

Controlling the Size and Surface Morphology of Carboxylated Polystyrene Latex Particles by Ammonium Hydroxide in Emulsifier-free Polymerization

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Abstract: In emulsifier-free, emulsion polymerization with ionizable comonomer, the ionization of the comonomer is critical in determining the size of the final polymeric particles at sub-micrometer scale. In this study, polystyrene latex beads with carboxylates on the surface were synthesized using acrylic acid as a comonomer. Specifically, ammonium hydroxide was added to the emulsifier-free polymerization system to promote the ionization of acrylic acid by increasing pH. Smaller polystyrene latex particles were produced by increasing the ammonium hydroxide concentration in the reaction system, due to the enhanced stability promoted by the ionization of acrylic acid during the nucleation step. In addition, the surface morphology of the polystyrene latex particles was controlled by the concentration of acrylic acid, the dissociation of which was influenced by the ammonium hydroxide concentration.

Keywords: polystyrene, acrylic acid, ammonium hydroxide, emulsifier-free polymerization, solubility.

Introduction

Applications of monodisperse polystyrene nanoparticles are expanding to various engineering fields such as photonic band gap crystals,^{1,2} lithographic photo masks,³ and drug delivery systems⁴ from the conventional usages of painting, papers, and adhesives.⁵ For the advanced application of polystyrene latex particles in electronic and photonic devices, surface-functionalized monodisperse particles with high purity are necessary. In general, the polystyrene particles are fabricated via mini/micro-emulsion technique where the emulsifier is added in for the control of particle size and colloidal stability.⁶ However, due to the emulsifier locating at surface, it is limited to control the surface functional groups and the emulsifier could work as a contamination source in electrical devices. Moreover, the colloidal stability can be lost during purification process. Emulsifier-free emulsion polymerization is a well-known synthesis method for preparing polystyrene latex particles precluding contamination by the emulsifier. Thereby, polystyrene nanoparticles prepared emulsifier-free emulsion polymerization method have been used as a good model system for the advanced applications.

In the general emulsifier-free emulsion polymerization, the reaction system consists of styrene, potassium persulfate, and divinyl benzene as a monomer, initiator, and cross-

linker, respectively. In addition, water-soluble comonomer and salt are used for controlling the size and surface functional groups. In particular, surface functional groups were produced from initiator and comonomer, which is of primary importance because they control stability that determines the product size and morphology during the polymerization. In previous reports, researchers have investigated the effects of monomer, comonomer, and initiator on the particle size and degree of polymerization with feasible mechanisms. However, the size dependency to the initiator concentration is not clarified yet specifically when additional ions are engaged in the polymerization system.^{5,7} It is believed that the size reduction is explained not only by the promoted nucleation of polystyrene seed with increase of initiator concentration but by the enhanced stabilization of polymerized particles by additional ions in the aqueous medium.⁸ From these findings, the surface electrostatic repulsion of particles should be controlled for the synthesis of stable monodisperse polystyrene particles in emulsifier-free emulsion polymerization. The electrostatic repulsion forces between polystyrene particles are dependent to the density of adsorbed ionized groups at the surfaces. The ionization of comonomer is dependent to the amount of added ammonium hydroxide.

In this study, the influences of ammonium hydroxide on the average size and morphology of polystyrene latex particles are investigated. Ammonium hydroxide was chosen as

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additional ion source because it is expected to improve stability during the polymerization process by increasing pH. Subsequently, the average particle size effectively will be controlled by the addition of ammonium hydroxide solution as well as adjustment of comonomer concentration.

Experimental

Chemicals and Equipments. Styrene monomer (99%), divinyl benzene (ACS technical grade, 80%), potassium persulfate (ACS grade, 99%) were purchased from Aldrich and used without further purification. Acrylic acid (Aldrich 99%) was chosen as a comonomer that is soluble in water. Ammonium hydroxide solution (Duksan Chemical, 30 wt%) was used for pH control. Polymerization was carried out in a jacketed cylindrical glass reaction vessel which equipped with a reflux condenser and a teflon stirrer. The stirrer with anchor type baffle was positioned 1 cm from the bottom. Stirring rate was maintained at 400 rpm during the reaction. Temperature of the reactor was kept constant at 70 °C with the use of a circulating temperature bath. The reaction vessel was purged with nitrogen to remove dissolved oxygen in the reaction solution at the initial stage and then the nitrogen environment was kept during the whole reaction process.

