

Self film-forming and opaque hollow latexes fabricated via seeded emulsion polymerization followed by alkali post-treatment

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ABSTRACT: In order to obtain novel hollow latexes with both opaque and self film-forming properties, the four-layer core/shell latex particles—sequentially consisting of a high carboxyl-containing soft core, a transition layer, a rigid supporting layer, and an outermost film-forming layer—are first designed and prepared by emulsion polymerization, and then treated with alkali to fabricate self film-forming hollow latexes. On the basis of the previous research on the three-layer core/shell latex, influences of the composition and thickness of the film-forming layer on the properties and morphologies of the four-layer core/shell and the final hollow latexes are investigated. Results show that under optimized conditions with butyl acrylate/styrene (BA/St) mass ratio of 2/1, divinyl benzene (DVB) content of 1 wt %, and core/film-forming layer mass ratio of 1/6 in the film-forming layer preparation, the final hollow latex particles exhibit best morphology considering both light scattering efficiency and film-forming capability at room temperature. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42541.

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INTRODUCTION

Hollow polymer particles have attracted great attention and strong commercial interests owing to its unique properties of low density, opacity, encapsulation, and controllable release. Over the past few decades, much effort has been made to develop its synthetic methods as well as to investigate its applications in filler, coating, diagnostics, drug delivering, microencapsulation, nanoreactors, and stimuli-responsive systems.^{1–5} And among them, the osmotic swelling method is the earliest and dominant for obtaining submicron-size hollow polymer particles, which was invented by Kowalski and his colleagues and then commercialized in Rohm & Hass Company.⁶ The typical concept is to prepare core/shell latexes with a soft carboxyl-containing core and a rigid shell followed by neutralizing the carboxyl to generate polyelectrolyte inside and expanding the core by osmotic swelling mechanism. Based on this principle, many investigations have been focused on the better understanding of the mechanism as well as on the effective controlling of latex particle morphology, and good progresses have been achieved.

In order to obtain a more uniform and complete encapsulation of the shell, Chips *et al.* introduced an interlayer with intermediate polarity as a transition between the core and the shell.⁷ Choi *et al.* revealed that proper cross-linking of both the core

and the shell polymers was necessary for minimizing the interpenetration of copolymer chains.⁸ Vanderhoff *et al.* optimized sophisticated kinetics and thermodynamic factors for obtaining the three-layer soft hydrophilic core/hard hydrophobic shell latexes and performed a neutralizing process of the carboxyls before the preparation of the second shell layer copolymer.⁹ Using similar process, the hollow latexes were also prepared, and the conditions of polymerization and post-treatment were optimized by Pavlyuchenko *et al.*^{10,11} As for post-treatment, stepwise alkali/acid method and alkali/cooling method have also been utilized to prepared submicron-sized multi-hollow polymer particles by different researchers.^{12–15}

In our previous work, the submicron-sized hollow latex particles with different composition and different morphology were prepared via multistep seeded emulsion polymerization followed by alkali post-treatment.^{16,17} Recently, by using a pre-emulsified feed mode of monomers, the hollow latexes with high methacrylic acid (MAA) content in the core preparation were successfully prepared.^{18,19} And the effects of many factors including MAA content, monomer feeding mode, core size, core/shell mass ratio, and cross-linking level on hollow latexes were revealed.

In order to afford the expansion and shrinkage of latex particles during the post-treating and further drying processes, a rigid

Table I. Typical Recipes of the Four-Layer Core/Shell Latex Preparation

Ingredients	Core (g)	Transition layer (g)	Supporting layer (g)	Film-forming layer (g)
MMA	26.8	7.32	0	0
MAA	17.8	0.840	0	0
St	0	2.00	23.6	5.00
BA	0	0	0.900	10.0
EGDMA	0.250	0	0	0
DVB	0	0	0.900	0.150
SDS	0.240	0.025	0.100	0.100
OP-10	0.670	0.075	0.150	0.300
APS	0.400	0.150	0.300	0.150
Water	130	55.0	37.0	50.0
Core latex ^a	-	25.0	-	-
3-layer c/s latex ^b	-	-	-	60.0

^aCore latex represented the latex prepared according to the core recipes.

^bThree-layer c/s latex represented the latex prepared according to the core, the transition layer, and the supporting layer recipes.

shell copolymer with a relatively high T_g is usually preferred in hollow latex preparation.¹ However, because the shell is too hard to deform under interfacial surface tension and capillary forces with the evaporation of water, and diffusion of copolymer chains across particle boundaries and further coalescence of particles are also limited by cross-link network and high T_g , the current hollow latexes cannot form a continuous and intact film by themselves at room temperature, which only can be used as white pigments.^{20–23} For obtaining opaque coatings at ambient condition, hollow latexes must be applied together with other film-forming resins, hindlers, or coalescents.^{24,25} In this work, based on the osmotic swelling method and the previous research on the three-layer core/shell latex,^{18,19} a four-layer core/shell polymer latex with an outermost soft film-forming layer was designed to prepare the hollow latex with both opaque and self film-forming properties, and effects of the BA/St mass ratio, DVB content, and the core/film-forming layer mass ratio in the film-forming layer preparation on the four-layer core/shell latex and the final hollow latex were investigated.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), and styrene (St) (all A. P. grades, First Chemical Reagent Factory, Tianjin, China) were purified by distillation under reduced pressure and stored in a refrigerator. Ethylene glycol dimethacrylate (EGDMA) (98.0% purity, Alfa Aesar, Tianjin, China), divinyl benzene (DVB) (*meta* and *para* mixture *ca* 55% in ethyl vinyl benzene, and diethyl benzene, J&K Scientific, Beijing, China), sodium dodecyl sulfate (SDS), alkylphenol polyoxyethylene (10) ether (OP-10), and NaOH (all A. P. grades, Beijing Chemical Works, Beijing, China) were used without further purification. Ammonium persulfate (APS) (A. P. grade, Aijian Modern Reagent Factory, Shanghai, China) was purified by recrystallization twice in water before use. Distilled and deionized water was used throughout this work.

Preparation of Four-Layer Core/Shell Latexes

Preparation of the four-layer core/shell latexes included four sequential steps of the core, the transition layer, the supporting layer, and the film-forming layer synthesis, and the typical recipes with the BA/St mass ratio of 2/1, the DVB content of 1 wt %, and the core/film-forming layer mass ratio of 1/6 were listed in Table I. The emulsion polymerization was carried out in N₂ atmospheres in a four-necked 250-mL round-bottom flask equipped with an inlet of nitrogen gas, a reflux condenser, an electric mechanical stirrer, and a thermometer, and the stirring speed was around 250 r/min.

In the core latex preparation, 40 g H₂O, 0.22 g SDS, 0.67 g OP-10, and all of MMA, MAA, and EGDMA were first charged into a flask and stirred for 10 min by a high-speed mixer (Ultra-Turrax T25, Ika) to obtain monomer emulsion. Then, 4 g monomer emulsion, 66 g H₂O, 0.08 g APS, and 0.02 g SDS were charged into the reactor, and after polymerizing at 80°C for 40 min, the residual monomer emulsion and solution of APS (0.32 g APS dissolved in 24 g water) were simultaneously drop-wise added into the reactor at 80°C within 5 h and maintained for 30 min after the feeding, and then cooled down to room temperature.

The transition layer of the core/shell latex particles was prepared as follows: the mixture of MMA, MAA, and St was first emulsified in 5 g H₂O with SDS and OP-10 as emulsifiers. Then, the core latex was diluted with 40 g H₂O, and the seeded emulsion copolymerization onto the cores was performed at 80°C by constant feeding the monomer emulsion and APS solution (APS dissolved in 10 g water) simultaneously into the diluted core latex within 50 min, and maintained for 40 min after the feeding to obtain the two-layer core/shell latex.

