Effects of −COOH Groups on Organic Particle Surface on Hydrous Alumina Heterogeneous Coating

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The effects of the −COOH groups on polystyrene particle surface on the heterogeneous coating of hydrous alumina in an aqueous process were studied. Pure polystyrene particles and particles loaded with different densities of −COOH groups were used in the hydrous alumina coating process. The particles were synthesized by the emulsifier-free emulsion polymerization of pure styrene, and copolymerization of styrene and methacrylic acid (MAA), with potassium persulfate ($K_2S_2O_8$) as initiator. The amount of the −COOH groups on the copolymerized particle surface was determined by conductometric titration. High-resolution transmission electron microscopy (HRTEM) images showed that, when the density of −COOH groups loaded on the particle surfaces was high enough, the particles could be easily heterogeneously coated with hydrous alumina; when it was too low, there was much homogeneous nucleation on the coated particles and in the bulk. In the absence of −COOH groups, i.e., pure polystyrene, the particles could hardly be coated under the same conditions. It is inferred that the precipitation and reaction occurred at the sites of −COOH groups on the particle surfaces in the coating process.

1. Introduction

The synthesis of composite particles consisting of a core particle coated with a functional shell as well as hollow particles has opened new promising directions for advanced materials. Many factors affect the coating process and the product quality. Surface groups on the core particles conceivably play a key role in the coating, but there are few reports in the literature with the details of this. In this research, the effects of the surface groups on the coating were studied using core particles of the same composition, except that these were with and without functional groups. Polystyrene and styrene/methacrylic acid copolymerized particles are used because of their clean surface, controllable size, and surface functional groups, which make the particles easily coated. The inorganic coating of organic particles provides a promising way to prepare hollow particles by calcining, leading to cost and weight reduction and property improvement on mechanical, electrical, thermal, acoustic, etc. when the hollow spheres were used as fillers, and they can be used as microreactors and catalyst support.[1,2]

Spherical monodispersed copolymer particles can be synthesized by emulsifier-free emulsion polymerization, precipitation polymerization, and dispersion polymerization.[3,4] Emulsifier-free emulsion polymerization is particularly effective for preparing functional polymer particles with a very narrow size distribution.[5] In emulsion polymerization, the introduction of −COOH groups onto the polystyrene (PS) particles can be achieved by the copolymerization of styrene with comonomers containing −COOH such as methacrylic acid (MAA) or acrylic acid (AA).[6] The properties of the copolymerized particles depend on the reactants and the synthesis conditions, which affect not only the particle sizes but also their surface groups. These particles can be stabilized by ionized −COOH groups, and the density of the −COOH groups on the particle surface is controllable. Therefore, these particles are suitable for studying the effect of surface groups on the heterogeneous coating process.

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In this paper, particles with a narrow size distribution and different surface densities of −COOH groups were synthesized. The effects of the −COOH groups on the polystyrene particle surface on the heterogeneous coating process were studied. High-resolution transmission electron microscopy (HRTEM) and conductometric titrations were used to characterize the coating morphology and −COOH group density, respectively.

2. Experimental Section

2.1. Reagents. Styrene (St) monomer was purified by 5% (wt) NaOH. Methacrylic acid (MAA) was used as the comonomer, and potassium persulfate ($K_2S_2O_8$) was used as the initiator. Deionized water with a resistance of >16 MΩ was used in all the syntheses. Other chemicals used were analytical reagents of analytical reagent (AR) grade.

2.2. Particle Preparation. The particles were prepared by an emulsifier-free polymerization.[5] St (70 mL) was dissolved into 500 mL of deionized water in a 1000 mL four-necked flask equipped with a reflux condenser, a N_2 inlet, a thermometer, and a stirrer. N_2 was bubbled into the solution to remove oxygen from the monomeric solution during the whole polymerization process. After thorough deoxygenation of the solution (about 30 min), the temperature was increased to 70 °C. Then, a specific amount of MAA was added into the flask as the comonomer. Polymerization was initiated by adding 15 mL of saturated $K_2S_2O_8$ solution (20 °C). After 2 h of reaction, the milky white product was filtered and washed three times.

2.3. Measurement of −COOH Groups on Particle Surface. Conductometric titration[7,8] was carried out in a flask equipped with a conductivity meter and a peristaltic pump. All titrations were carried out at 20 °C under N_2 protection to prevent CO_2 dissolution into the suspension. A typical conductometric titration was performed as follows: (1) 0.1 g of particles was dispersed into 100 mL of deionized water to form a suspension; (2) 0.2 mL of 0.10 mol·L^{-1} HCl solution was uniformly mixed into the suspension; (3) 0.0256 mol·L^{-1} NaOH solution was titrated into the suspension.

