

Preparation and Structure Control of Hollow Polymer Particles: Influence of Seeded Emulsion Polymerization and Alkalization Treatment Process

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Received 27 April 2008; accepted 1 November 2008

DOI 10.1002/app.29631

Published online 16 March 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Hollow polymer latex particles containing a hydrophilic core were prepared by seeded emulsion polymerization with MAA/BA/MMA/St as comonomers, followed by stepwise alkalization treatment with ammonia. The size and morphology of composite latex particles was determined by TEM. The effects of the seeded emulsion polymerization conditions and alkalization treatment on the size and hollow structure of latex were investigated. The results showed that the optimum content of crosslinking agent in the shell polymers was about 0.5–1.0 wt %, emulsifier was about 0.8–1.1 wt %, and the

core/shell weight ratio was 1/7. To obtain uniform hollow latex particles with large size, the starved feeding technique should be adopted in seeded emulsion polymerization, and the neutralization temperature should equal to the T_g of the shell polymer. Then, the obtained polymer particles under this condition had an excellent hollow structure. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 207–215, 2009

Key words: hollow particles; alkalization swelling; seeded emulsion polymerization; morphology

INTRODUCTION

The design and control of the morphology of latex particles has been an intensive area of research in polymer emulsion science for the past decades.^{1,2} These composite latex particles create a class of materials with unique colloidal and physical properties that differ from homogeneous and solid particles.³ Submicrometer hollow polymer microsphere is a kind of latex particle with unique structure and morphology, which has excellent opacifying performance for the refractive index difference between the shell polymer and the internal substance with small molecular weight, such as air or water.^{4–6} This hollow polymer particle also has many other excellent characters such as deformation performance, good stability, and light specific gravity.^{7–9}

The needed structure and properties of opaque hollow polymers can be obtained by changing the composition of shell, the size of particles, and holes or the kinds of internal substance.^{10,11} Therefore, hollow polymer particles are utilized as an opacifying agent or a white pigment with excellent optical properties such as opacity and whiteness, which also enhance the performance of industrial coatings and potentially are useful in other technologies such as microencapsulation and controlled-release.^{12–14}

A significant number of techniques for obtaining hollow particle lattices have been developed.^{15–17} One prominent synthetic approach to hollow polymer particles is based on core/shell emulsion polymerization and alkalization swelling.^{6,10,18} In this method, seeded emulsion polymerization is adopted to prepare the core/shell polymer latex which is hydrophilic in core and hydrophobic in shell. The core contained some amounts of polymer with carboxyl groups. Then alkali was used to swell the core/shell latex in some conditions and opaque polymer hollow microspheres were obtained after cooling.

This article describes the preparation of hollow particle lattices that we consider to meet the controlled ideal morphology. To obtain stable, uniform-sized, and clear-structured hollow polymer microsphere, the influence of several factors on the sizes, morphologies, and volume expansions of hollow polymer particles were investigated, such as core/shell emulsion polymerization techniques, dosages, and feeding methods of shell comonomers and emulsifiers, ratio of the core monomers to shell ones and alkalization swelling conditions. Appropriate polymerization techniques and conditions of alkalization swelling were confirmed.

EXPERIMENTAL

Materials

Styrene (St), methyl methacrylate (MMA), methacrylic acid (MAA), and *n*-butyl acrylate (BA) were

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purchased from Wulian chemical Co. (China) and distilled under reduced pressure. Diallyl maleate (DAM), purchased from Hangzhou kaimen chemical Co., was used as crosslinking comonomer without preliminary purification. Potassium persulfate (KPS, initiator), sodium dodecyl sulfate (SDS, surfactant), and Octyl Phenol Polyethoxylate with 10 ethylene oxide units per molecules (OP-10, surfactant) were analytical grade and used as received without further purification. Alkali NH_4OH was used as 20 wt % solutions in water.

