

Effect of the Shell Crosslinking Level and Core/Shell Ratio on the Morphology of Latex Particles in the Preparation of Hollow Latexes

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Abstract Three-layer core/shell latex particles with various shell crosslinking level and shell thickness were prepared by multistep emulsion polymerization, and the hollow latex particles with different morphologies were then obtained after alkali post-treatment. Influences of divinyl benzene (DVB) content and the core/shell mass ratio on emulsion polymerization and particle morphology were investigated. Results showed that with the increase of DVB content, the percentage of total amount of $-\text{COOH}$ on the particle surface and free in aqueous phase (PSF_a) decreased, and the morphology of the post-treated particles underwent evolution from cracked, intact hollow to deficient swelling structure. Decreasing the core/shell mass ratio could not only make more carboxyl groups encapsulated by the shell, but also increase the shell resistance to the swelling of the core. The uniform hollow latex particles with intact morphology were obtained when the DVB content was 3.54 wt% and the core/shell mass ratio was 1/6.

Keywords: Emulsion polymerization; Hollow morphology; Crosslinking agent; Core/shell mass ratio.

INTRODUCTION

Design and control of the particles with specified morphology have been an intensive area in colloid and polymer science for more than 30 years. A variety of structured latex particles with different compositions have been obtained owing to the development of synthetic methods based on a greater understanding of the thermodynamic and kinetic aspects of emulsion polymerization^[1, 2]. Among them, the hollow latex particles with low density and excellent opacity have shown great commercial value as plastic pigment^[3–5], and their potential applications in nano-reactors, diagnostics, encapsulation, controllable release and stimuli-responsive systems have also drawn great attention^[6–8].

Kowalski and his colleagues first developed a preparation process of hollow latexes based on osmotic swelling principle, which has become a prominent synthetic approach to hollow particles^[9, 10]. Since then, great effort has been made to extend the synthetic techniques and applications^[11–15]. The typical process mainly includes the preparation of core/shell latex particles and the expansion of these particles through creating ions in the core under the appropriate conditions, and this process was subsequently improved by Vanderhoff, Okubo and others^[16–20].

Many important factors including ingredients, polymerization processes and post-treatment conditions are connected and interfered in the preparation of hollow latexes. Structural factors such as composition, core/shell mass ratio, and crosslinking level are critical to the morphology and properties of the core/shell and the hollow latexes. Vanderhoff *et al.* prepared soft hydrophilic core/hard hydrophobic shell latex particles and optimized the

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kinetics and thermodynamic factors to achieve the preferred morphology^[16]. An interlayer with moderate polarity was also introduced into the core and the shell to encapsulate the hydrophilic core with the hydrophobic shell more effectively^[13, 15, 21]. Choi *et al.* demonstrated that the encapsulation uniformity of the core/shell latex particles and the morphology of the hollow latex particles could be improved by introducing crosslinking structure and by gradually decreasing the hydrophilicity from the inner to the outer of the shell^[22].

In our previous work, hollow latex particles with different composition and different morphology were prepared *via* multistep seeded emulsion copolymerization followed by alkali post-treatment. It was revealed that the type and content of carboxyl monomers in the core preparation had significant effects on the emulsion polymerization process and the final particle morphology^[14, 23]. Recently, we found that the driving force to expand the core/shell latex particles could be adjusted not only by changing the content of carboxyl monomer in the core preparation, but also by controlling the size of core under a high carboxyl monomer content^[24]. No doubt, besides the core size and core swelling ability, the shell thickness and its crosslinking level are also critical structural requirements to obtain intact hollow particles. In this article, using the same latex with 40 wt% MAA in its preparation as core, the three-layer core/shell latex particles with different shell crosslinking levels and shell thicknesses were first prepared *via* multistep pre-emulsified seeded emulsion polymerization, and then the hollow latex particles with different morphologies were obtained by the alkali post-treatment. The influences of the DVB content in the shell monomers and the core/shell mass ratio on the emulsion polymerization, the carboxyl distribution of the core/shell latex and the morphology of latex particles were investigated, and the forming mechanism of different particle morphologies was proposed.