In the supporting layer preparation, the mixture of St, BA, and DVB was first emulsified in 20 g H₂O with SDS and OP-10 as emulsifiers, and the monomer emulsion and APS aqueous solution (APS dissolved in 17 g water) were then simultaneously drop-wise added into the above two-layer core/shell latex system

Table II. Properties of the Core, the Two-Layer Core/Shell and the Three-Layer Core/Shell Latexes

Sample	Conv. (wt %)	D^{DSL} (nm)	PDI	ζ (mV)
Core latex	99.2	171.4	0.019	-53.9
Two-layer c/s latex	98.9	221.3	0.002	-46.7
Three-layer c/s latex	99.3	303.7	0.007	-44.8

at 90°C within 3 h. After additional 90 min, the system was cooled down to room temperature to obtain the three-layer core/shell latex.

The film-forming layer of the core/shell latex particles was prepared as follows: the mixture of St, BA, and DVB was first emulsified in 15 g H₂O with SDS and OP-10 as emulsifiers. Then, 60 g of the three-layer core/shell latex was diluted with 25 g H₂O, and the seeded emulsion copolymerization was

performed at 90°C by constant feeding the monomer emulsion and APS solution (APS dissolved in 10 g water) into the above three-layer core/shell latex system within 3 h. After additional 90 min, the system was cooled down to room temperature to obtain the four-layer core/shell latex.

Alkali Post-Treatment

Thirty grams of the original four-layer core/shell latex was first charged into a reactor which was immersed in a water bath at 90°C, and then certain amount of 10 wt % NaOH aqueous solution was added into the reactor to keep the mole ratio of NaOH to the total MAA used in the recipes at 1/1. After 2 h of treatment, the latex was cooled down to room temperature to obtain the final hollow latex.

Characterization

Monomer conversion was measured by gravimetric analysis. The hydrodynamic diameter (D^{DSL}), polydispersity index (PDI), and zeta potential (ζ) of the latex particles were measured on a Zetasizer 3000HS (Malvern, UK) at 25°C. The morphology of

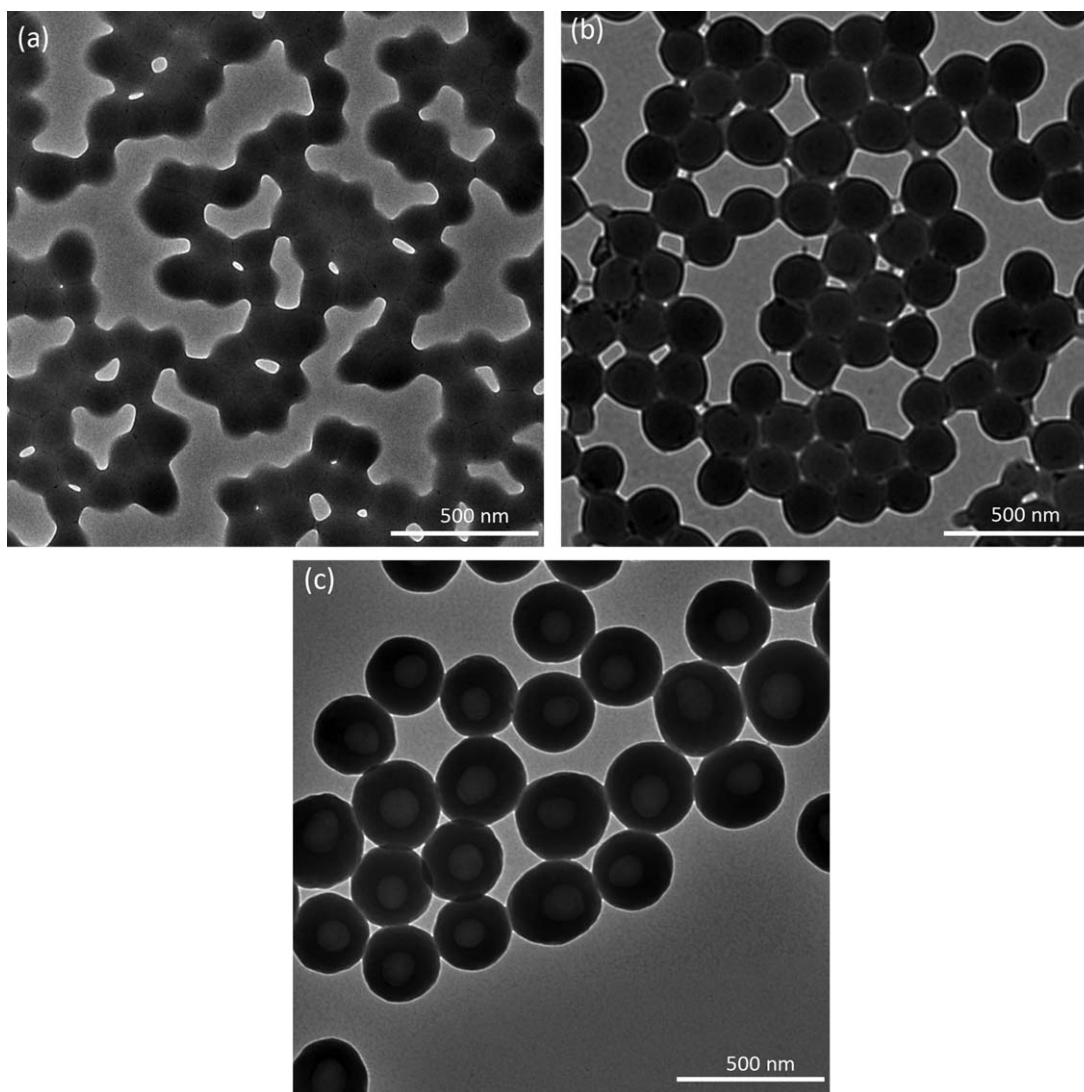


Figure 1. TEM photos of (a) the core latex, (b) the two-layer core/shell latex, and (c) the three-layer core/shell latex.

Table III. Effect of BA/St Mass Ratio in the Film-Forming Layer Preparation on the Four-Layer Core/Shell Latex Properties^a

Sample no.	BA/St mass ratio in the film-forming layer preparation	Conv. (wt %)	D^{DLS} (nm)	PDI	ζ (mV)	MFT of the four-layer c/s latex (°C)	T_g^{Theo} of the film-forming layer copolymer ^b (°C)
1	1/1	99.4	369.4	0.003	-36.9	22.7	1.4
2	2/1	99.7	366.7	0.015	-38.0	7.2	-20.8
3	3/1	98.6	361.3	0.037	-36.1	<0	-30.7

^aThe film-forming layers with varied BA/St mass ratio were prepared under the same condition with 1 wt % of DVB content in the film-forming layer monomers and 1/6 mass ratio of the core/ film-forming layer.

^b T_g^{Theo} was calculated by the Fox equation without consideration of the cross-linking agent DVB.

the dried latex particles was characterized using transmission electron microscopy (TEM, JEOL JEM-2100EX, Japan) at 70 KV. The samples used for TEM characterization were prepared as follows: the latex was first diluted with water to a solid content about 1 wt %, and then mounted on carbon-coated copper grids and dried overnight at room temperature.

The minimum film formation temperature (MFT) of the hollow latex was measured using the MFT Tester (Bar) (Rhopoint, UK). The latex film with the thickness of about 10 μm , which was used to do opaque evaluation, was prepared by coating the hollow latex on a glass substrate and drying at about 25°C.