Preparation of carboxylated core latex

Model latex synthesis was performed in a 100-mL glass reactor equipped with a mechanical stirrer, a reflux condenser, and a nitrogen gas inlet tube. The carboxylated core lattices were prepared by a conventional semicontinuous emulsion polymerization process. The typical recipe is illustrated in Table I. First, about 5 wt % of the monomer mixture was used in the seeding stage. Although the reactor temperature rose to 80°C , 5% of surfactant and initiator solution were added into the reactor. Polymerization was carried out under a nitrogen atmosphere. After the seeds were almost fully formed (the conversion is above 90%), the remaining monomer mixture, surfactant, and initiator solution were continuously fed into the reactor by syringe pump at constant rates in 2 h. When the feeds were finished, the reaction was allowed to continue for another 1.5 h.

Preparation of core/shell latex

The core/shell copolymer latex was synthesized by seeded emulsion polymerization process based on carboxylated core latex. Table I gives a typical recipe

for the synthesis of the core/shell latex particles. After the core polymerization stage finished, a part of the emulsion obtained (16.5 g) was used as the seed emulsion for the core/shell polymerization. Polymerization was carried out in the same reactor under a nitrogen atmosphere. The shell stage monomer mixture, surfactant, and initiator solution were continuously fed into the seed emulsion system by syringe pump at constant rates in 2 h. When the feeds were finished, the reaction was allowed to continue for another 1.5 h, and the polymerization proceeded to completion. And, well-defined core/shell latex particles with a narrow size distribution could be synthesized.

Alkalization treatment

To prevent the coagulation of particles during the neutralization at high temperatures, an additional amount of SDS was charged into the obtained latex. Thirty grams of the original core/shell composite latex, diluted to 20%, was charged into a one-neck round-bottom flask equipped with a stirrer, followed by alkalization treatment. The pH value of the latex was adjusted to 10.5 with a 20 wt % solution of NH_4OH . The alkalization treatment was maintained for 3 h at 85°C . Finally, the flask was cooled to room temperature, and clear-structured hollow polymer particles could be obtained. The typical recipe is illustrated in Table I.

Analysis and characterization

The conversion of monomers in progress of polymerization was determined gravimetrically.

Electron microscopy was performed with a JEM 1200EX transmission electron microscope operating at 100 kV. The diluted colloidal solutions were applied to a 400 mesh carbon-coated copper grid and left to dry at room temperature.

The particle sizes were characterized from the number-average diameter measured by TEM, and the counted number of particles for size analysis is 300. The following equations are used for evaluation of the number-average size of the latex. Where D_n is the number-average diameter, δ is the standard deviation; $P(\delta/D_n)$ equals the distribution of latex particles size. The lesser the value of δ/D_n is, the narrower the size distribution will be.

$$D_n = \sum d_i/n \quad (1)$$

$$\delta = \sqrt{\sum (d_i - D_n)^2 / (n - 1)} \quad (2)$$

$$P = \delta/D_n \quad (3)$$

TABLE I
Recipe for the Preparation of Carboxylic Core,
Core/Shell Latex, and Alkalization Treatment

Components	Core latex	Core/shell latex	Alkalization swelling
MMA	9.42 g		
BA	5.15 g	1.24 g	
MAA	6.03 g		
St		11.1 g	
DAM	0.1 g	0.12 g	
SDS	0.063 g	0.03 g	0.05 g
OP-10	0.12 g	0.06 g	
KPS	0.025 g	0.12 g	
NH_4OH (20 wt %)			0.65 g
Core latex		16.5 g	
Core/shell latex			30 g
Water	65 g	18 g	22 g
Temperature ($^\circ\text{C}$)	80	80	85
Conversion	98.5%	98.7%	
Solid content	24%	35%	20%

TABLE II
Sizes and Distributions for Latex Particles at Different Emulsifier Contents

Emulsifier contents (w %)	Average diameter, D_n (nm)	Distribution of particles size (δ/D_n)
2.0	386	0.526
1.4	426	0.343
1.1	488	0.108
0.8	505	0.016

RESULTS AND DISCUSSION

Synthesis of core/shell latex

To obtain clear-structured hollow polymer latex swelled by Alkalization, the core/shell polymer emulsion should be first synthesized by semicontinuous seeded emulsion polymerization process based on carboxylated core lattices. As we all know, seeded emulsion polymerization parameters, such as emulsifier dosage used, shell monomer mixture feeding rate, ratio of core monomers to shell ones, and composition of shell copolymers, can affect the morphology of core/shell polymer emulsion and hollow particles structure.^{8,19} Herein, the influences of these polymerization parameters were studied.