Synthesis of Polystyrene Latex Particles. Emulsifier-free emulsion polymerization was carried out in a batch reactor. A volume of 12 mL styrene and 0.12 mL divinyl benzene were injected in reaction vessel containing 400 mL deionized water and various amounts of ammonia solution. The temperature was increased to 70 °C for the decomposition of initiator, potassium persulfate. In order to remove oxygen inside, nitrogen gas was purged in the reactor for 30 min and then various amount of acrylic acid and 25 mL of 37 mM potassium persulfate solution were injected. The reaction was left to reflux for 8 h. Nitrogen purge and stirring at a rate of 400 rpm were maintained throughout the polymerization.

Characterization. Size distribution of polystyrene latex particles was determined using a dynamic light scattering equipment (ELS-Z, Otsuka electronics). The hydrodynamic radii were measured five times for each sample, then the average and standard deviations were calculated. The morphologies of polystyrene nanoparticles were observed using scanning electron microscopy (SEM, S4700, Hitachi, 10 kV) and field-emission transmission electron microscopy (FE-TEM, FEI Co., 300 kV).

Results and Discussion

Effects of Ammonium Hydroxide Concentration on Polystyrene Particle Size in the Absence of Acrylic Acid.

Firstly, the effects of ammonium hydroxide concentration on the average size of polystyrene nanoparticles were examined in the absence of comonomer, acrylic acid. While

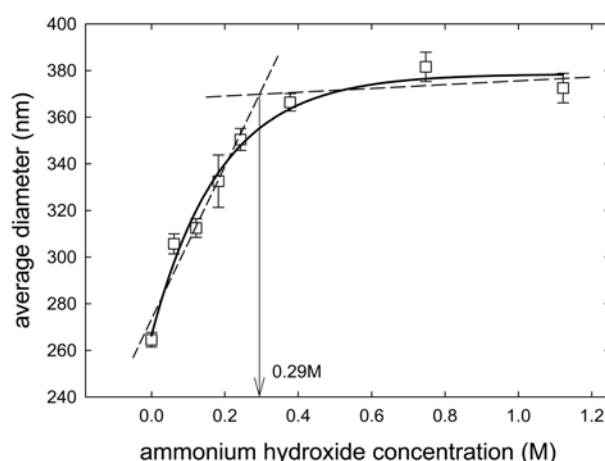


Figure 1. Average diameter of polystyrene latex particles prepared without acrylic acid (solid line is guide for eye).

keeping the reaction concentrations of initiator, styrene monomer, and crosslinker constant, emulsifier-free emulsion polymerization was carried out with variance of ammonium hydroxide concentration. In Figure 1, the average diameter of polystyrene particles was plotted against the concentration of ammonium hydroxide. Under the ammonium hydroxide concentration of 0.28 M, the average diameter increased almost linearly. This size increment is similar to the size increase driven by salting out effect.⁹⁻¹¹ In contrast, over the ammonium hydroxide concentrations of 0.28 M, particle size increased with small slope and saturated. This saturation of particle size at high ammonium concentration is likely due to the saturated salting out effect where the solubility of styrene changes little by the addition of ammonium hydroxide. The crucial concentration of 0.28 M was determined from the cross point where two different slope of size increment meets.

With the observation of particle size, conversion was monitored during the polymerization. In order to observe the ammonium hydroxide effect clearly, two conditions were chosen from Figure 1 where the product particle sizes are different obviously. In Figure 2, plots of conversion and size change are present. The first interval of the reaction increased with the increase of ammonium hydroxide contents as present in Figure 2(a). This behavior is similar to the commonly observed salt addition effect that reduces solubility of monomer.¹²

From the plot of particle sizes against conversion, the size difference was clearly observed with increment of conversion. In Figure 2(b), the size variation with the conversion is present where larger product particles were obtained at high ammonium hydroxide concentration. In a condition of low ammonium hydroxide concentration, particle grows large even at a low conversion. These particles grew up slowly with progress of polymerization. In contrast, when large amount of ammonium hydroxide was added, relatively