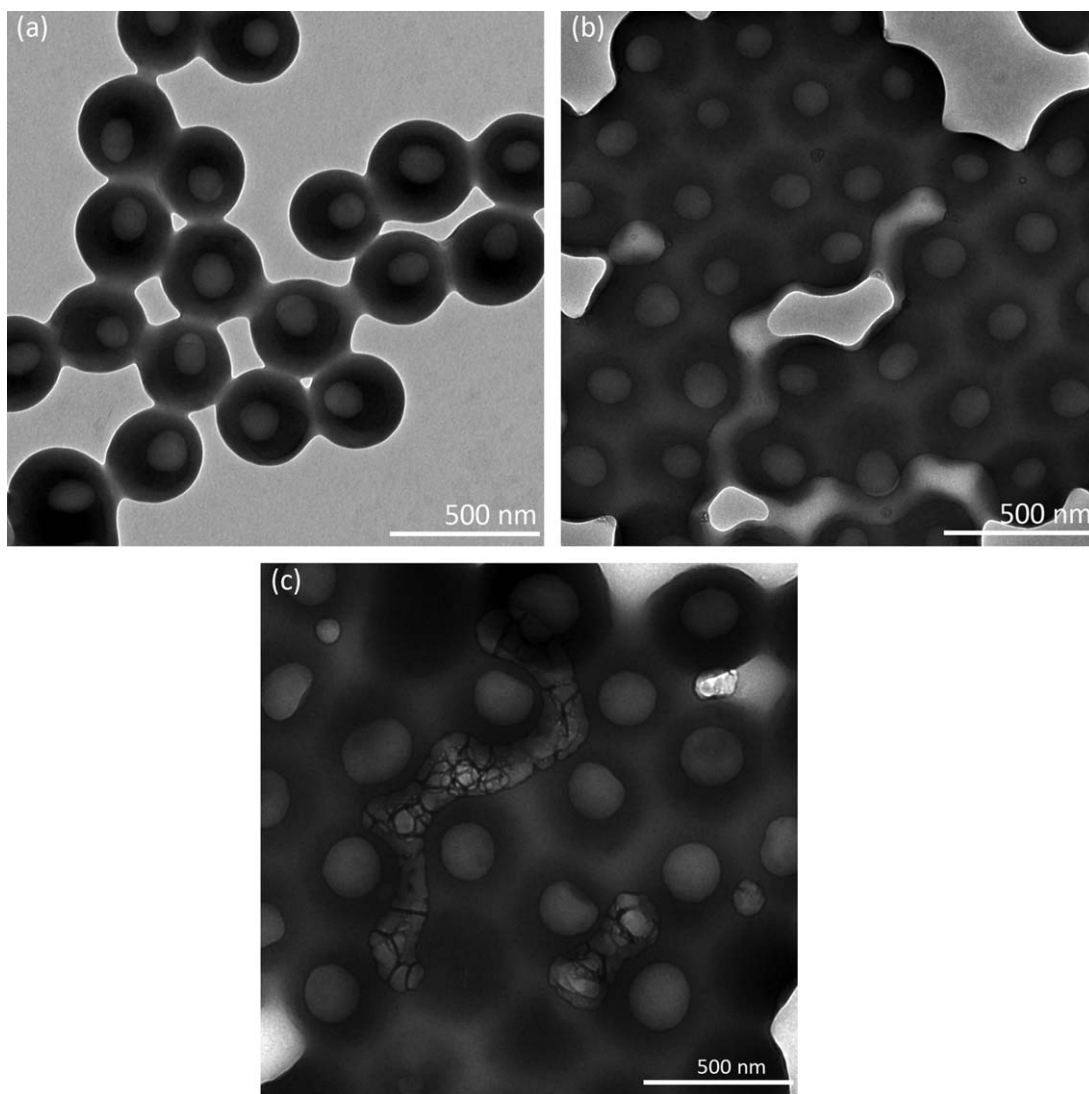


Figure 2. TEM photos of the four-layer core/shell latexes with different BA/St mass ratios in the film-forming layer preparation: (a) 1/1, (b) 2/1, and (c) 3/1.

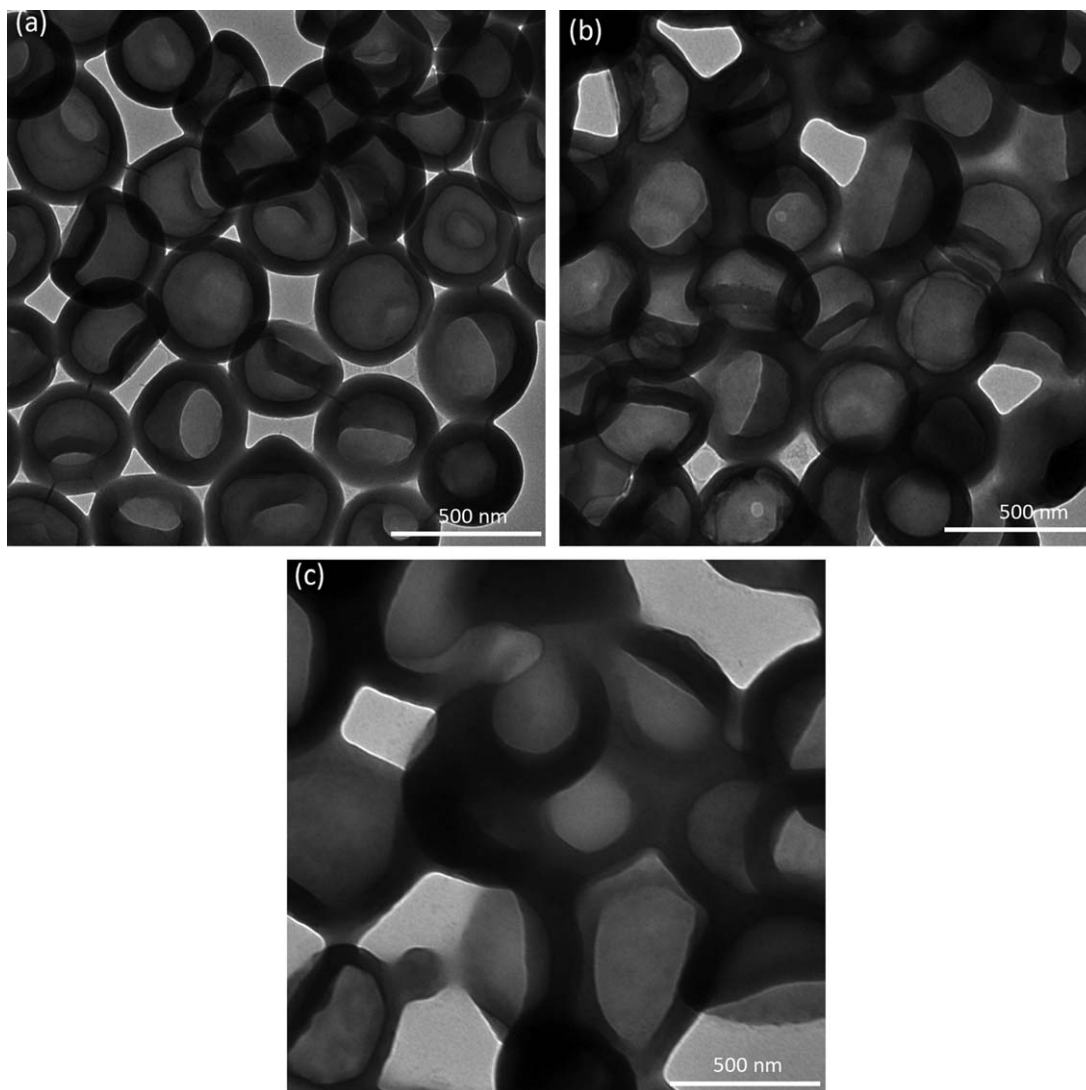


Figure 3. TEM photos of the final hollow latexes with different BA/St mass ratios in the film-forming layer preparation: (a) 1/1, (b) 2/1, and (c) 3/1.