Influence of emulsifier dosage used in seeded emulsion polymerization

The diameter of core polymer particles will continuously increase with the addition of shell monomers in core/shell polymerization process. That means the whole surface area of the latex enlarge, and the number of the surfactant absorbed on the surface of average polymer particle decreases accordingly. To maintain the stability of the latex, it is necessary to add an amount of surfactant into the core/shell latex system. In this experiment, the additional surfactants were the composite of SDS and OP-10 (SDS/OP-10 = 1/2 by weight).

There are no carboxylated monomers, which obviously influence the stability of emulsion polymerization, used in the core/shell stage. The dosage of

surfactant and feeding method are the key factors for the stability of core/shell emulsion polymerization.² The concentration of surfactants fed into the emulsion by stepwise should be under the CMC value. In other words, there are no free micelles in emulsion system and the second micelle nucleation will be avoided. Table II shows the effects of the surfactant dosage on the size and structure of core/shell particles. From Table II, increasing the dosage of the surfactants, the size of the latex particles is observed to decrease, and polydispersity index increase accordingly. Figure 1 shows the TEM images of core and core/shell particles prepared with different surfactants dosage. As the surfactants dosage decreased to 0.8% w/w based on the total shell monomers, the size of the core/shell particles enlarged from 300 (core particles) to 505 nm, accordingly, the polydispersity index decreased to 0.016, and almost no new particles appeared. At high surfactant concentration (>1.4 wt %), an amount of new small particles were formed. The reason was new micelles came into being when the surfactant concentration increased from below the CMC to above and the shell monomers entered into the micelle followed by producing large number of new small particles.

Influence of Feeding rate of shell monomers

It has been commonly recognized that the feeding rate in emulsion polymerization is quite important, especially for obtaining a special core/shell particles with the core composed of a highly carboxylated hydrophilic polymer and the shell composed of a hydrophobic polymer.²⁰

The TEM images in Figure 2 demonstrate the characteristics and morphology of the core/shell particles obtained at various feeding rate of the shell monomer mixture. As seen in Figure 2, when the feeding time of shell monomers was less than 1 h, the instantaneous conversions was less than 75% and a great number of new latex particles were produced because of the rapid feeding rate. New smaller particles formed by shell monomers are shown in Figure 2(a,b). This is because the feeding

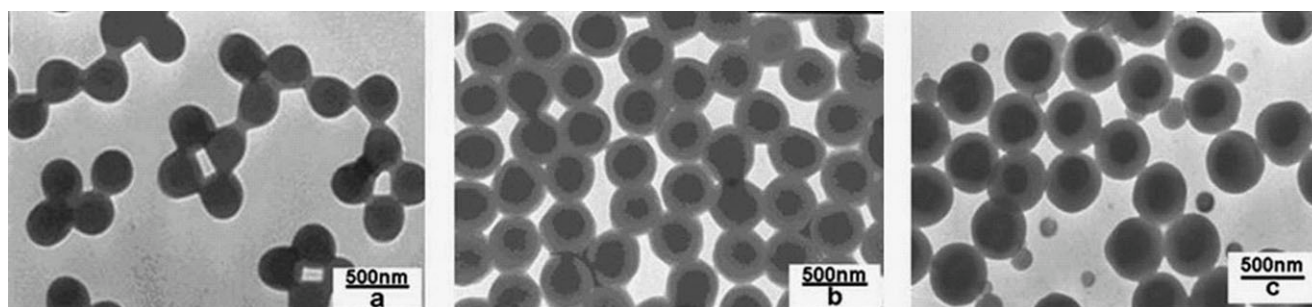


Figure 1 TEM images of core (a) and core/shell latex particles (surfactants dosage b: 0.8%, c: 1.4%).