2.4. Particle Coating. The particle coating was carried out in a flask with the temperature and pH measured online with a

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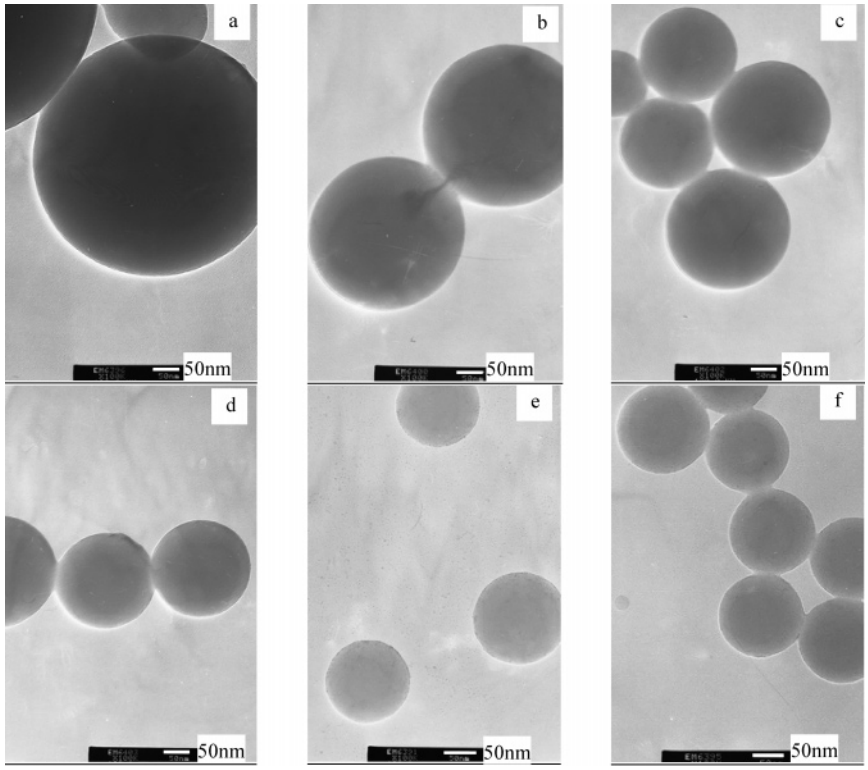

Figure 1. Morphologies of polymerized particles at different MAA/St ratios; MAA/ St: (a) 0; (b) 0.01; (c) 0.05; (d) 0.10; (e) 0.15; and (f) 0.20.

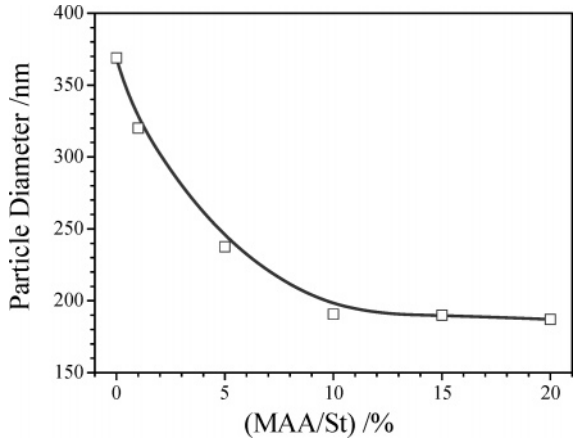

Figure 2. Mean size of the polymerized particles vs MAA/St ratio.

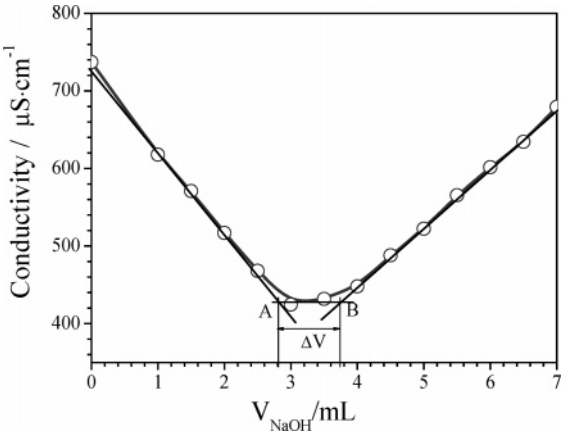

Figure 3. Conductometric titration for determining the volume of NaOH solution reacted with −COOH groups on the particle surface.