RESULTS AND DISCUSSION

Design and Preparation of the Four-Layer Core/Shell Latex

In order to fabricate the hollow latex with self film-forming property, a four-layer core/shell latex was designed, in which a three-layer core/shell latex was encapsulated with a soft polymer shell. For this purpose, the three-layer core/shell latex consisting of a high carboxyl-containing soft core, a transition layer, and a rigid supporting layer was prepared by monomer pre-emulsified seeded emulsion copolymerization according to Ref. [19], and results are given in Table II and Figure 1. Here, the transition layer with a moderate polarity was introduced to help the supporting layer to encapsulate the hydrophilic core more effectively, while the supporting layer with high T_g of copolymer was to support the latex particle during post-treating process and to resist the hollow particle shrinkage or collapse during the drying process.

Experiments showed that each step of the emulsion polymerization processes performed smoothly with a high monomer

conversion, and the stable latexes with narrow size distribution were obtained. It was notable that there was a small void in the center of each three-layer core/shell latex particle [Figure 1(c)], and it was believed that because of the hydration of carboxyl groups of the core copolymer, the core was actually swelled with water and encapsulated by polymer layers in the seeded emulsion polymerization. During the drying process and the TEM observation, the internal water diffused from the core through the outer layers into the ambience, leaving a small void in the center of the particle. This phenomenon was also observed by Vanderhoff *et al.*⁹

However, similar small void was not observed in the two-layer core/shell latex particles as shown in Figure 1(b). This is because that the transition layer is too thin to embed all core carboxyls inside and to avoid the interpenetration of the two layers, and the strength of transition layer is also too weak to resist particle shrinkage. In this case, the evaporation of water inside the two-layer core/shell particles and the shrinkage of the

Table IV. Effect of BA/St Mass Ratio in the Film-Forming Layer Preparation on the Hollow Latex Properties^a

Sample no.	BA/St mass ratio in the film-forming layer preparation	D^{DLS} (nm)	PDI	ζ (mV)	MFT of the hollow latex (°C)
1	1/1	483.1	0.052	-37.5	30.8
2	2/1	486.7	0.232	-38.9	18.5
3	3/1	563.2	0.468	-41.9	<0

^aThe film-forming layers with varied BA/St mass ratio were prepared under the same condition with 1 wt % of DVB content in the film-forming layer monomers and 1/6 mass ratio of the core/ film-forming layer.

particle occurred simultaneously during drying, and no small void was left.

With the three-layer latex as the seed, the seeded emulsion copolymerization of BA, St, and DVB was carried out to prepare the four-layer core/shell latex using the pre-emulsified monomer feeding model, and the final hollow latex was then fabricated by alkali post-treating the core/shell latex. Because the film-forming layer afforded the self film-forming property of the hollow latex, its composition and amount were significant. Thus, effects of the BA/St mass ratio, the DVB content, and the core/film-forming layer mass ratio in the film-forming layer preparation on the four-layer core/shell latex and the final hollow latex were investigated.

Effect of BA/St Mass Ratio in the Film-Forming Layer Preparation on the Four-Layer Core/Shell Latex

According to film-forming mechanism of the polymer latex, a soft film-forming layer copolymer with a relatively low T_g was designed to ensure that once the latex particles contacted to each other with the water evaporation during the drying process, the film-forming layer could deform and the copolymer chains could diffuse across boundaries of particles to form a continuous and intact latex film.^{20–22} It is well known that the mobility of the polymer chains increase with the decrease of T_g , which is beneficial for forming a latex film at room temperature. However, too high mobility of the copolymer can lead to aggravate the interpenetration of the polymers between the film-forming layer and the supporting layer, and make the formed latex film sticky. As for the four-layer latex, T_g of the film-forming layer copolymer varied along with the change of BA/St mass ratio. Here, effects of the BA/St mass ratio on the four-layer core/shell and the final hollow latexes were investigated under the same conditions with 1 wt % of DVB content in the film-forming layer monomers and 1/6 mass ratio of the core/film-forming layer.

Table III illustrated that the MFT of the four-layer core/shell latex increased with the increase of St in the film-forming layer monomers. It was noticed that when the BA/St mass ratio was equal to or more than 3/1, some gel was generated in the preparation of the film-forming layer, indicating that excessive amount of soft monomer BA made the polymerization process unstable.

TEM photos of the four-layer core/shell latexes were given in Figure 2. When the BA/St mass ratio was 1/1, all of the latex particles presented uniformly spherical though slightly adhesion

of particles was observed. However, the edges of particles with a higher BA/St mass ratio of 2/1 or 3/1 became blurred and even disappeared, demonstrating that the mutual diffusion of the film-forming layer copolymer chains of the adjacent particles increased as the increase of BA content in the film-forming layer monomers. A small void also existed in the center of the particle as observed in the three-layer core/shell latex particles.

Effect of BA/St Mass Ratio in the Film-Forming Layer Preparation on the Hollow Latex

After post-treating the four-layer core/shell latex, the distinct hollow structures inside the particles were generated as shown in Figure 3, and the hollow latex properties were given in Table IV and Figure 4. Compared with the untreated core/shell latexes, the diameter of all the hollow latex particles increased significantly.

During post-treating process, since the particle volume expansion by osmotic swelling led all of the layers to be much thinner, the interpenetration of the supporting layer and the film-forming layer copolymer chains increased significantly, resulting in simultaneous decreases of both the supporting strength of the supporting layer and the mobility of the film-forming layer. And as a result, MFT of the hollow latex was much higher than that of the four-layer core/shell latex (Table IV). For example,

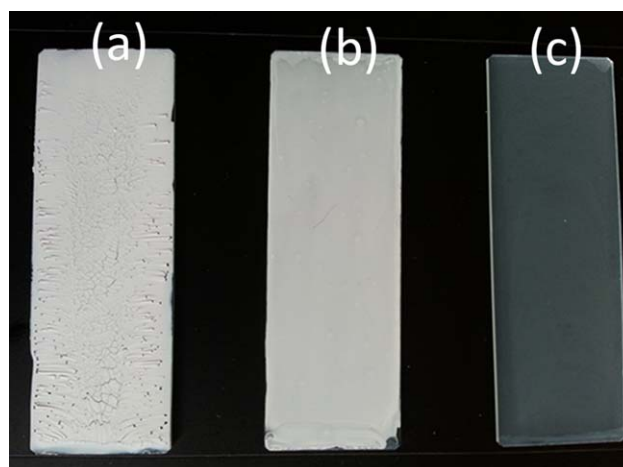


Figure 4. Optical images of the hollow latex films with different BA/St mass ratios in the film-forming layer preparation: (a) 1/1, (b) 2/1, and (c) 3/1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Effect of DVB Content in the Film-Forming Layer Preparation on the Four-Layer Core/Shell Latex Properties^a

Sample no.	DVB content in the film-forming layer preparation (wt %)	Conv. (wt %)	D^{DLS} (nm)	PDI	ζ (mV)	MFT of the four-layer c/s latex (°C)
4	0.5	98.5	367.0	0.015	-35.1	5.0
2	1.0	99.7	366.7	0.015	-38.0	7.2
5	2.0	98.8	367.6	0.037	-36.0	8.0

^aThe film-forming layers with varied DVB content were prepared under the same condition with 2/1 mass ratio of BA/St in the film-forming layer monomers and 1/6 mass ratio of the core/ film-forming layer.

