acta. A*, **56**, 1731 (2000).
- (18) M. T. Benaniba, N. B-Bensemra, and G. Gelbard, *Polym. Degrad. Stabil.*, **74**, 501 (2001).