thermometer and a pH meter. The temperature was controlled by a constant-temperature bath.[9] The particles, at a concentration

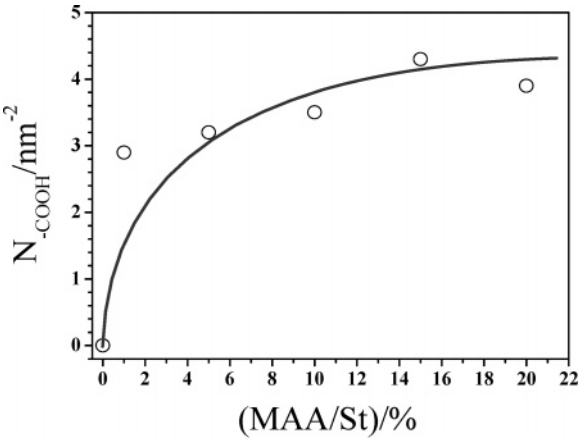

Figure 4. Surface density of −COOH groups on the polymerized particle surface vs MAA/St ratio.

of about 80 g·L^{-1}, were dispersed in deionized water by a continuous ultrasonic treatment for 30 min before titrating with the coating reagent. The coating process was operated under strong stirring with 21 mL of 0.3 mol·L^{-1} $Al_2(SO_4)_3$ solution and a 1 mol·L^{-1} NaOH solution titrated into the suspension by peristaltic pumps simultaneously. The suspension was titrated with the $Al_2(SO_4)_3$ solution at the rate of 0.5 mL·min^{-1}, and the titration rate for the NaOH solution was adjusted to keep the solution at a set pH. After titration, the suspension was aged for 1.5 h under stirring. Then, the samples were taken from the suspension for further characterization.

2.5. Characterization. The morphology and structure of the hydrous alumina coating on the particle surface were examined by high-resolution transmission electron microscopy (HRTEM, JEM-2011, JEOL Co., Tokyo, Japan). The size and zeta-potential of the particles were measured by a particle sizer and zeta-potential meter (ZetaPALS, Brookhaven Instruments, USA). The conductivity was measured by a conductivity meter (DDSJ-308, Shanghai Jinmai Co., China).

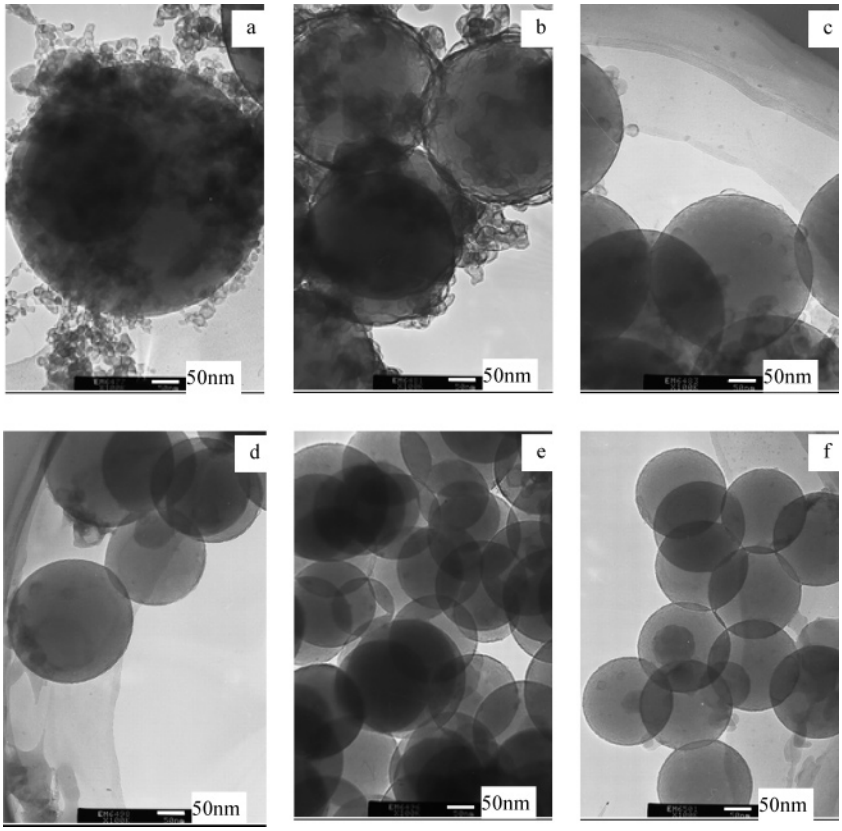

Figure 5. Morphologies of coated polymerized particles at different MAA/St ratios (pH 5, 60 °C); MAA/St: (a) 0; (b) 0.01; (c) 0.05; (d) 0.10; (e) 0.15; and (f) 0.20.