MFT of the final hollow latex with the BA/St mass ratio of 1/1 reached up to 30.8°C, and isolated spherical hollow particles from one another were observed in the TEM photo [Figure 3(a)], indicating that this latex could not form a continuous film at room temperature as shown in Figure 4(a). However,

when BA amount was excessive such as for the core/shell latex prepared with the BA/St mass ratio of 3/1, the final hollow latex particles suffered from significant decline of the supporting strength of the supporting layer, leading the particles to messy morphologies with collapse and distortion [Figure 3(c)], and

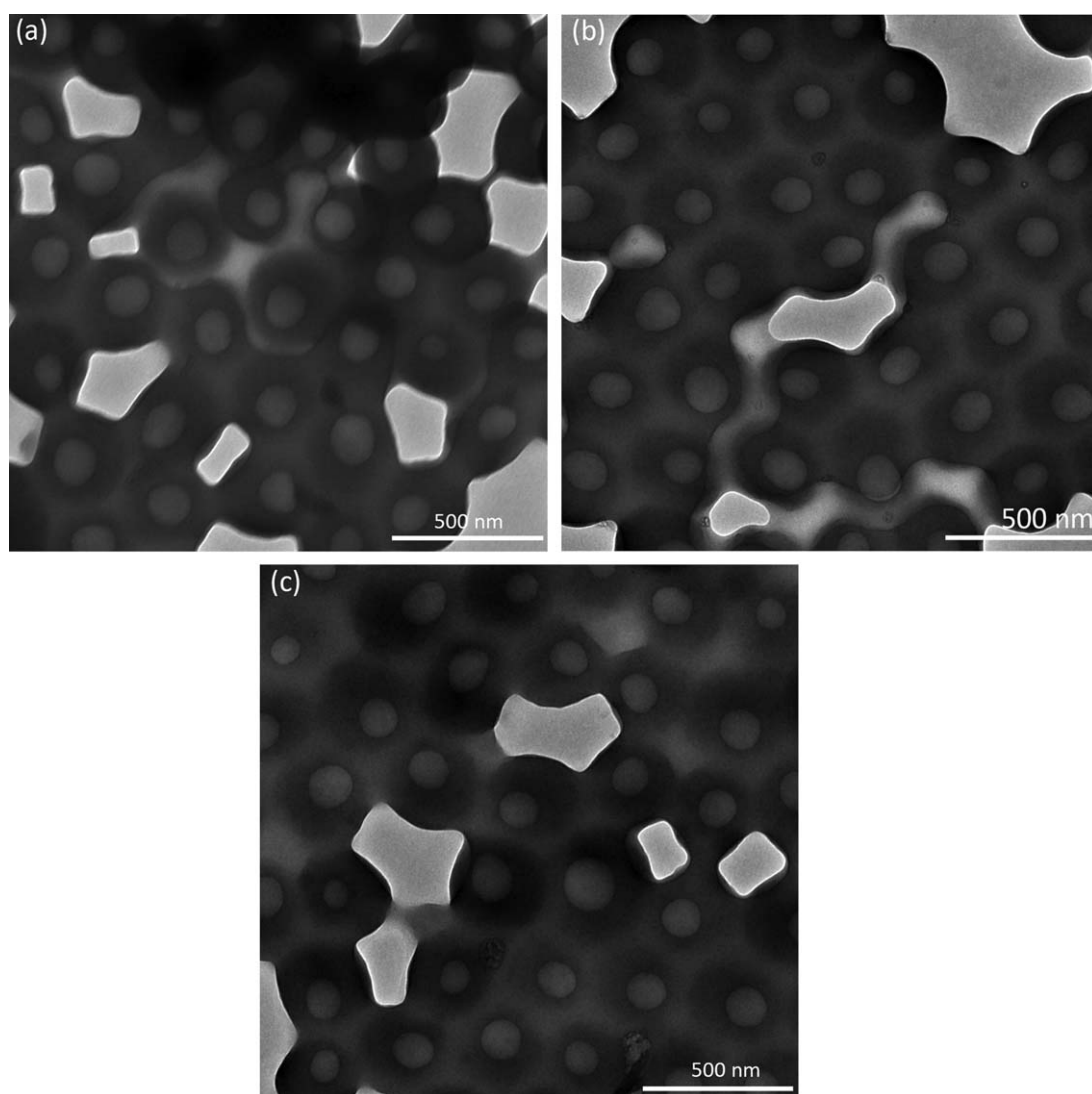


Figure 5. TEM photos of the four-layer core/shell latexes with different DVB contents in the film-forming layer preparation: (a) 0.5 wt %, (b) 1 wt %, and (c) 2 wt %.

Table VI. Effect of DVB Content in the Film-Forming Layer Preparation on the Final Hollow Latex Properties^a

Sample no.	DVB content in the film-forming layer preparation (wt %)	D^{DLS} (nm)	PDI	ζ (mV)	MFT of the hollow latex (°C)
4	0.5	498.3	0.149	-38.1	12.5
2	1.0	486.7	0.232	-38.9	18.5
5	2.0	476.3	0.442	-42.9	21.7

^aThe film-forming layers with varied DVB content were prepared under the same condition with 2/1 mass ratio of BA/St in the film-forming layer monomers and 1/6 mass ratio of the core/ film-forming layer.

the film formed at room temperature was translucent and lack of hiding power [Figure 4(c)].

Considering both the extent of opacity and the capability of film forming, the hollow latex with the BA/St mass ratio of 2/1 in the film-forming layer preparation was the best, as the optical image of the latex film in Figure 4(b) showed.

Effect of DVB Content in the Film-Forming Layer Preparation on the Four-Layer Core/Shell Latex

As mentioned above, the interpenetration of the film-forming layer and the supporting layer copolymer chains occurred in some extent, which would reduce the supporting strength of the supporting layer. And as a result, latex particles would crack