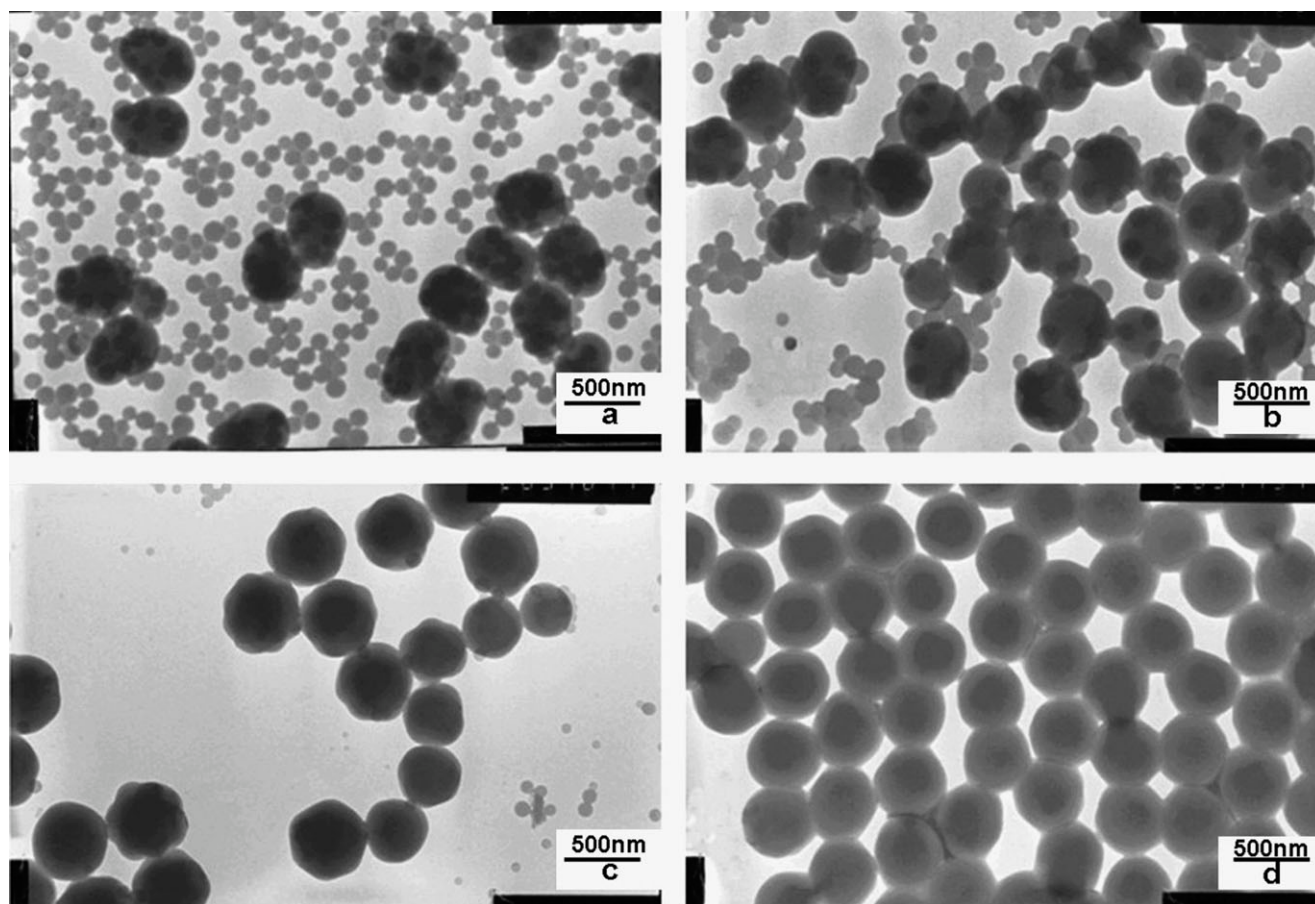


Figure 2 TEM images of core/shell latex particles for different feeding time of shell monomer: (a) 0.5 h; (b) 1 h; (c) 1.5 h; (d) 2 h.