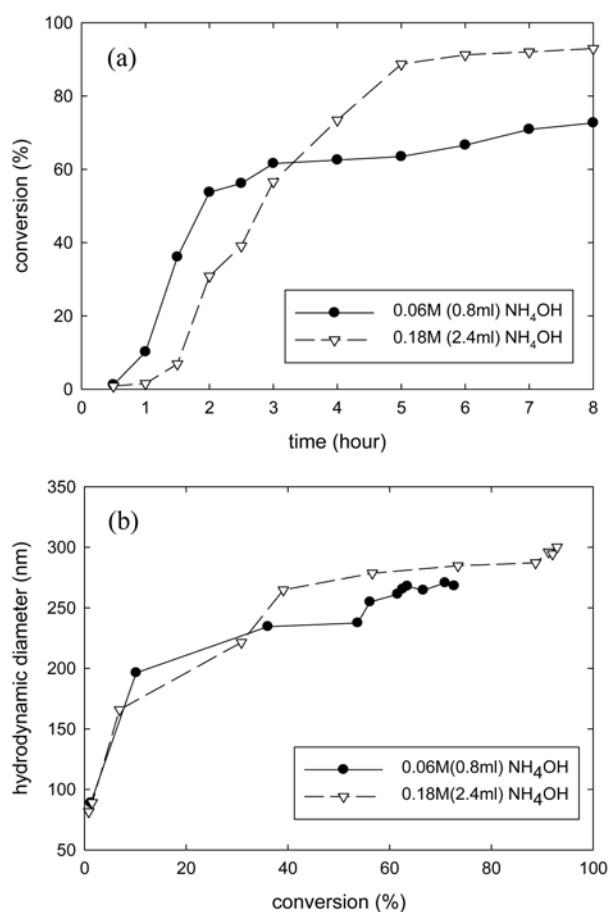


Figure 2. Conversion and particle size changes with the progress of reaction (a) conversion changes with time, (b) particle size change against conversion (lines are guides for eye).

small particles were formed at the low conversion and they grew up continuously with the polymerization. This particle growth behavior is reported to be due to the monomer solubility change, and larger particle would be harvested when the solubility is low.¹³ Since the solubility of monomer is dependent to the ammonium hydroxide concentration in this system, it can be inferred that the ammonium hydroxide might have caused salting out effect during the polymerization.

SEM images of polystyrene particles prepared with different concentrations of ammonium hydroxide are present in Figure 3. The particles keep their spherical shape with smooth surface in all cases. This spherical shapes indicate that the coagulation of styrene oligomers were done at the initial stage of polymerization due to the salting out effect.¹⁴

The size dependency of polystyrene nanoparticles to the ionic concentration could be predicted with a model equation proposed by Goodwin *et al.*¹⁵ In Figure 4, by comparing our experimental data with model equation, all data was fitted well into the following equation;

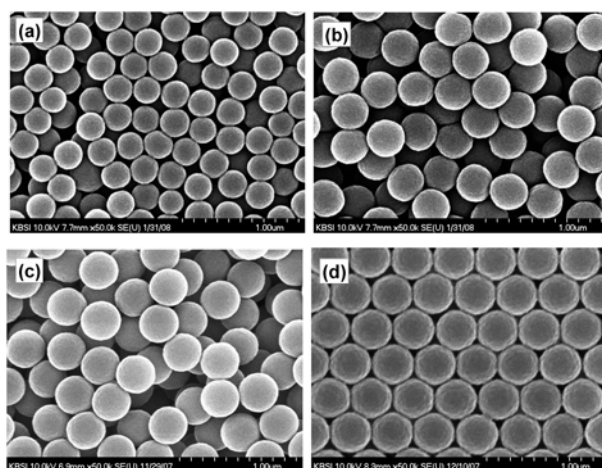


Figure 3. SEM images of polystyrene latex particles synthesized without acrylic acid with variation of ammonium hydroxide concentrations. (a) 0.0 M, (b) 0.18 M, (c) 0.24 M, (d) 0.75 M of ammonium hydroxide.

