

Morphology Control of Hollow Polymer Latex Particle Preparation

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ABSTRACT: Hollow polymer latex particles containing a hydrophilic core fully encapsulated with a hydrophobic shell were prepared by multistage polymerization followed by neutralization with a base. The diameters of the particles were monodispersed and void fractions of the prepared latex particles as high as 50% were achieved. High instantaneous monomer conversion was found to be the key point to minimize the interdiffusion of the core-shell polymer chains. The influences of the shell crosslinking agent and

shell carboxyl content on the hollow morphology were also investigated. The maximum hollow diameter was observed with crosslinking agent contents of 7.5–12.5 wt %. The shell carboxyl content had an appropriate value, and an excess of it resulted in an excentric hollow structure. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 860–863, 2005

Key words: hollow particles; core-shell polymers; emulsion polymerization; morphology; monodisperse

INTRODUCTION

The morphology control of latex particles has been a fascinating area in emulsion polymer science, because it significantly enhances the application areas of latex. Latex particles with a hollow structure have a wide variety of applications such as photonic crystals, delivery vehicle systems, fillers, pigments, and catalysts.^{1–3} Consequently, preparation and characterization of the hollow-structured latex particles have been extensively investigated.

One of the approaches for the synthesis of hollow-structured particles is the employment of a micron-sized or nanometer-sized particle as a template. The research laboratories of the Rohm and Haas Company developed a method using a carboxylated polymer as the template.^{4–7} The process involved synthesizing a structured particle with a carboxylated polymer core and one or more outer shells, followed by neutralizing of the carboxylated core with a base under an appropriate temperature, which resulted in the expansion of the particles by osmotic swelling and the formation of water-filled hollow particles. The advantage of this method lies in the formation of hollow particles with a definite morphology (particles containing one central hollow), compared to other techniques.^{8–11} In the few

academic studies about the method, Vanderhoff et al. used heterocoagulation as the mechanism of particle growth.¹² Pavlyuchenko et al. investigated the effect of neutralization conditions and shell copolymer thickness on the final hollow-particle geometry.¹³ However, the factors influential on the morphology during the encapsulated stage were infrequently mentioned or deficient in quantitative data. Because the core latex copolymer was introduced, high levels (20–35 wt %) of carboxylic acid, which is known to be connected to instability and coagulation, will influence the following polymerization to encapsulate the core copolymer, especially a hydrophilic core fully encapsulated with a hydrophobic shell. Therefore, controlling the conditions of the method in the encapsulated stage is very important and difficult to complete.

We investigated the factors influential on the morphology of hollow latex particles prepared during the shell polymerization stage. Monodispersed hollow particles were fabricated by emulsifier-free emulsion polymerization without the occurrence of a coagulate latex. Hollow particles have a nearly uniform void morphology.

EXPERIMENTAL

Materials

Methyl methacrylate, vinyl acetate, styrene, methacrylic acid, acrylic acid, and *n*-butylacrylate were used for latex preparation. All of the monomers were purified by vacuum distillation before use. Ethylene glycol dimethacry-

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TABLE I
Recipe for Synthesis of Core Copolymer Latex

Components	Seed charge (g)	Rest charge (g)
MMA	0.64	15.86
MAA	0.03	10.02
BA	0.57	14.13
EGDM		0.25
SDS	0.005	
KPS	0.10	0.30
Water	90	

late, divinyl benzene, potassium persulfate, and sodium dodecylbenzenesulfonate were used as received. Twenty percent aqueous NaOH and HCl were used to adjust the pH of the polymerized latex.

Emulsion polymerization

The emulsion was prepared in a 250-mL glass reactor equipped with a reflux condenser, a mechanical stirrer, an inlet for nitrogen supply, and inlet tubes for the continuous feed of materials. The temperature was controlled to vary within $\pm 1^\circ\text{C}$.