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) (*m*- and *p*- 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 sodium hydroxide (NaOH) 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 the Three-layer Core/shell Latexes

The preparation of three-layer core/shell latexes included three sequential steps of the core, the interlayer and the shell syntheses, and the typical recipes with the core/shell mass ratio of 1/6 and the DVB content of 3.54 wt% are listed in Table 1. The emulsion polymerization was carried out 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 of H₂O, 0.22 g of SDS, 0.67 g of 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, Ikea) to obtain monomer emulsion. Then, 4 g of the monomer emulsion, 60 g of H₂O, 0.10 g of APS and 0.02 g of SDS were charged into the reactor, and after polymerizing at 80 °C for 40 min, the residual monomer emulsion and solution of APS (0.30 g of APS dissolved in 25 g water) were simultaneously drop-wise added into the reactor at 80 °C within 5 h. After that, the reaction system was heated to 90 °C for 30 min, and then cooled down to room temperature.

The interlayer of the core/shell latex particles was prepared as follows; the mixture of MMA, MAA and St was first emulsified in 5 g of H₂O with SDS and OP-10. Then, the core latex was diluted with 40 g of 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

45 min, and maintained for 40 min after the feeding.

Finally, the shell monomer mixture of St, BA and DVB was first emulsified in 30 g of H₂O with SDS and OP-10, and the monomer emulsion and APS aqueous solution (APS dissolved in 25 g water) were then simultaneously drop-wise added into the above core-interlayer latex system at 90 °C within 4 h. After additional 90 min, the system was cooled down to room temperature to obtain the three-layer core/shell latex.

By varying the amount of shell monomers with the same St/BA proportion and fixed DVB content at 3.54 wt% and keeping the emulsifier and initiator amount in proportion to the total amount of shell monomer, the three-layer core/shell latex with different core/shell mass ratios was prepared with the same core and interlayer recipes as shown in Table 1.

Table 1. Typical recipes of the three-layer core/shell latex preparation *via* multistep emulsion copolymerization (the core/shell mass ratio was 1/6)

Ingredients	Core (g)	Interlayer (g)	Shell (g)
MMA	26.8	7.32	0
MAA	17.8	0.840	0
St	0	2.00	35.4
BA	0	0	1.35
EGDMA	0.250	0	0
DVB	0	0	1.35
SDS	0.240	0.025	0.150
OP-10	0.670	0.075	0.225
APS	0.400	0.150	0.375
Water	125	55.0	55.0
Core latex ^a	—	25.0	—

^a Core latex represented the emulsion prepared according to the core recipe.

Preparation of the Hollow Latex Particles

30 g of the original three-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 in the core and interlayer preparation at 1.3/1. After 2 h of treatment, the latex was cooled down to ambient temperature.

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 number-average diameter (D^{TEM}) and morphology of the dried latex particles were 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 carboxyl distribution of the core/shell latex was determined by conductometric titration as follows^[23]. 0.5 g of the original latex was diluted with 50 g of water and its solid content was measured by gravimetric method. pH value of the diluted latex was first adjusted to 11.5 ± 0.02 using a 0.385 mol/L NaOH aqueous solution, and then the latex was titrated with 0.04 mol/L H₂SO₄ aqueous solution, and its conductance was recorded using a DDS-307 conductometer (Leici, Shanghai, China). The conductometric titration curve was plotted with the conductance of latex versus the amount of H₂SO₄ aqueous solution. The total amount of —COOH on the particle surface and free in aqueous phase (SF_a) expressed as per gram polymer was calculated directly based on conductometric titration curve. The value of PSF_a expressed as the percentages of SF_a to the total carboxyl groups of the core/shell latex (T_a).

RESULTS AND DISCUSSION

In this work, the core latex with a high MAA content of 40 wt% and the core-interlayer latex were first synthesized, and results are given in Table 2 and Fig. 1. Then, using this core-interlayer latex as seeds, the three-layer core/shell latexes were prepared *via* pre-emulsified seeded emulsion polymerization, and the effects of the shell crosslinking level and core/shell mass ratio on the three-layer core/shell latexes and the hollow latexes were investigated.