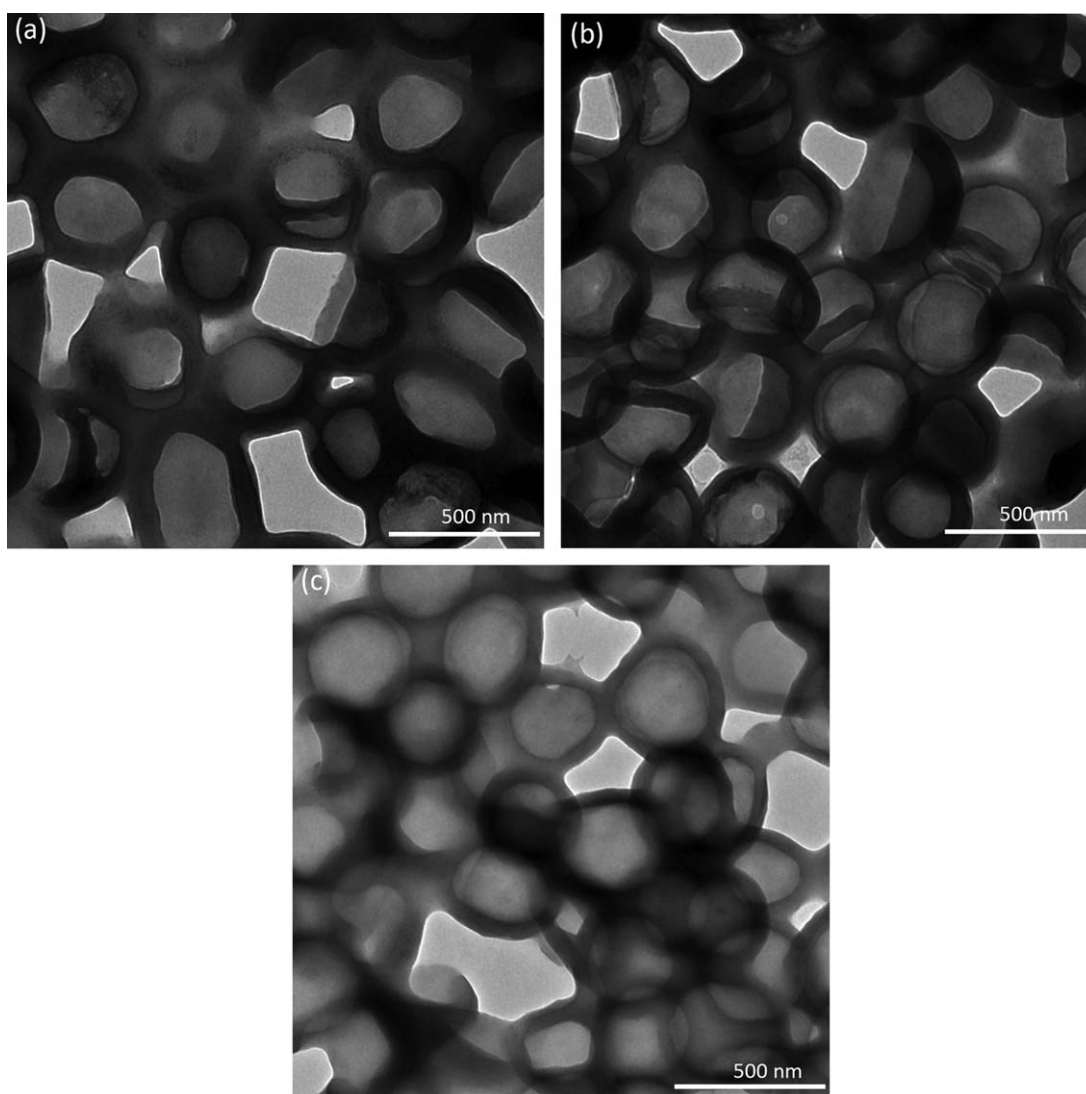


Figure 6. TEM photos of the final hollow latexes with different DVB contents in the film-forming layer preparation: (a) 0.5 wt %, (b) 1 wt %, and (c) 2 wt %.

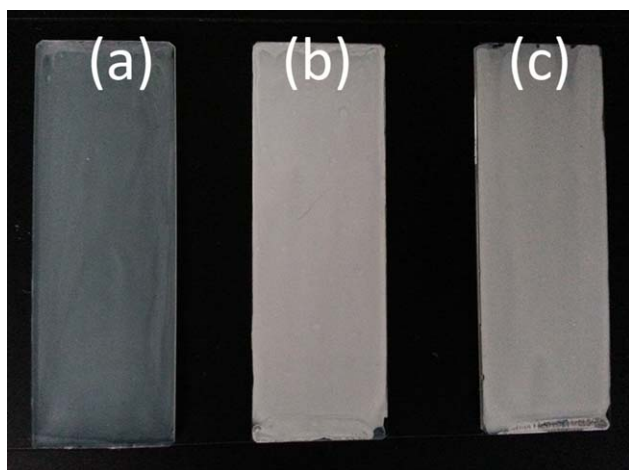


Figure 7. Optical images of the hollow latex films with different DVB contents in the film-forming layer preparation: (a) 0.5 wt %, (b) 1 wt %, and (c) 2 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and collapse in the post-treating and film-forming processes, and the formed film would lose its opacity. It was demonstrated that cross-linking of the copolymer could reduce the interpenetration of different layer copolymer chains.¹⁹ Here, using the same BA/St mass ratio of 2/1 and the core/film-forming layer mass ratio of 1/6, the four-layer core/shell latexes with various DVB content in the film-forming layer preparation were obtained.

The properties of the four-layer core/shell latexes (Table V) indicated that all the emulsion polymerization processes went smoothly, and MFT of the four-layer core/shell latexes increased slightly as the cross-linking degree of the film-forming layer increased. As the TEM photos in Figure 5 indicated, all of the latex particles presented multilayer structure with a small void in the center, although the internal boundary-layer boundaries and the edges of particles were blurred because of the mutual diffusion of polymer chains.

Effect of DVB Content in the Film-Forming Layer Preparation on the Hollow Latex

The properties of the final hollow latexes were listed in Table VI, and the particle morphologies and the optical images of the latex films were given in Figures 6 and 7, respectively. It was obvious that the size of the post-treated latex particles slightly decreased while the size distribution increased as the DVB content increased. The hollow particles with DVB content of 0.5 wt

% showed defective morphology [Figure 6(a)] owing to the interpenetration of the two outer layer copolymers, and the formed latex film was lack of effective light scattering structures, showing weaker opacity [Figure 7(a)]. This situation was improved as DVB content increased to 1 and 2 wt %. Results in Figure 6(b,c) demonstrated that a moderate cross-linking level was beneficial for the latex particles to maintain spherical hollow structures during post-treating and film-forming process, and the formed latex films at room temperature exhibited a good hiding power as shown in Figure 7(b,c). Considering an excessive cross-linking level of the film-forming layer copolymer would raise swelling resistance as well as lower mobility of the film-forming layer copolymer chains, which results in deteriorating both light scattering and film-forming capabilities of the hollow latex, 1 wt % of DVB content was appropriate in the film-forming layer preparation.

Effect of Core/Film-Forming Layer Mass Ratio on the Four-Layer Core/Shell Latex

A proper thickness of the film-forming layer was another important factor for the final hollow latexes to form continuous film and maintain spherical hollow structures simultaneously. In order to investigate the effect of the core/film-forming layer mass ratio, the four-layer core/shell latexes with different core/film-forming layer mass ratio were prepared by keeping the BA/St mass ratio and DVB content constant at 2/1 and 1 wt %, respectively. Experiments showed that the emulsion polymerization processes went smoothly, and results were listed in Table VII and Figure 8. As expected, the diameter of the core/shell latex particles increased with the increase of core/film-forming layer mass ratio. It is worth pointing out that because the effect of interpenetration of the polymer chains on the particle morphology was lessened with the increase of the film-forming layer thickness, MFT value of the core/shell latexes decreased and adhesion between the particles increased with the decrease of the core/film-forming layer mass ratio.

Effect of Core/Film-Forming Layer Mass Ratio on the Hollow Latex

The properties of the hollow latexes were listed in Table VIII, and TEM photos of the hollow latexes and the optical images of the latex films were shown in Figures 9 and 10, respectively. Although the hollow latex with the core/film-forming layer mass ratio of 1/4 presented spherical hollow morphology [Figure 9(a)] and its film showed the best opacity [Figure 10(a)] among the three, the film-forming layer of the corresponding core/shell latex particles was too thin to maintain a high mobility as the supporting layer copolymer chains penetrated into.

Table VII. Effect of the Core/Film-Forming Layer Mass Ratio on the Four-Layer Core/Shell Latex Properties^a

Sample no.	Core/film-forming layer mass ratio	Conv. (wt %)	D^{DLS} (nm)	PDI	ζ (mV)	MFT of the four-layer c/s latex (°C)
6	1/4	99.2	342.4	0.019	-33.7	14.5
2	1/6	99.7	366.7	0.015	-38.0	7.2
7	1/8	98.5	393.6	0.182	-39.4	<0

^a The film-forming layers with varied core/film-forming layer mass ratio were prepared under the same condition with 2/1 mass ratio of BA/St and 1 wt % of DVB content in the film-forming layer monomers.