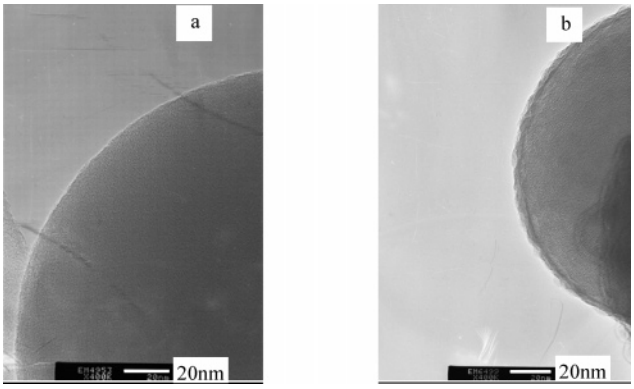

Figure 6. Magnified images of coated and noncoated polymerized particles (pH 5, 60 °C): (a) noncoated particle; (b) coated particle (MMA/St = 0.1, N_{-COOH} = 3.5 nm^{-2}).

3. Results and Discussion

On inorganic particles, the −OH groups on the particle surface can accept or donate different amounts of protons at different pHs.[10,11] They are acidic when they provide protons and basic when they accept protons, and the −OH groups act as the reaction or condensation sites to give a heterogeneous coating process.[12] However, organic particles are generally without −OH groups on the surface. Then, can they be heterogeneous coated with hydrous alumina if they are loaded with other kinds of functional groups that can also provide or accept protons, e.g., −COOH groups? Do the −COOH groups act as reaction or condensation sites?

3.1. Effects of MAA/St Ratio on Particle Size. A previous work on the emulsifier-free emulsion copolymerization of St and MAA showed that the size, size distribution and particle morphology are affected by many factors, including the concentration of the initiator, the ionic strength of the aqueous phase, the comonomer concentration, and the ratio of comonomers.[6] In this research, methacrylic acid (MAA) was copolymerized with styrene in order to load −COOH groups onto the polystyrene particle surface. To simplify the situation, the comonomer concentration was set as the only variable and all the other parameters were fixed.

Figure 1 shows the morphologies of the polystyrene particles and the copolymerized particles of styrene and MAA. It can be seen that the prepared particles were spherical and clean and had diameters in the range of 180−360 nm.

The mean particle size was measured by a ZetaPALS sizer using dynamic light scattering. The mean particle size change with an increase of the MAA/St ratio is shown in Figure 2. When the MAA/St ratio was below 10%, the mean size decreased sharply as the ratio increased, and the mean size tended to be constant when the ratio was over 10%. Because the hydrophilic −COOH groups of the MAA reduced the interface tension of the styrene droplet and the water, it resulted in the decrease of the droplet size and the decrease of the polymerized particle size with the increase of the MAA/St ratio.

3.2. Effects of the MAA/St Ratio on the Surface Density of the −COOH Groups. When MAA copolymerizes with styrene, the −COOH groups are apt to remain on the interface of the latex because of their hydrophilicity; thus, there exist −COOH groups on the copolymerized particle surface. The volume of NaOH solution that reacted with the −COOH groups on the particle surface can be determined from the titration curve, as shown in Figure 3.

In the first stage of the titration, because the acidity of H^+ in the solution is stronger than that of −COOH, the H^+ in the solution was first neutralized when NaOH was titrated. Because the limiting molar conductivity of H^+ (0.03498 S·m^2·mol^{-1} at

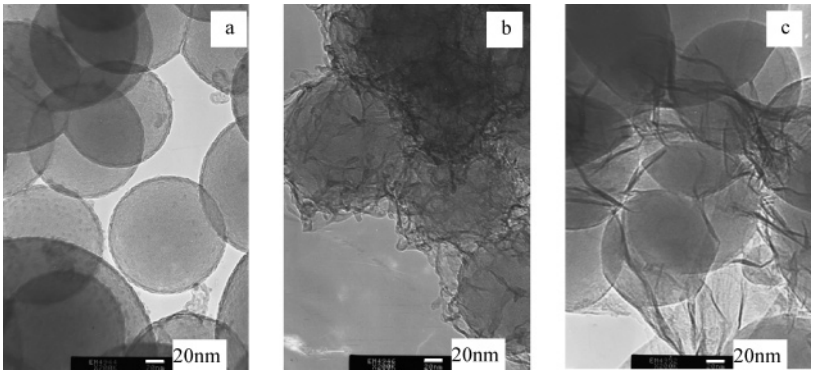

Figure 7. Morphologies of coated polymerized particles under different pH values (60 °C); pH: (a) 5; (b) 7; (c) 9 (MMA/St = 0.2, N_{-COOH} = 3.9 nm^{-2}).