Table 2. Properties of the core and core-interlayer latexes

Sample	Conv. (wt%)	D^{DSL} (nm)	D^{TEM} (nm)	PDI	ζ (mV)
Core latex	98.65	173.4	140	0.004	−53.0
Core-interlayer latex	99.23	225.7	198	0.021	−46.7

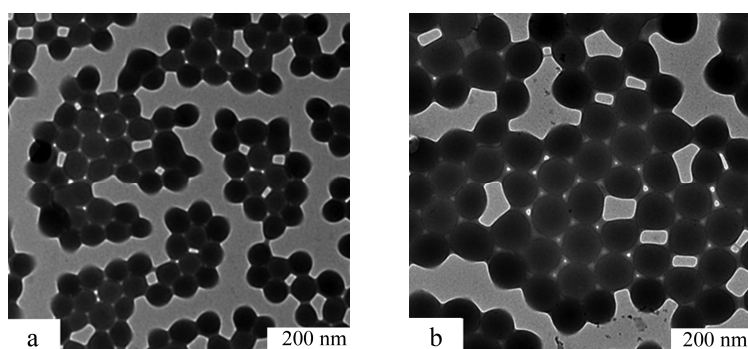


Fig. 1 TEM photos of the core latex (a) and the core-interlayer latex (b)

Effect of DVB Content in the Shell Monomers on the Core/Shell Latex

An appropriate crosslinking level of the shell polymer is of importance, which can prevent the interpenetration of the core and shell polymers in the core/shell latex preparation and improve the shell strength to keep the latex particles unbroken during the swelling process. Furthermore, network structure of the shell can also provide the swelled particles with enough resistance to shrink during the drying process. In order to investigate the crosslinking effect of shell polymer, the core/shell mass ratio was fixed at 1/6 and DVB content in the shell monomers was varied in the preparation of core/shell latex, and results are given in Table 3. The emulsion polymerization performed smoothly with the monomer conversion over 98%, and DVB content had little influence on the particle size, size distribution, as well as the stability of core/shell latexes.

Table 3. Effect of DVB content in the shell monomers on the core/shell latex properties

DVB (wt%)	Conv. (wt%)	D^{DSL} (nm)	D^{TEM} (nm)	$D^{\text{Theo a}}$ (nm)	PDI	ζ (mV)
0	99.2	340.2	324	297	0.0646	−32.9
2.39	98.7	349.0	330	297	0.0570	−41.9
3.54	98.4	349.2	327	298	0.0135	−43.3
4.78	99.5	345.3	325	300	0.0501	−40.2

^a D^{Theo} represented the theoretical diameter of core/shell particles assuming all of the shell monomers were polymerized onto the core latex particles.

It has been demonstrated that the amount of $-\text{COOH}$ embedded inside the particles is an essential of forming hollow structure^[14]. The carboxyl distribution of the core/shell latexes is shown in Fig. 2 and Table 4. The percentage of total amount of carboxyl groups on the particle surface and free in aqueous phase (PSF_a) decreased significantly from 35% to 22.9% when DVB content rose from 0 to 2.39 wt%, and then the value of PSF_a decreased gradually with the DVB content further increased to 4.78 wt%. It is clear that even small amount of DVB could make the shell polymer cross-linked, and the mobility of the carboxyl-enriched core polymer could be restricted by the cross-linked shell. In this case, it is hard for the core polymer segments/chains to

traverse the shell to the particle surface or into the aqueous phase, and as a result, more $-\text{COOH}$ groups were embedded inside the particles, which was beneficial for the core/shell particles to form the hollow structure in the following post-treatment process.