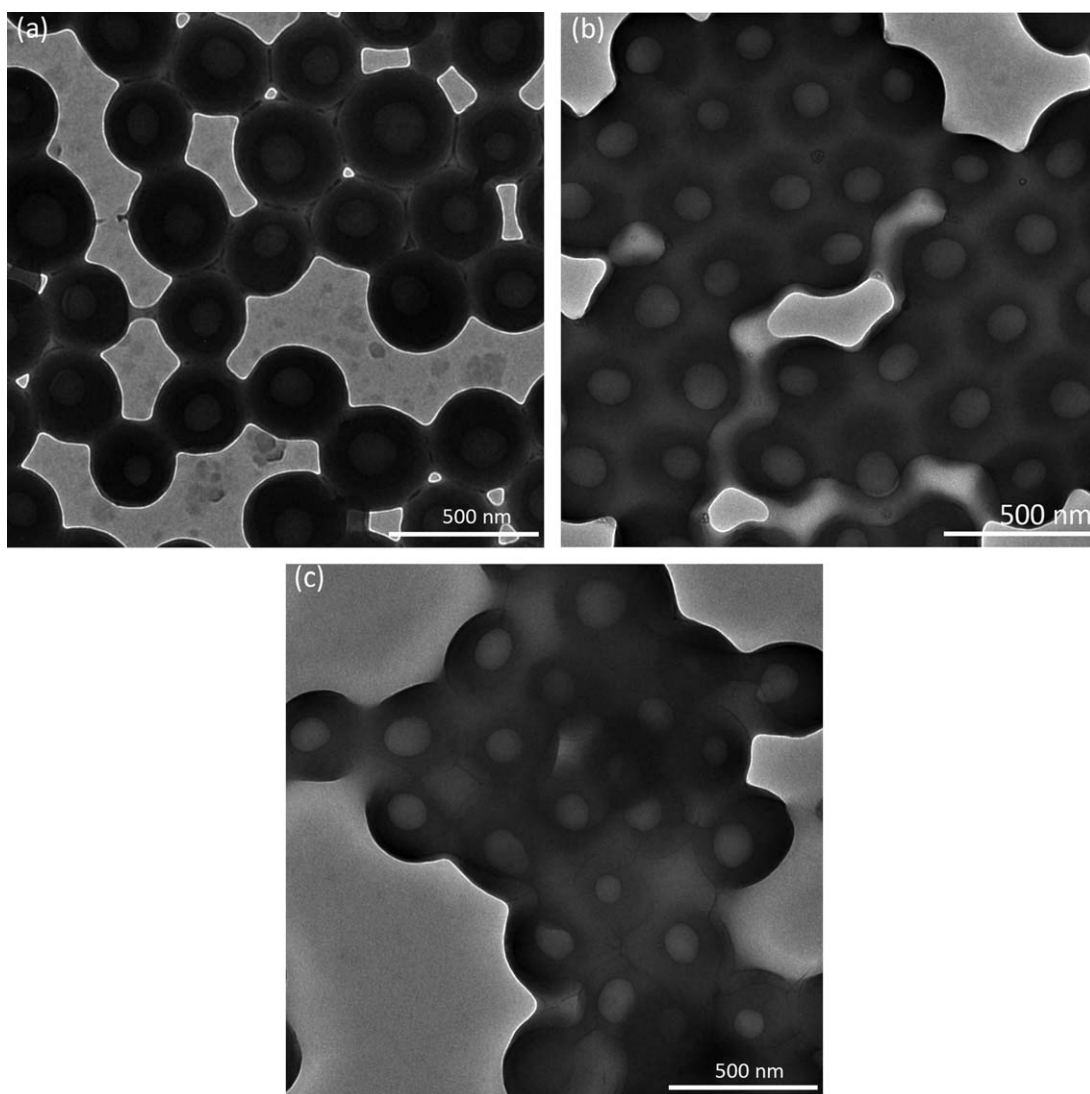


Figure 8. TEM photos of the four-layer core/shell latexes with different the core/film-forming layer mass ratios: (a) 1/4, (b) 1/6, and (c) 1/8.

And as a result, this kind of hollow latex with a MFT above 25°C could not form a continuous film at room temperature, and some very tiny cracks were observed in Figure 10(a). When the core/film-forming layer mass ratio was controlled at 1/6, the latex particles showed recognizable spherical hollow structures [Figure 9(b)], and the obtained hollow latex could form an intact film [Figure 10(b)], resulting in an effective light

scattering. However, when the core/film-forming layer mass ratio increased to 1/8, the hollow latex particles showed collapse and messy structures [Figure 9(c)], and the resulted latex film exhibited a poor opacity [Figure 10(c)] owing to the lack of light scattering capability. This is probably because that excessive thickness of the film-forming layer aggravated penetration of the film-forming soft layer copolymer chains into the

Table VIII. Effect of the Core/Film-Forming Layer Mass Ratio on the Hollow Latex Properties^a

Sample no.	Core/film-forming layer mass ratio	D^{DLS} (nm)	PDI	ζ (mV)	MFT of the hollow latex (°C)
6	1/4	465.1	0.092	-37.2	34.2
2	1/6	486.7	0.232	-38.9	18.5
7	1/8	540.0	0.782	-38.8	3.8

^a The film-forming layers with varied core/film-forming layer mass ratio were prepared under the same condition with 2/1 mass ratio of BA/St and 1 wt % of DVB content in the film-forming layer monomers.

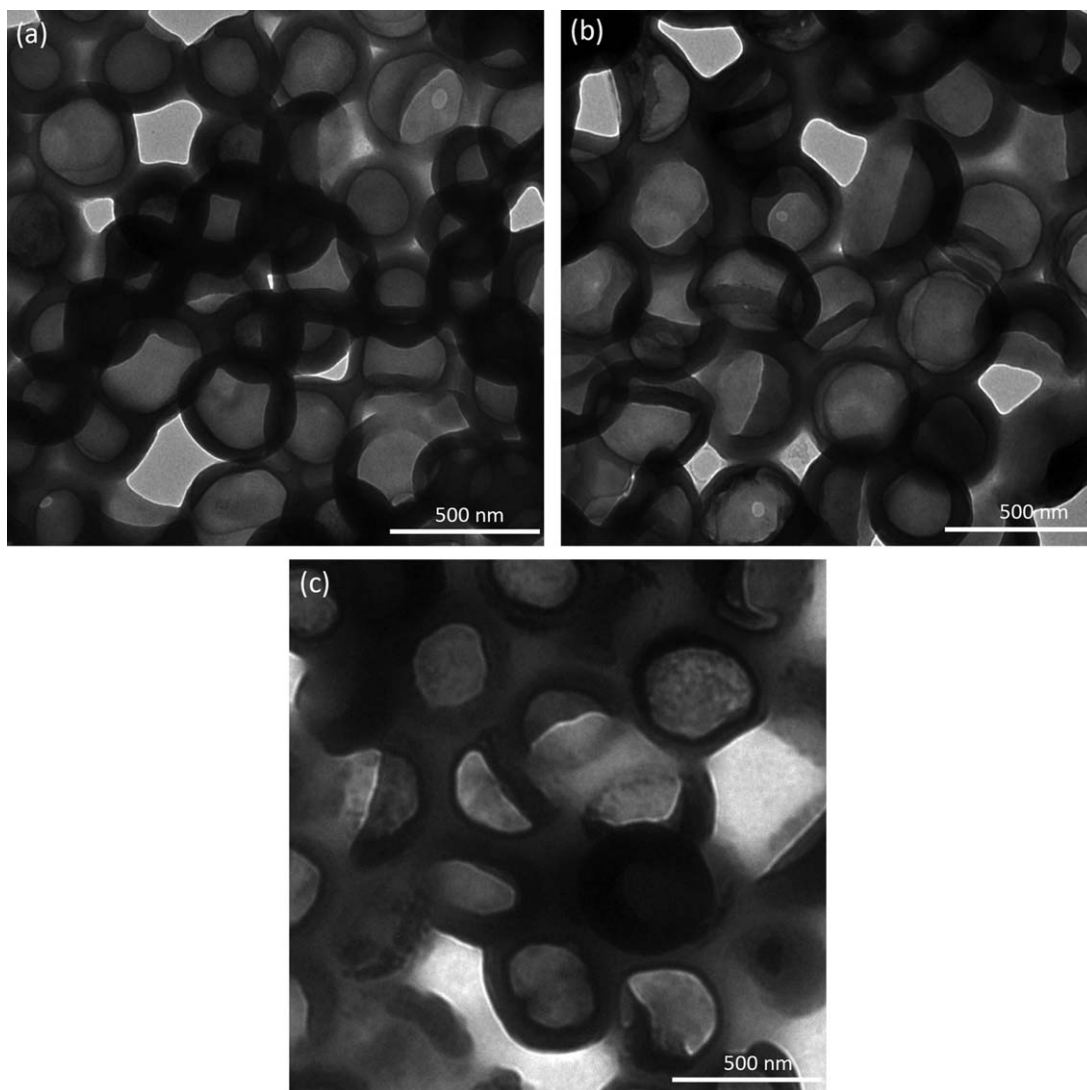


Figure 9. TEM photos of the final hollow latexes with different core/film-forming layer mass ratios: (a) 1/4, (b) 1/6, and (c) 1/8.