rate of shell monomer mixture was faster than the seeded emulsion polymerization rate, and the concentration of monomer became high enough in the emulsion system. Then, a great number of new particles with no carboxylated monomer were produced, and this new particles from only shell monomers could not exhibit core/shell morphology as precursors of the hollow particles.

The ratio of smaller particles to core/shell composite ones decreased rapidly with prolonging the feeding time, and when the feeding time reached 2 h, and the instantaneous conversions can achieve 93%, almost no new small particles existed in the core/shell latex systems. That meant the feeding rate was lower than the polymerization rate of the shell monomers, and all of the feeding monomers entered into the particles rapidly and formed shell layer covering the carboxylated hydrophilic core. As shown in Figure 2(d), the entire core particles were covered by the shell polymers and clear core/shell structure latex was formed. From this result, the obstacles of second nucleation in seeded emulsion polymerization with low surfactant dosage can be overcome by starved feeding conditions.

Influence of crosslinking agent content in shell polymer

The use of crosslinking agent in shell polymer is necessary during the preparation of stable core/shell particles. First, the crosslinking agent can prevent the molecules of carboxylated core from penetrating to the outside, and favor the formation of core/shell structure. Second, a proper dosage of crosslinking agent will improve the heat resistance and solvent resistance in application. The crosslinking agent used in this work is diallyl maleate (DAM) with three vinyl groups, which is a very effective crosslinking agent.²¹ Figure 3 shows the effect of crosslinking agent on the hollow structure of latex particles.

As seen in Figure 3, the shell crosslinking agent content brings a great effect on the structure of the hollow particles. If the crosslinking agent used in shell polymer was below 0.5 wt % of shell polymer, the shape of the hollow particles become abnormal, and the shell layer collapsed after alkalization treatment without crosslinking agent in shell polymer. As the crosslinking agent content was increased to 1 wt %, as shown in Figure 3(c), the shape of the hollow particles became regular, and the clear