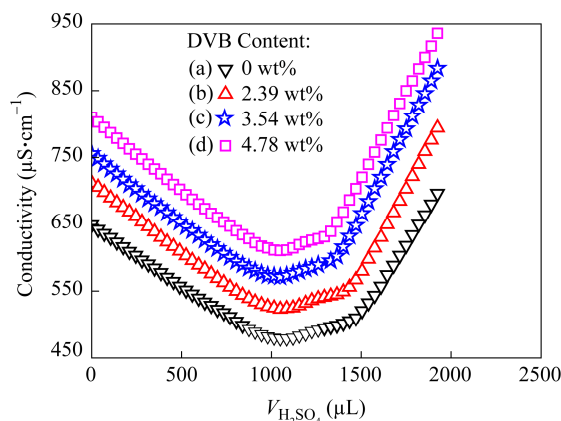


Fig. 2 Conductometric titration curves of the core/shell latexes prepared with different DVB contents in the shell monomers: (a) 0 wt%, (b) 2.39 wt%, (c) 3.54 wt% and (d) 4.78 wt%

Table 4. The carboxyl distribution of the core/shell latexes prepared with different DVB contents in the shell monomers

DVB (%)	$SF_a \times 10^4$ (mol/g)	$T_a \times 10^4$ (mol/g)	PSF_a (%)
0	2.52	7.19	35.0
2.39	1.62	7.07	22.9
3.54	1.53	7.01	21.8
4.78	1.44	6.96	20.7

The particle morphology was also affected by DVB content. It can be seen that most of the core/shell particles prepared without DVB (Fig. 3a) were not uniform spheres, and even some heteromorphic particles were observed. The spherical degree of the core/shell particles could be improved significantly by introducing DVB in the shell preparation. This is because that the morphology of hydrophilic core/hydrophobic shell latex particles was thermodynamically unfavorable, the carboxyl-enriched core polymer segments/chains had tendency to penetrate through the hydrophobic shell to the particle surface or into the aqueous phase, and at the same time, the hydrophobic shell polymer segments/chains would also transfer towards the core if the shell polymer was not cross-linked, resulting in the heteromorphic particles. When DVB was used in the shell preparation, the interpenetration of the core and shell polymer chains could be prohibited efficiently by the shell crosslinking structure, and uniformly spherical core/shell latex particles were obtained as shown in Fig. 3 from (b) to (d).

Effect of DVB in the Shell Monomers on the Morphology of Hollow Particles

It has been known that in the alkali post-treating process, the carboxyl groups of the core polymer were neutralized to form carboxylate polyelectrolyte, and the subsequent imbibing of water into the interior of the particles due to the osmotic pressure led to the volume expansion of the particles^[11, 20]. During the drying process, the interior water gradually evaporated from the swelled latex particles, leaving a hollow in the center of the dried particles. Obviously, the generation and morphology of the hollow latex particles depended not only on the osmotic pressure resulted from carboxyl groups of the core polymer, but also on the properties of the shell polymer, which acted as a hard layer to isolate the swelled core and resist the shrinkage of the swelled particle during the drying process. Here, using the same core latex with 40 wt% MAA and the core/shell mass ratio at 1/6, the influence of DVB content in the shell monomers on the morphology of the post-treated particles was investigated, and TEM images are shown in Fig. 4.