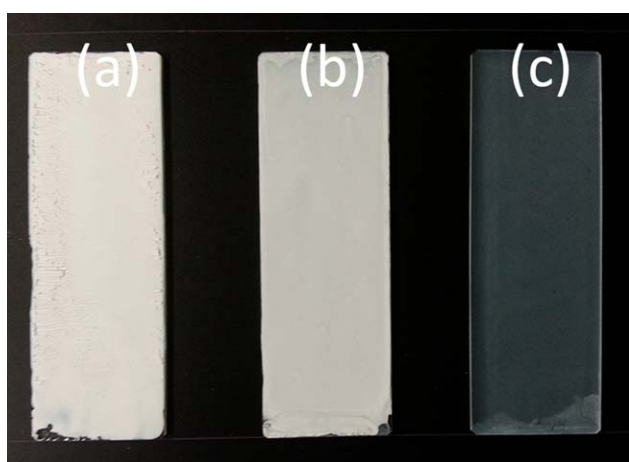


Figure 10. Optical images of the hollow latex films with different core/film-forming layer mass ratios: (a) 1/4, (b) 1/6, and (c) 1/8. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

supporting layer, leading the supporting layer to be too weak to stand swelling force during the post-treating process, and to resist particle collapse during the drying process.

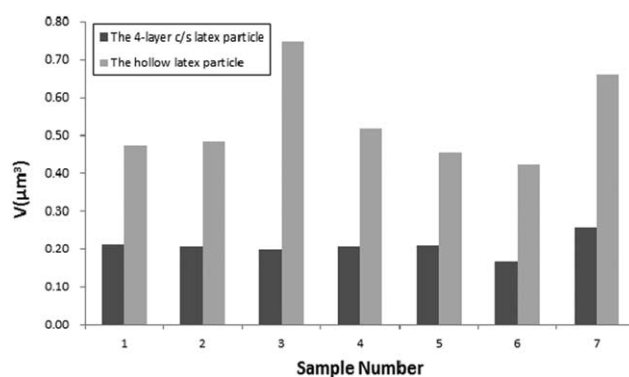


Figure 11. Volumes of the four-layer core/shell latex particles and the hollow latex particles.

Finally, in order to make the expansion of the core/shell latex particles clearer, the particle volume variations before and after treatment were calculated based on the particle diameter, and the volumes of all four-layer core/shell particles and hollow particles were given in Figure 11. The expansion of the core/shell latex particle is a crucial step to obtain the final hollow structures. However, it was notable that the hollow latex of sample 3 with the most significant expansion after treatment did not present a good performance considering both opaque and film-forming properties. Instead, as discussed above, the hollow latex of sample 2 could form an opaque and integral film at room temperature, showing the best result. Thus, the expansion of the core/shell latex particles should be appropriate to obtain an effective light scattering hollow structure and maintain film-forming capability at the same time.

CONCLUSION

The four-layer latexes sequentially consisting of a high carboxyl-containing soft core, a transition layer, a rigid supporting layer, and an outermost film-forming layer were first fabricated via multistep monomer pre-emulsified seeded emulsion polymerization, and followed by alkali post-treatment, the hollow latexes with both opaque and self film-forming properties were obtained. Results showed that the efficient reduction of diffusion and interpenetration of polymer chains between the film-forming layer and the supporting layer was the most important, which could be realized by optimizing the composition and amount of the outermost film-forming layer. When the optimized recipe with BA/St mass ratio of 2/1, DVB content of 1 wt %, and core/film-forming layer mass ratio of 1/6 was utilized in the film-forming layer preparation, the self film-forming hollow latex with the best opaque property was obtained. Accordingly, this kind of hollow latexes might have prospective applications in various fields, such as waterborne coating, ink, paint, biomedicine, and so on.

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REFERENCES

1. Kawaguchi, H. *Prog. Polym. Sci.* **2000**, *25*, 1171.
2. McDonald, C. J.; Devon, M. J. *Adv. Colloid Interface Sci.* **2002**, *99*, 181.
3. Guan, G. J.; Zhang, Z. P.; Wang, Z. Y.; Liu, B. H.; Gao, D. M.; Xie, C. G. *Adv. Mater.* **2007**, *19*, 2370.
4. Yang, X. Y.; Chen, L. T.; Huang, B.; Bai, F.; Yang, X. L. *Polymer* **2009**, *50*, 3556.
5. Fu, G. D.; Li, G. L.; Neoh, K. G.; Kang, E. T. *Prog. Polym. Sci.* **2011**, *36*, 127.
6. Kowalski, A.; Vogel, M.; Blankenshi, R. M.; Rohm and Haas E.P. Patent 0,022,633, January 21, **1981**.
7. Chip, G. K.; Rudin, A. U.S. Patent 4,985,469, January 15, **1991**.
8. Choi, S. B.; Jang, T. H.; Yoo, J. N.; Lee, C. H. U.S. Patent 5,618,888, April 8, **1997**.
9. Vanderhoff, J. W.; Park, J. M.; El-Aasser, M. S. In *Polymer Latex: Preparation, Characterization, and Applications*; Daniel, E. S., Sudol, E. D., El-Aasser, M. S., Eds.; ACS Symposium Series 492; American Chemical Society: Washington, DC, **1992**; p 272.
10. Pavlyuchenko, V. N.; Byrdina, N.; Ivanchev, S.; Skrifvars, M.; Halme, E.; Laamanen, H.; Koskinen, J. W. O. Patent 9,839,372, September 11, **1998**.
11. Pavlyuchenko, V. N.; Sorochinskaya, O. V.; Ivanchev, S. S.; Klubin, V. V.; Kreichman, G. S.; Budtov, V. P.; Skrifvars, M.; Halme, E.; Koskinen, J. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 1435.
12. Okubo, M.; Ito, A.; Kanenobu, T. *Colloid Polym. Sci.* **1996**, *274*, 801.
13. Okubo, M.; Mori, H. *Colloid Polym. Sci.* **1997**, *275*, 634.
14. Kang, K.; Kan, C. Y.; Du, Y.; Yeung, A.; Liu, D. S. *Eur. Polym. J.* **2005**, *41*, 1510.
15. Kang, K.; Kan, C. Y.; Du, Y.; Liu, D. S. *J. Appl. Polym. Sci.* **2006**, *99*, 1934.
16. Deng, W.; Li, R. L.; Zhang, M. J.; Gong, L. X.; Kan, C. Y. *J. Colloid Interface Sci.* **2010**, *349*, 122.
17. Deng, W.; Ji, W. J.; Jiang, Y. M.; Kan, C. Y. *J. Appl. Polym. Sci.* **2013**, *127*, 651.
18. Jiang, Y. M.; Li, B. T.; Deng, W.; Li, X. Y.; Kan, C. Y. *Chin. J. Polym. Sci.* **2014**, *32*, 21.
19. Jiang, Y. M.; Wang, W. J.; Xu, M.; Kan, C. Y. *Chin. J. Polym. Sci.* **2014**, *32*, 177.
20. Winnik, M. A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 2, 192.
21. Keddie, J. L. *Mater. Sci. Eng. R* **1997**, *21*, 101.
22. Steward, P. A.; Hearn, J.; Wilkinson, M. C. *Adv. Colloid Interface Sci.* **2000**, *86*, 195.
23. Mu, Y. C.; Qiu, T.; Li, X. C.; Guan, Y. D.; Zhang, S. W.; Li, X. Y. *Langmuir* **2011**, *27*, 4968.
24. Rennel, C. *Colloid. Polym. Sci.* **1994**, *272*, 1111.
25. Cardinal, C. M.; Francis, L. F.; Scriven, L. E. *J. Coat. Technol. Res.* **2009**, *6*, 457.