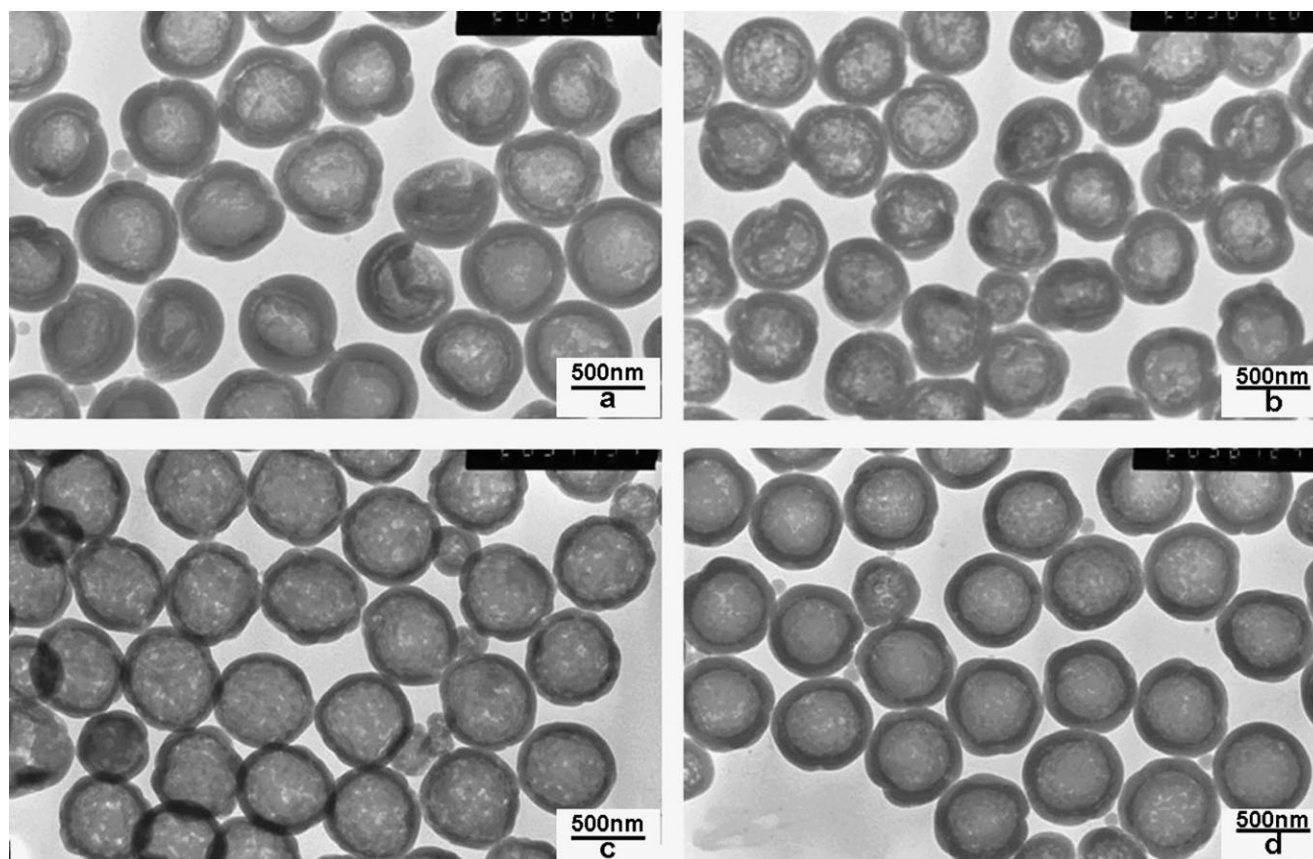


Figure 3 Effect of crosslinking agent on volume expansion of latex particles (the core/shell monomer ratios is set at 1/4): (a) 0 wt %; (b) 0.5 wt %; (c) 1 wt %; (d) 2 wt %.

hollow structure with a complete shell layer came forth. Therefore, appropriate content of crosslinking agent can promote the size-keeping of shell and prevent collapse. However, excess crosslinking will harm the swelling of the shell. If the crosslinking agent increases to 2 wt %, the crosslinked shell layer prevents the transfer of the molecules or segments of the core polymers containing $-\text{COO}^-$ group, and just small hollow volume form with a thick shell.

Influence of core/shell monomers ratio

The coverage shape of shell polymers on the surface of core particles is affected by the weight ratio of core monomers to shell monomers.²² Lower ratio of core/shell will lead a thick shell, which prevent the alkali from penetrating into the particles and swelling. TEM images in Figure 4 demonstrate the characteristics of the hollow particles at different shell thickness under different weight ratios of the core monomer to shell one, and Table III shows the sizes of the hollow lattices.

The movement of the molecules or segments containing $-\text{COO}^-$ groups is critical to the formation of the hollow structure. As seen in Figure 4 and Table III, the sizes of hollow polymer particles swelled by

alkalization increased with the decrease of core/shell ratio, but the hollow ratio and expansion ratio decreased. This is because the shell thickness increases with the decrease in the core/shell ratio, so that the alkaline solution becomes more difficult to diffuse into the interior of the core/shell particles and the segments with $-\text{COO}^-$ groups are wrapped tightly with the crosslinked thick shell. As a result, the movement of the molecules or segments with $-\text{COO}^-$ groups toward the outside and the swelling of the cores become more difficult as well. By contrast, too high core/shell ratio will lead a thin shell layer, which can not encapsulate the core particles completely. After alkalization swelled, the morphology and structure can not maintain an entire globe hollow particle. When the core/shell ratio is 1 : 7 the obtained hollow latex particles keep a more preferable balance between the rigidity of the shell polymers and the hollow percentages.