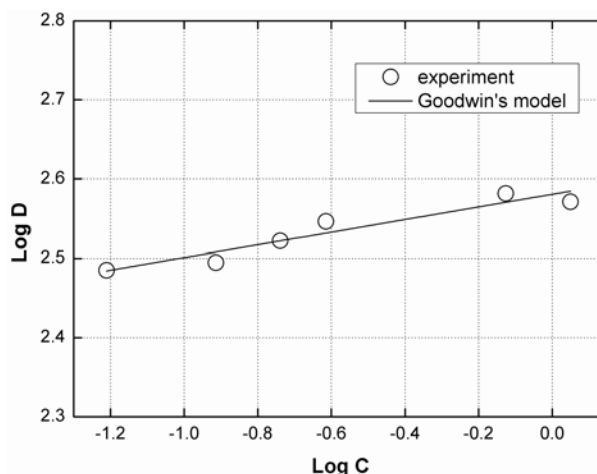


Figure 4. Polystyrene latex particle size dependence to the ion concentration. The experimental data were fitted with Goodwin's model.

$$\log D = 0.0795 \log C + 2.581 \quad (\text{at } 70^\circ\text{C})$$

where, D is the diameter of particle and C is the ionic strength dissolved in. This experimental trend of increasing particle size with ammonium hydroxide concentration agrees with Goodwin's model, though the slope of the fitted equation was lowered around one-third of the original Goodwin's equation. This small value of slope suggests that the particle size change is less dependent to the ammonium concentration comparing to other salts used in Goodwin's experiments.

Effects of Ammonium Hydroxide Concentration on the Polymerization of Polystyrene Particles with Acrylic Acid. When comonomer of acrylic acid was added to the above polymerization system, the average particle size was

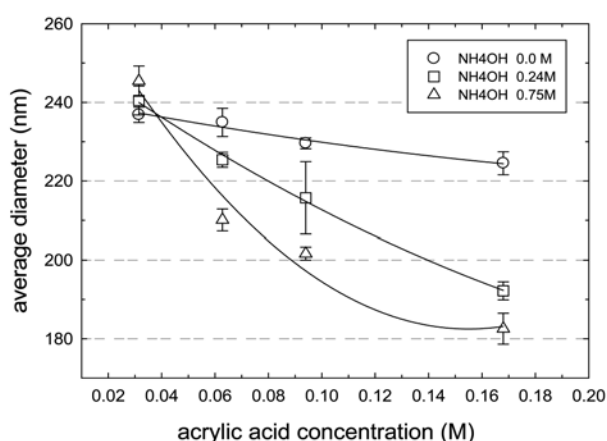


Figure 5. Average diameter of polystyrene latex particles prepared with different concentrations of acrylic acid with and without ammonium hydroxide (lines are guide for eye).

reduced with both increases of acrylic acid and ammonium hydroxide concentrations. The average particle sizes are shown in Figure 5 with the both changes of acrylic acid and ammonium hydroxide concentrations. In most of cases, particle sizes were reduced comparing to the sizes of particles that were prepared without acrylic acid. In the absence of ammonium hydroxide, the particle size was not changed much even when the concentration of acrylic acid was increased to 0.17 M. This slight change of particle size is because of the acidity of acrylic acid. As noted in Table I, the pH of reaction system was maintained lower than 3.0 in the absence of ammonium hydroxide. Since acrylic acid would not fully dissociate at such a low pH, under the pKa of carboxylate, acrylic acid would contribute little to stabilize the polystyrene particle at the early stage. Subsequently, the polystyrene particle size would not be influenced by the increase of acrylic acid. On the while, pH of the reaction system changes when the amounts of ammonium hydroxide and acrylic acid are balanced. Changes of pH resulted in particle size variation as present in Figure 5. In each experiment, changes of the pH during the polymerization were negligible as far as the pH maintained above pKa of acrylic acid, around 4.3. In the pH range above pKa, over 90% of acrylic acid would be dissociated and affected little by the slight pH change during the polymerization.