298 K) is about 7 times that of Na^+ (0.005011 $S \cdot m^2 \cdot mol^{-1}$ at 298 K),[13] the conductivity of the solution decreased rapidly along with the H^+ substituted by Na^+. In the second stage, when the H^+ in the solution was completely neutralized, the OH^- ions reacted with the acidic −COOH groups on the particle surface, resulting in a slow increase of the solution conductivity with the introduction of Na^+. After all the −COOH groups on the particle surface reacted with OH^- ions, namely, in the third stage, the solution conductivity sharply increased with the increase of Na^+ and OH^-, since the limiting molar conductivity of OH^- (0.01980 $S \cdot m^2 \cdot mol^{-1}$ at 298 K)[13] is about 4 times of that of Na^+.

In Figure 3, the tangent intersection between the first and second stages was marked as A, and the tangent intersection between the second and third stages was marked as B. In the region AB only, the −COOH groups on the particle surface reacted with OH^-, and the volume of NaOH solution consumed in AB was marked as ΔV. The amount of −COOH groups on the particle surface was obtained by conductometric titration. The particle number and total surface area of a given mass can be estimated from the mean size and density of the spherical particles to give the average number of −COOH groups per unit surface area, N_{-COOH} (nm^{-2}), which can be calculated from the following equation,

$$N_{-COOH} = AC\Delta V\rho R \times 10^{-27}/(3M) \qquad (1)$$

where A is Avogadro's constant, 6.022×10^{23} mol^{-1}; C is the concentration of NaOH solution, $mol \cdot L^{-1}$; ΔV is the consumption volume of NaOH solution in the second stage of the conductometric titration, mL; ρ is the density of the copolymerized particles, $kg \cdot m^{-3}$; R is the radius of the particles, nm; and M is the mass of the copolymerized particles, g.

Figure 4 shows that the surface densities of the −COOH groups on the particles changed with the increase of the MAA/St ratio. When the MAA/St ratio was below 5%, the densities of −COOH groups increased sharply with the MAA/St ratio; when the ratio was over 10%, the densities of the −COOH groups tended to be constant. Because of the hydrophilicity of the −COOH groups, they were apt to locate on the surface of the polymerized particles in the slurry. Because of the limited surface of the particles in the suspension, the −COOH groups will exist not only on the surface but also in the body of the polymerized particles when the MAA/St ratio was higher than a critical value. So, when the MAA/St ratio was >10%, the density of the −COOH groups on the polystyrene particle surface became constant, which paralleled the trend of the size change.

3.3. Effects of the −COOH Groups on the Particle Coating. Figure 5 shows the coating morphologies of particles with different surface densities of −COOH groups for the same coating condition. The surface densities of the −COOH groups were 0, 2.9, 3.2, 3.5, 4.3, and 3.9 nm^{-2}, corresponding to the MAA/St ratios of 0%, 1%, 5%, 10%, 15%, and 20%, respectively. The coating reagents were all $Al_2(SO_4)_3$ solutions, and the coating condition was pH 5 and 60 °C, under which the coating morphologies should be film coating according to the morphology "phase diagram" of hydrous alumina coating on TiO_2 particles as our previous work.[14] However, it was seen that the coating morphologies of the six samples were different. Figure 5a shows a homogeneous precipitation of the coating materials, and parts b and c of Figure 5 show heterogeneous coating morphologies with some amount of homogeneous precipitation, while parts d, e, and f of Figure 5 show almost completely heterogeneous coating morphologies. The differences in the six samples were the particle size and surface density of −COOH groups. TEM inspection shows that the coating morphology under the same condition was not affected by the particle size, e.g., in Figure 5e, it is clearly shown that all the particles, large or small, were film coated. Thus, the different coating morphologies shown in Figure 5 were mainly brought about by the different surface densities. The images of the coated and noncoated particles (MMA/St = 0.1, N_{-COOH} = 3.5 nm^{-2}) with high magnification are shown in Figure 6. It is clearly shown that the film was uniform and continuous and had a thickness ≈ 5 nm. Combining Figures 4 and 5, it can be concluded that, when the ratio of MAA/St is >10%, i.e. the surface density of −COOH groups is >3.5 nm^{-2}, the particles are easily film coated.