Influence of Alkalization treatment on the structure of hollow particles

The formation of hollow particles with narrow size distribution requires the synthesis of a core/shell-structured particle by sequential emulsion polymerization,

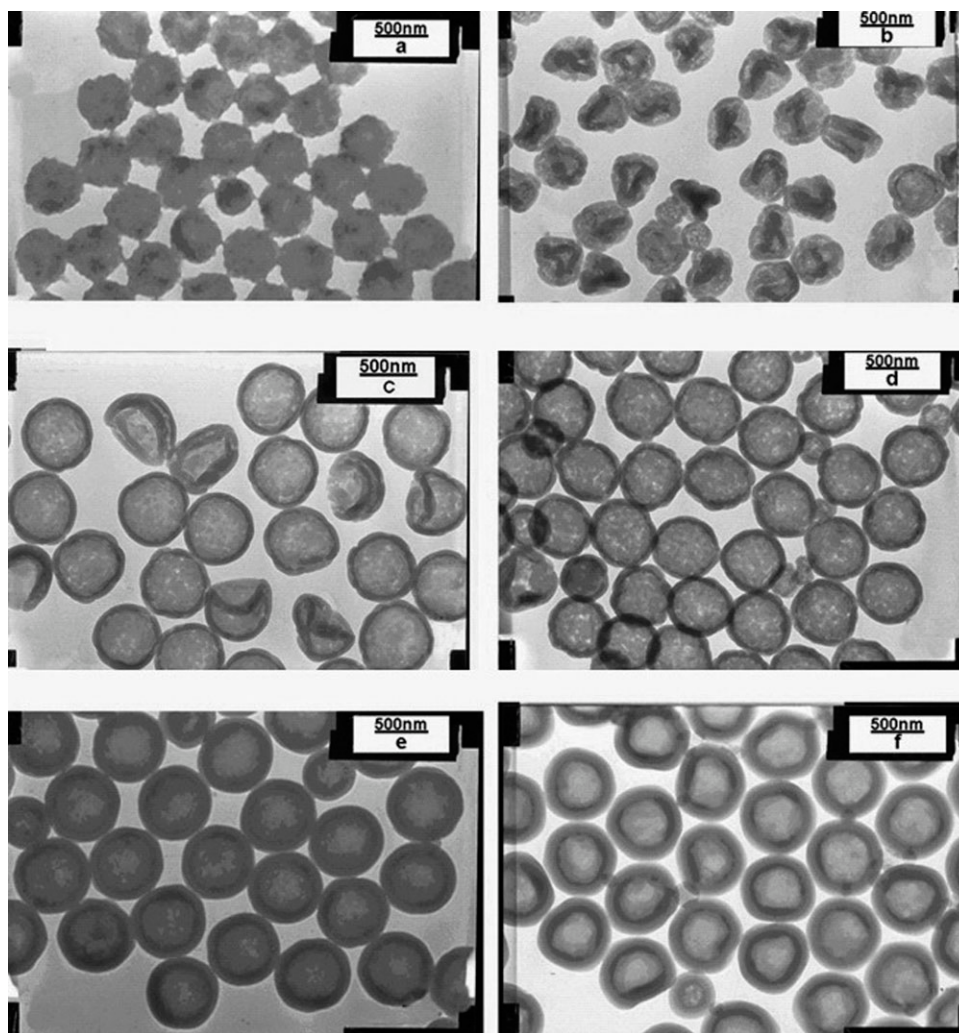


Figure 4 TEM images of latex particles with different core/shell ratio: (a) 1 : 1; (b) 1 : 2; (c) 1 : 3; (d) 1 : 4; (e) 1 : 7; (f) 1 : 10.

and the core is designed to be ionizable based on alkalization swelling, which imbibes water into the center of the particle. Except the synthesis process of core/shell latex, the structures of hollow particles were also influenced by alkalization treatment conditions.⁶