The average particle size dramatically decreased when

ammonium hydroxide is added in. The addition of ammonium hydroxide makes reaction medium basic from acidic, which promotes the dissociation of carboxyl group of acrylic acid to form carboxylate anion. The ionized acrylic acid form more oligomers and these charged oligomers with carboxylates would diffuse to the particle surface. By the association of charged oligomer, the nanoparticles were stabilized at the early stage of reaction. The rich carboxyl groups from acrylic acid provide sufficient electrical repulsive force that stabilizes polystyrene particle.^{16,17} In the same fashion, the particle sizes were reduced with increase of ammonium hydroxide concentration at the same acrylic acid concentration. The addition of ammonium hydroxide resulted in increase of pH promoting the acrylic acid dissociation. A similar behavior is reported for the well-known comonomer of methacrylic acid. The promoted dissociation of methacrylic acid is observed with pH increase.^{18,19} The enhanced dissociation of methacrylic acid resulted in reduction of reaction rate suggesting reduction of product particle size.²⁰

All of these observations consistently indicate that the polystyrene particle size can be adjusted by controlling the ionization of comonomer of acrylic acid, which can be promoted by addition of ammonium hydroxide. By adjusting the pH above the pKa of carboxylate, more acrylic acid would dissociate to stabilize the polystyrene particles at the early stage of formation. This dissociation also explains well the decrease of particle diameter with increase of acrylic acid concentration at high ammonium hydroxide concentration.

Particle Morphology Dependence to Ammonium Hydroxide and Acrylic Acid Concentrations. Morphologies of polystyrene nanoparticles were strongly affected by the comonomer and ammonium hydroxide concentrations. As shown in images of scanning electron microscopy of Figure 6, wrinkled surfaces of polystyrene particle are observed with the increase of acrylic acid concentration. In addition, increment of acrylic acid concentration resulted in size reduction with broadening of the size distribution. The roughened surface of polystyrene particle is clearly observed in the TEM picture present in Figure 7. As observed in Figure 6, the higher concentration of acrylic acid would result in rough surface with irregular surface morphology.

As described in the reference cited, such non-smooth surface of particles might be from deposition of polymeric materials such as oligomers and tiny nanoparticles in the

Table I. pH of the Polystyrene System Present in Figure 4

*pH of the Reaction System	Acrylic acid (mL)			
	0.03 M (1.0 mL)	0.06 M (2.0 mL)	0.09 M (3.0 mL)	0.17 M (5.0 mL)
Ammonium Hydroxide Concentration (added volume)				
0.0 M (0 mL)	2.8	2.8	2.8	2.9
0.24 M (3.2 mL)	9.3	9.4	7.5	5.8
0.75 M (10.0 mL)	10.1	10.0	9.9	9.6

* pH was measured after completing the reaction.