Preparation of core latex

All seed monomers and initiator were charged into the reactor simultaneously at 80°C within 30 min. The remaining monomers and the initiator were fed into the seed latex within 300 min. Then, the reaction mixture was kept at 80°C for 30 min (see recipe in Table I).

Shell latex synthesis

Before the synthesis of the shell structure, the prepared core latex was diluted to a solid content of 10%. The reaction was carried out at 80°C by constant feeding of the first sheath stage monomers and initiator into the diluted core latex. To provide high polymerization rates, a portion of the initiator was charged into the latex before feeding of the components. After completion of the first sheath stage feeding, the second-stage monomers and initiator were added to the reactor while the reaction temperature and the corresponding feed rate were adjusted to various values. The reaction was carried out for an additional 30 min after completion of the feeding (see recipe in Table II).

Latex neutralization

To prevent the coagulation of particles during the neutralization at high temperatures, an additional amount of sodium dodecylbenzenesulfonate was charged into the above latex. The pH of the emulsion was adjusted to 10 with aqueous NaOH and then kept

at 90°C for 180 min. After the treatments, the emulsion was rapidly cooled to room temperature and neutralized to pH 7 with aqueous HCl.

Measurements

The solid contents of the latexes were determined by weighing the remaining solid weight after IR drying of 1–2 g of latex to constant weight.

The morphology of the prepared latex particles was observed using a Hitachi model H-800 transmission electron microscope with Formvar-coated copper grids at an accelerating voltage of 200 keV. The mean particle diameter and hollow size were determined from at least 300 particles on the microscope photos.

RESULTS AND DISCUSSION

Effect of instantaneous percent monomer conversion

The hydrophilic core introduces especially high levels of carboxylic acid encapsulated in a hydrophobic shell, so the mutual diffusion of polymer chains is unavoidable. For preventing interdiffusion, the polymerization speed needs to be increased. Only if the polymer shell is formed rapidly enough can the interdiffusion of the polymer chain be efficiently prevented. Thus, we introduced the control factor of instantaneous percent monomer conversion. The instantaneous percent monomer conversion of the polymerization of the shell can be adjusted by changing the reaction temperature and the feed rate of the monomers and the initiator. A variety of polymerization conditions were examined to optimize the morphology, reduce polymerization time, and minimize any coagulated polymer produced in the process. Table III lists the conditions for shell formation. The corresponding instantaneous percent monomer conversion with the polymerization time is plotted in Figure 1.

TABLE II
Recipe for Polymer Shell Formation onto Core Latex Particles

Components	First sheath stage charge (g)	Second-stage charge (g)
Core latex (10% solids)	82.2	
MMA	7.33	
AA	0.84	1.36
ST	2.03	23.67
DVB		4.88
KPS1 ^a	0.10	
KPS2 ^a	0.10	0.30
Water	10	10

^a KPS1 and KPS2 are the amounts of the initiator added into the reaction mixture before the polymerization and during the feeding of the components, respectively.

TABLE III
Conditions for Polymer Shell Formation
onto Core latex Particles

Synthesis conditions	A1	B1	C1	D1
First sheath stage charge				
Polymerization temperature (°C)	80	80	80	80
Time of components feeding (min)	30	30	30	30
Second-stage charge				
Polymerization temperature (°C)	80	85	90	90
Time of components feeding (min)	180	160	130	110/130 ^a

^a Initiator/monomer feeding time.

The instantaneous monomer conversion was increased with the increase of the reaction temperature and feed rate of the initiator.

The morphology of the latex particles prepared at the corresponding synthesis conditions after neutralization treatment are provided in Figure 2. We found that, with the increase of instantaneous monomer conversion, the hollow volume of the latex particles increased and the hollow structure became increasingly regular. High instantaneous conversion during the stages of the process is ideal in terms of the morphology. The swelling of the core and thickening of the sheath can be minimized by the polymerized monomer and the shell formed promptly.