Then, it can be inferred that the coating process is controlled by the kinetic competition between two reactions: the heterogeneous condensation between the −COOH groups on the particle surface and OH−Al species, which leads to the growth of the coating, and the homogeneous condensation of the OH−Al species, which leads to the particle formation of alumina hydroxide in the bulk phase. The increase in surface energy for heterogeneous precipitation is lower than that for homogeneous nucleation, so generally, the former reaction is favored over the latter. However, the heterogeneous precipitation is limited by the density and reactivity of the −COOH groups on the particle surface. Therefore, when the density of −COOH groups increased, heterogeneous condensation was enhanced and homogeneous nucleation was restricted, which can be verified by the six images in Figure 5.

Figure 7 shows the coating morphologies of copolymerized particles (with 3.9 nm^{-2} −COOH groups on the surface) at 60 °C and pH 5, 7, and 9, respectively. It is seen that the coating

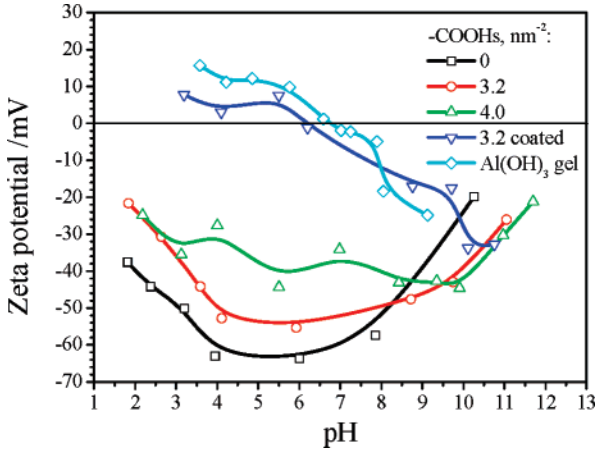

Figure 8. Zeta-potential vs pH for coated and noncoated polymerized particles.

morphologies were film coating, floccule coating, and flake coating, which coincide with the morphology "phase diagram" of the hydrous alumina coating on TiO_2 particles.[14] This shows that, whether the core particles are organic copolymerized or inorganic oxides, when these have surface functional groups that can provide enough condensation sites, the particles can be heterogeneously coated and the coating morphologies can be easily changed from film, via floccule, to flake by increasing the pH. Thus, different coating morphologies can be easily obtained by using particle surfaces that had been loaded with a particular density of functional groups.

Figure 8 shows the zeta-potential vs pH curves for coated and noncoated copolymerized particles. The surface densities of the −COOH groups of the copolymerized particles were 0, 3.2, and 4.0 nm^{-2}. It is seen that the zeta potentials of the three noncoated copolymerized particles were almost below −30 mV. In addition, the absolute value of the zeta potential decreased with the increase of the density of −COOH groups. The reason has to be further studied. Meanwhile, it can be seen that the zeta-potentials of the coated copolymerized particles were significantly changed. The zeta-potential vs pH curve and isoelectric points (IEPs) for the particles coated with hydrous alumina are similar to those of pure $Al(OH)_3$ gel, indicating that the properties of the particle surface were effectively changed.

4. Conclusion

MAA/St copolymerized particles loaded with different surface densities of −COOH groups were successfully synthesized and used to study their hydrous alumina coating. The density of −COOH groups on the particle surface increased and the particle size decreased with the increase of MAA/St ratio in the copolymerization. When MAA/St ratio was >10%, the surface density of −COOH groups and the particle size tended to be constant.

The coating morphologies of polystyrene particles loaded with −COOH groups were similar to those of inorganic particles with −OH groups. When the surface density of −COOH groups was >3.5 nm^{-2}, the particles can be easily heterogeneously coated with hydrous alumina and the surface coating morphologies can be readily controlled by changing the pH. A high density of −COOH groups on the particle surface increased heterogeneous coating and restricted homogeneous nucleation in the bulk. The −COOH groups acted as reaction or condensation sites during the precipitation in the coating process.

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Note Added after ASAP Publication. In the version of this paper that was published on the web 5/25/2007, the author list for ref 2 had errors. The correct version was posted 6/5/2007.

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