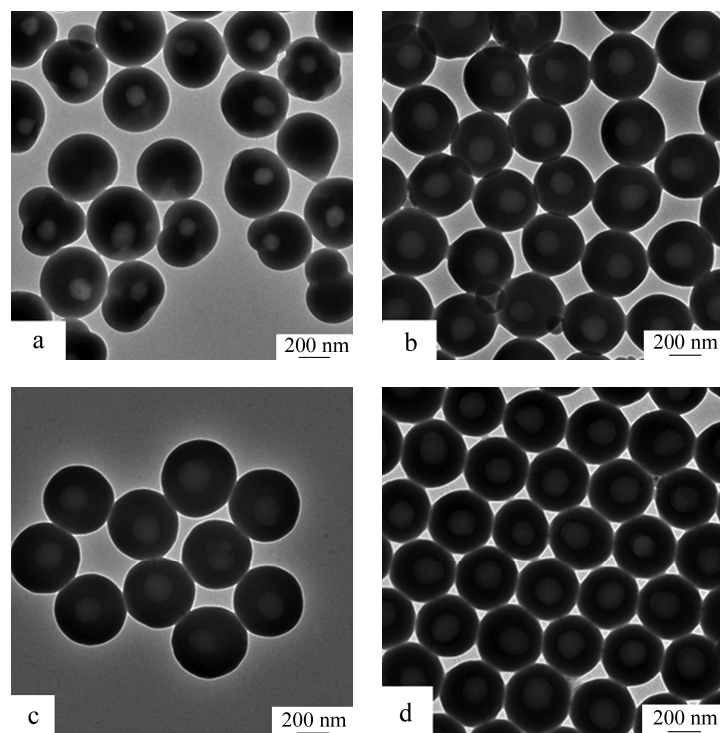


Fig. 3 TEM photos of the core/shell latexes prepared with different DVB contents in the shell monomers: (a) 0 wt%, (b) 2.39 wt%, (c) 3.54 wt% and (d) 4.78 wt%

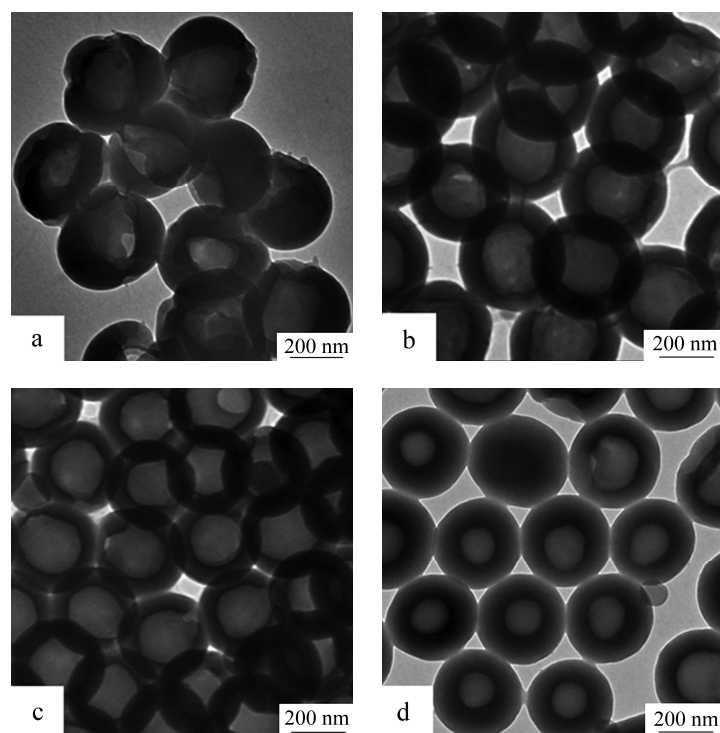


Fig. 4 TEM photos of the post-treated latexes prepared with different DVB contents: (a) 0 wt%, (b) 2.39 wt%, (c) 3.54 wt% and (d) 4.78 wt%

As mentioned above, the interpenetration of the core and shell polymer chains occurred in some extent in the core/shell latex particles prepared without using DVB. Because of their inhomogeneous structure, it is hard for this kind of latex particles to form spherical morphology in the alkali post-treating process. As shown in Fig. 4(a), although voided structure was generated in the post-treated particles, the shell thickness was not uniform, and even cracked structure could be identified in some particles. This morphological defect of hollow particles could be eliminated by using an appropriate amount of DVB in the shell preparation. For example, when DVB content was 2.39 wt% and 3.54 wt%, uniform hollow latex particles were obtained (Figs. 4b and 4c). As DVB content further increased to 4.78 wt%, excessive crosslinking of the shell would increase swelling resistance and as a result, the core/shell particles were inefficiently swelled in the post-treating process, and only a small void was observed in the post-treated particles (Fig. 4d).

Influence of Core/Shell Mass Ratio on the Core/Shell Latex

Besides the shell crosslinking level, shell thickness is another factor influencing the interpenetration of the core and shell polymers and the resistance of the shell to the core swelling. Here, with the same DVB content of 3.54 wt%, the three-layer core/shell latexes with different core/shell mass ratios were prepared, and results are listed in Table 5. Experiments showed that the polymerization process was smooth, and all of the core/shell latex particles were spherical (Fig. 5). As expected, the size of the core/shell latex particles increased with the increase of shell monomer amount.