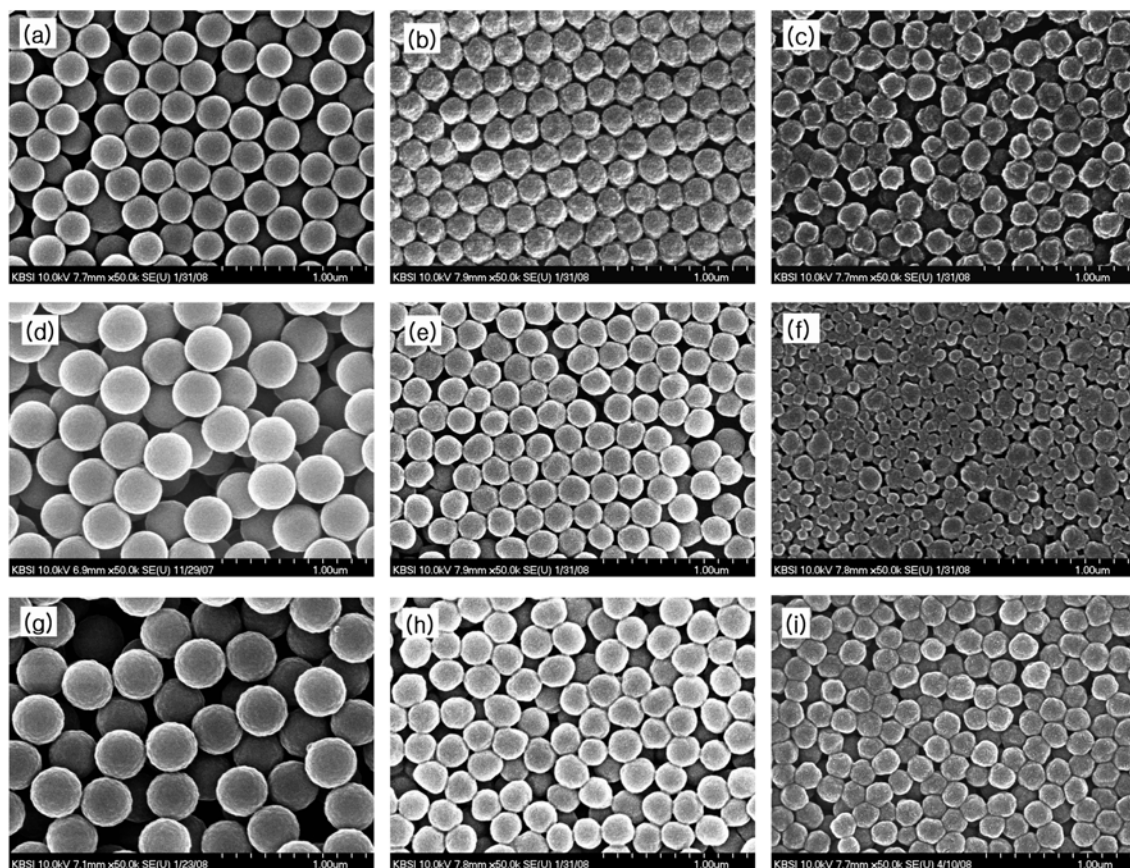


Figure 6. Surface morphology changes with respect to the comonomer and ammonium hydroxide concentrations. The acrylic acid concentrations were set 0.0, 0.06, and 0.17 M for each ammonium hydroxide concentration. The acrylic acid concentration increases from left to right. (a~c) particles prepared without ammonium hydroxide, (d~f) particles prepared with 0.24 M ammonium hydroxide, (g~i) particles prepared with 0.75 M ammonium hydroxide. SEM pictures were taken at 50,000 times magnification.

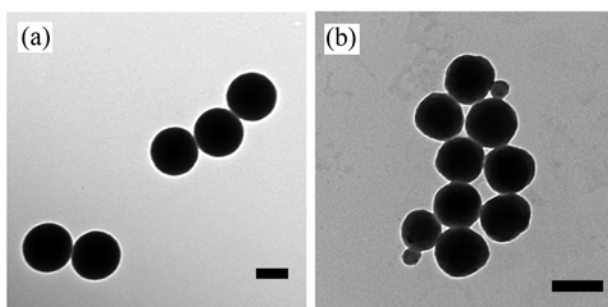


Figure 7. TEM images of polystyrene latex particles prepared different comonomer and ammonium hydroxide concentrations. (a) a smooth surface: 0.0 M of acrylic acid and 0.24 M of NH_4OH , (b) a rough surface: 0.06 M of acrylic acid and 0.24 M of NH_4OH (Scale bar: 200 nm).

bulk to the larger polystyrene particle surface and further polymerization was stopped due to the depletion of monomer.¹⁴ Formation of the hydrophilic oligomers were promoted with increase of acrylic acid at high pH working

polymeric materials.²¹ This kind of polymeric material deposition can be thought as the heterocoagulation between core latex particle and polymeric materials are taking place. The size reduction of the product latex particle is known due to the promoted formation of nuclei at the early stage of polymerization.²¹ It is reasonable that the increased acrylic acid concentration promotes hydrophilic oligomer formation working as nuclei. Therefore, the product latex particle size would decrease with the acrylic acid concentration.

Conclusions

The addition of ammonium hydroxide to the emulsifier-free polystyrene synthesis system was an effective way to control the average particle sizes. In the absence of acrylic acid, increased ammonium hydroxide concentration promoted salting out of styrene monomer resulting in particle size growth. On the contrary, the average particle size was reduced with a rise of ammonium and acrylic acid concentrations. The ionization of acrylic acid is the key factor leading particle size reduction, which was influenced by the

addition of ammonium hydroxide to the reacting solution. In addition, the surface morphology of nanoparticles was influenced by both acrylic acid and ammonium hydroxide concentrations. Rough surfaces were obtained when the acrylic acid concentration increased. Nanoparticle size adjustment through pH and ionic strength control is a promising way preparing emulsifier-free polystyrene nanoparticles.

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