Effect of shell crosslinking agent content

Crosslinking the shell polymer chains is another effective way to prevent diffusing of the hydrophobic shell

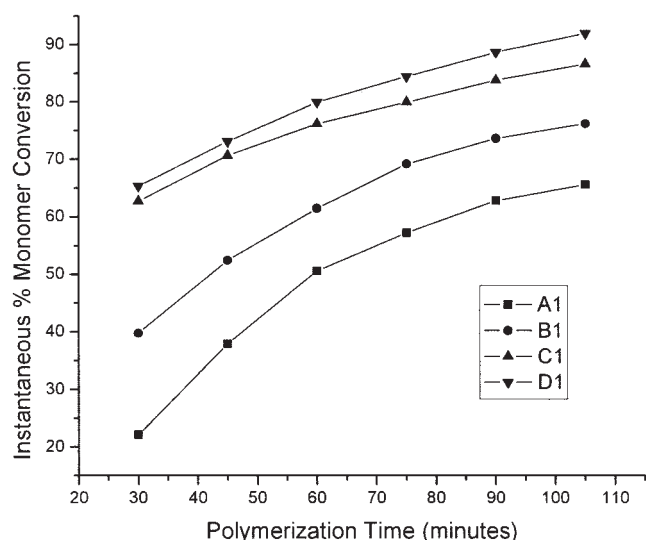


Figure 1 The instantaneous percent monomer conversion as a function of polymerization time under the conditions listed in Table III.

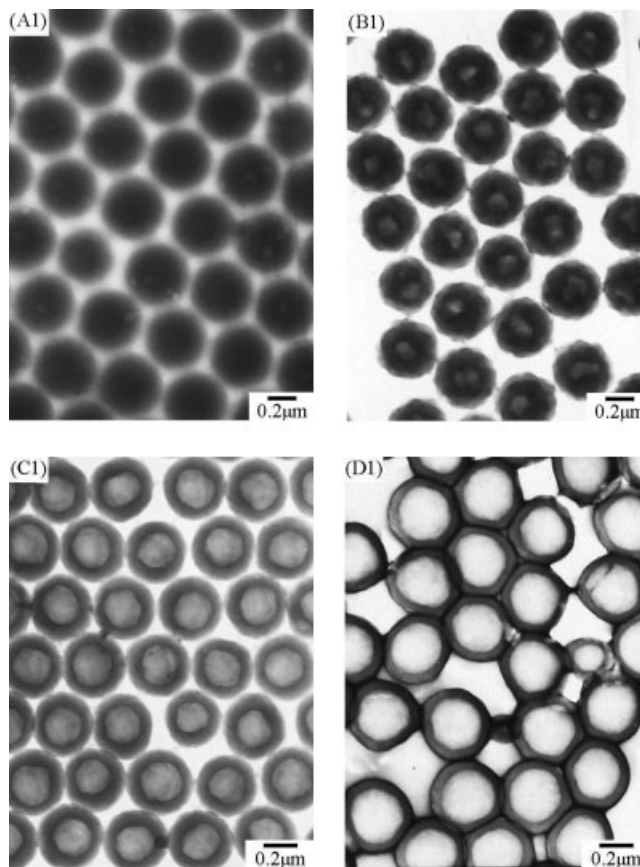


Figure 2 Transmission electron micrographs of the core-shell latex particles with different shell synthesis conditions after neutralization treatment. The synthesis conditions are listed in Table III.

polymer and swelling of the hydrophilic core component, which increased the encapsulation efficiency of the shell polymerization. After the neutralization of the latex, when the swelling agents were removed by drying, the shrinkage of the core tended to develop a void, the extent of which depended on the resistance of the shell to restore to its previous size. Appropriate crosslinking favors the shell being able to keep its size and prevent collapse. However, excess crosslinking harms the swelling of the shell.

Figure 3 illustrates the dependence of the hollow size on the shell crosslinking agent content. Clearly, an optimum crosslinking agent content existed. The maximum hollow diameter was observed at divinyl benzene contents of 7.5–12.5 wt %. Insufficient or excess crosslinking made the size decrease.