Table 5. Effect of core/shell mass ratio on the core/shell latex properties

C/S mass ratio	Conv. (wt%)	D^{DSL} (nm)	D^{TEM} (nm)	$D^{\text{Theo a}}$ (nm)	PDI	ζ (mV)
1/2	99.2	263.6	242	218	0.002	-43.6
1/4	98.9	293.7	276	245	0.0587	-44.8
1/6	99.7	328.9	304	267	0.0245	-42.5
1/8	98.5	353.3	330	287	0.0198	-40.9

^a D^{Theo} was the theoretical diameter of core/shell particles as shown in Table 3.

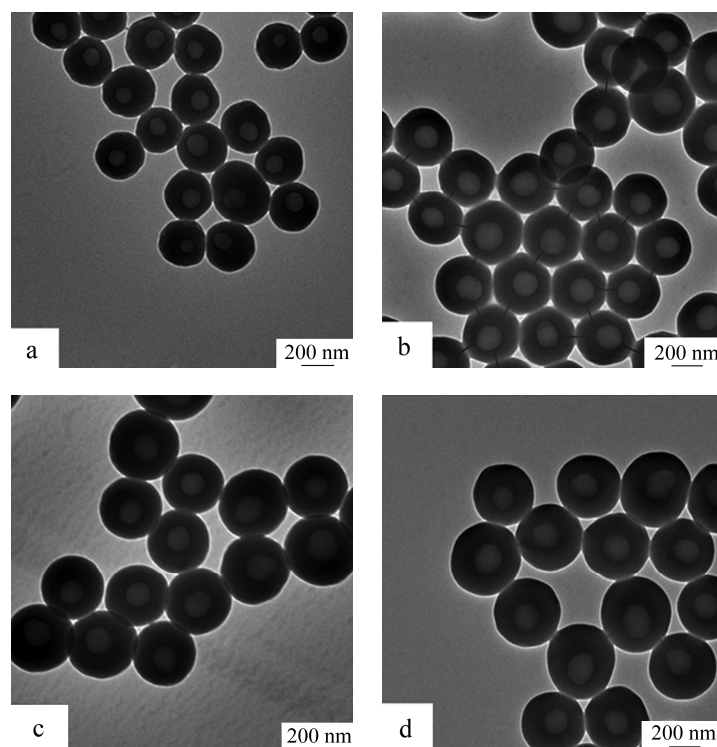


Fig. 5 TEM photos of the core/shell latexes with different core/shell mass ratios: (a) 1/2, (b) 1/4, (c) 1/6 and (d) 1/8

It is worth pointing out that the diameter of dried core/shell particles (D^{TEM}) was bigger than their theoretical value (D^{Theo}) which was calculated by assuming all of the monomers were polymerized onto the core particles, and similar phenomenon was observed in Table 3 and literature^[12]. The reason might come from the hollow structure of the core/shell particles as shown in Fig. 5. Because of the hydration of carboxyl groups of the core polymer, the core was actually swelled with water, and the swollen core was encapsulated by shell polymer in the seeded emulsion polymerization. Under the TEM observation, the encapsulated water was diffused through the hard shell from the core into ambient, leaving a small void in the center of the particle.

The carboxyl distribution of the core/shell latexes is given in Fig. 6 and Table 6. As the core/shell mass ratio decreased from 1/2 to 1/8, the percentage of total amount of carboxyl groups on the particle surface and free in aqueous phase (PSF_p) decreased from 23.3% to 17.8%, indicating that more carboxyl groups were embedded inside the latex particles.

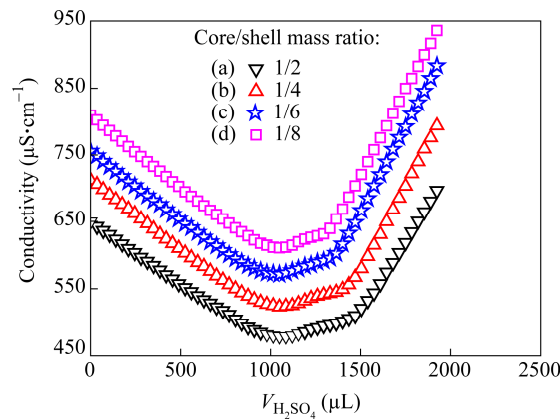


Fig. 6 Conductometric titration curves of the core/shell latexes with different core/shell mass ratios: (a) 1/2, (b) 1/4, (c) 1/6 and (d) 1/8

Table 6. The carboxyl distribution of the core/shell latexes with different core/shell mass ratios

C/S mass ratio	$SF_a \times 10^4$ (mol/g)	$T_a \times 10^4$ (mol/g)	PSF_a (%)
1/2	3.03	13.0	23.3
1/4	2.01	9.13	22.0
1/6	1.48	7.01	21.1
1/8	1.01	5.69	17.8

Influence of Core/Shell Mass Ratio on the Morphology of Hollow Particles

The core/shell latexes prepared with the same DVB content of 3.54 wt% and various core/shell mass ratios were post-treated under the same condition. As Fig. 7 demonstrated, when the core/shell mass ratio was 1/2, the shell was too thin to prevent the penetration of the core and the shell polymers, and the shell strength was too weak to support a spherical structure during the drying process, making the post-treated particles cracked or collapsed (Fig. 7a). Since the shell strength could be enhanced by increasing the shell thickness, the post-treated particles with the core/shell mass ratio of 1/4 exhibited general spherical morphology with a little collapse (Fig. 7b), and the intact hollow particles with uniform shell were obtained when the core/shell mass ratio reached 1/6 (Fig. 7c). If the mass ratio further increased to 1/8, the shell was too thick for the core/shell particles to swell efficiently, and only a small hollow generated in the post-treat particles (Fig. 7d).

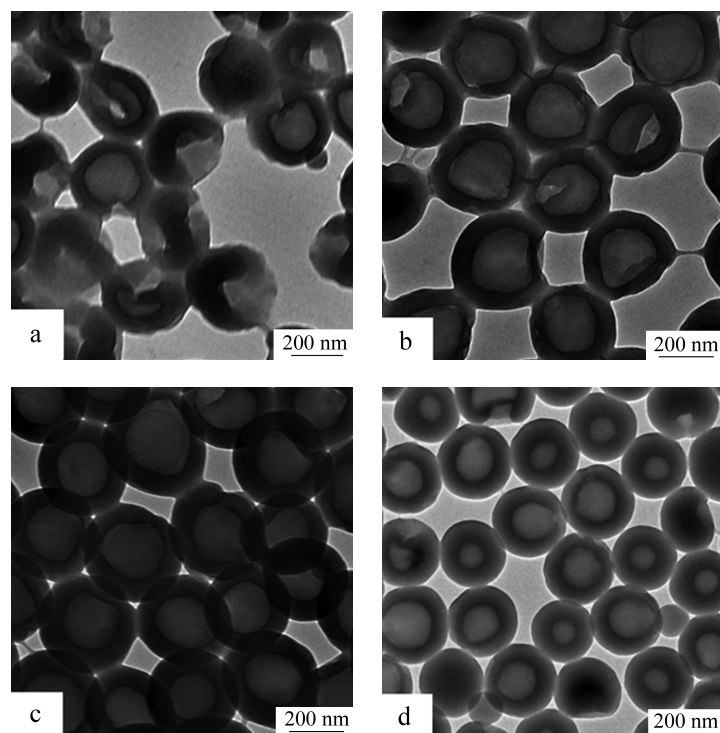


Fig. 7 TEM photos of the post-treated latexes prepared with different core/shell mass ratios: (a) 1/2, (b) 1/4, (c) 1/6 and (d) 1/8

CONCLUSIONS

The three-layer core/shell latex particles with various shell crosslinking levels and shell thicknesses were prepared by multistep pre-emulsified seeded emulsion polymerization, and the hollow latex particles with different morphologies were obtained followed by alkali post-treatment. Both the DVB content and the core/shell mass ratio had significant influences on the carboxyl distribution of the core/shell latexes, which resulted in different swelling degree of the core/shell particles and led to various hollow morphologies. When DVB content was 3.54 wt% in the shell monomers and the core/shell mass ratio was 1/6, the uniform hollow particles with intact morphology were obtained.

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