Effect of carboxylic acid functionalized polymer in sheath

The polar component of carboxylic acid in the shell copolymer facilitates the hydrophilic core to be fully encapsulated with the hydrophobic shell. In addition,

the carboxylic acid functionalized polymer in the sheath helps the water diffusion and core swelling during the neutralization stage. However, with the increase of the polar component content, the latex particles become polydispersed, producing the excentric hollow structure shown in Figure 4. Usually, the carboxylic acid functionalized polymer mostly distributes on the surface layer of the latex particles and reaches a balance value (about $6.9 \times 10^{-8} \text{ mol/m}^2$).¹⁴ When its content increases, more carboxylic acid functionalized polymers distribute in the sheath. The distribution of the polymer became uneven, which caused different diffusion and swelling velocities in the sheath. Ultimately, an excentric hollow structure formed.

We concluded from this study that high instantaneous monomer conversion was a key factor in controlling the morphology of the latex particles. The shell crosslinking agent and carboxyl group influenced the formation of the hollow structure.

CONCLUSION

Core-shell structured hollow polymer latex particles were successfully prepared. For making hollow particles, the most significant factors were certain synthesis conditions and recipes. The polymerization of the shell at high instantaneous monomer conversion was a necessary procedure to obtain latex particles with a thermodynamically unfavorable structure morphology, accompanied by no coagulation. The shell

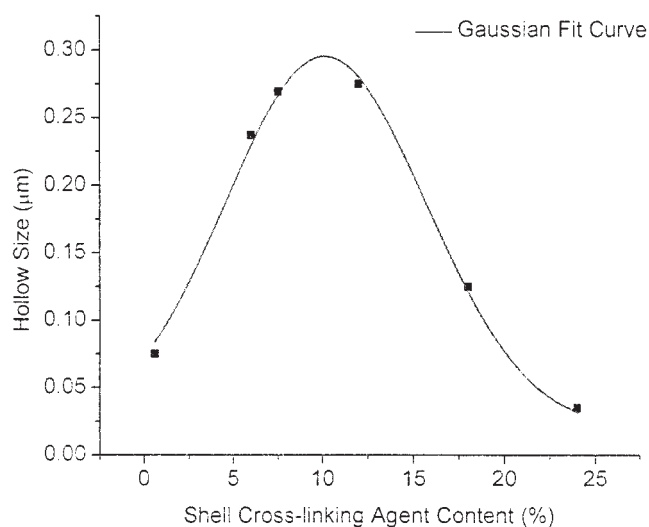


Figure 3 The hollow size of the core-shell latex particles with different shell crosslinking agent contents.

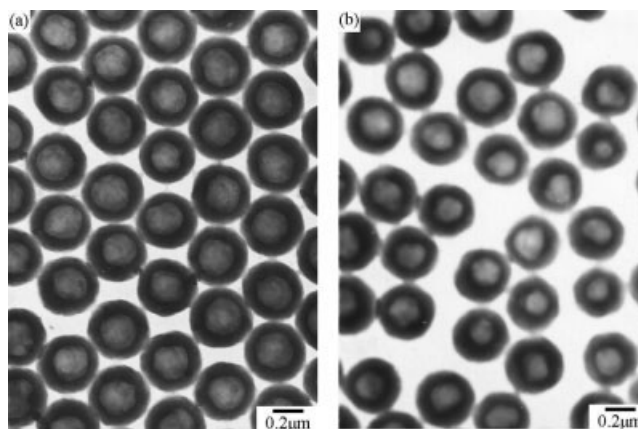


Figure 4 Transmission electron micrographs of the core-shell latex particles with different shell carboxylic acid contents after neutralization treatment: (a) 5% carboxylic acid or (b) 7% carboxylic acid.

crosslinking agent also played an important role in the formation of the hollow structure. The maximum hollow diameter was achieved at crosslinking agent contents of 7.5–12.5 wt %. The carboxyl group in the shell helped the water transport and swelling of the core. However, excess carboxylic acid content led to an excentric hollow structure.

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