As described in the experiment section, these prepared core/shell particles were heated in the presence of ammonia to a temperature near the softening point of the shell polymer. In this condition, the ammonia was transferred into the original core/shell particles and reacted with carboxylated group in core polymer, and the electrostatic repulsion and hydration of charged groups leads the polymer chain with carboxylated group to diffuse from core side to out. A subsequent swelling process imbibes water into the center of the particle and leaves a void upon evaporation.^{6,8} On the other hand, the thermodynamic equilibrium would favor the hydrophobic shell entering the core, and the two opponent influences make the shell thinner and the hollow structure clearer.

The behavior of carboxylated particle alkalization swelling depends on the applied base type and concentration. Among the bases, NH_4OH is probably more convenient technologically because its excess can be easily removed from the polymer.²³ Additionally, small distortions from the optimum pH value do not lead to considerable changes in the size of

TABLE 3
Properties of Hollow Polymer Particles
with Different Core-Shell Ratio

Core/shell ratio	D_1	D_2	D_3	Expansion ratio (%)	Hollow ratio (%)
1 : 3	465	642	521	163.2	53.4
1 : 4	488	664	516	151.7	46.9
1 : 7	575	695	495	76.6	36.1
1 : 10	663	713	425	24.4	19.6

D_1 , particles size before alkali treatment; D_2 , particles size after alkali treatment; D_3 , size of the hollow part; expansion ratio = $(D_2^3 - D_1^3)/D_1^3$; hollow ratio = D_3^3/D_2^3 .

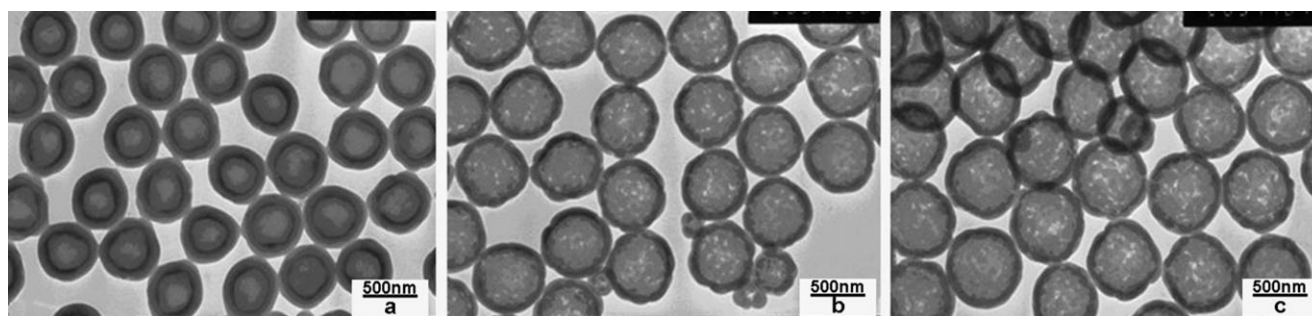


Figure 5 TEM images of hollow latex particles with different alkali-treating initial pH (the core/shell monomer ratios is set at 1/4): (a) pH = 8.5; (b) pH = 10; (c) pH = 11.5.

the particles. To evaluate the swollen ability of the synthesized carboxylated core/shell latex particles in water during the alkalization treatment, we studied the structure of hollow particles at different pHs of the aqueous medium.

Figure 5 shows TEM images of hollow particles after the alkalization treatment in the initial pH range from 8.5 to 11.5, in which the hollow size and total volume of the particle increased. The average size of

the particles only increased from 488 to 560 nm after alkalization treatment at pH of 8.5, and the hollow ratio is 20% (ratio of the hollow part size with the particle size after alkalization). As the pH of initial latex was increased to 11.5, the size of hollow particles increased to 680 nm, and the hollow ratio reach 48.5%. The results obtained show that the increase of pH values corresponds to high expansion and hollow ratio. But the excessive base in alkalization treatment

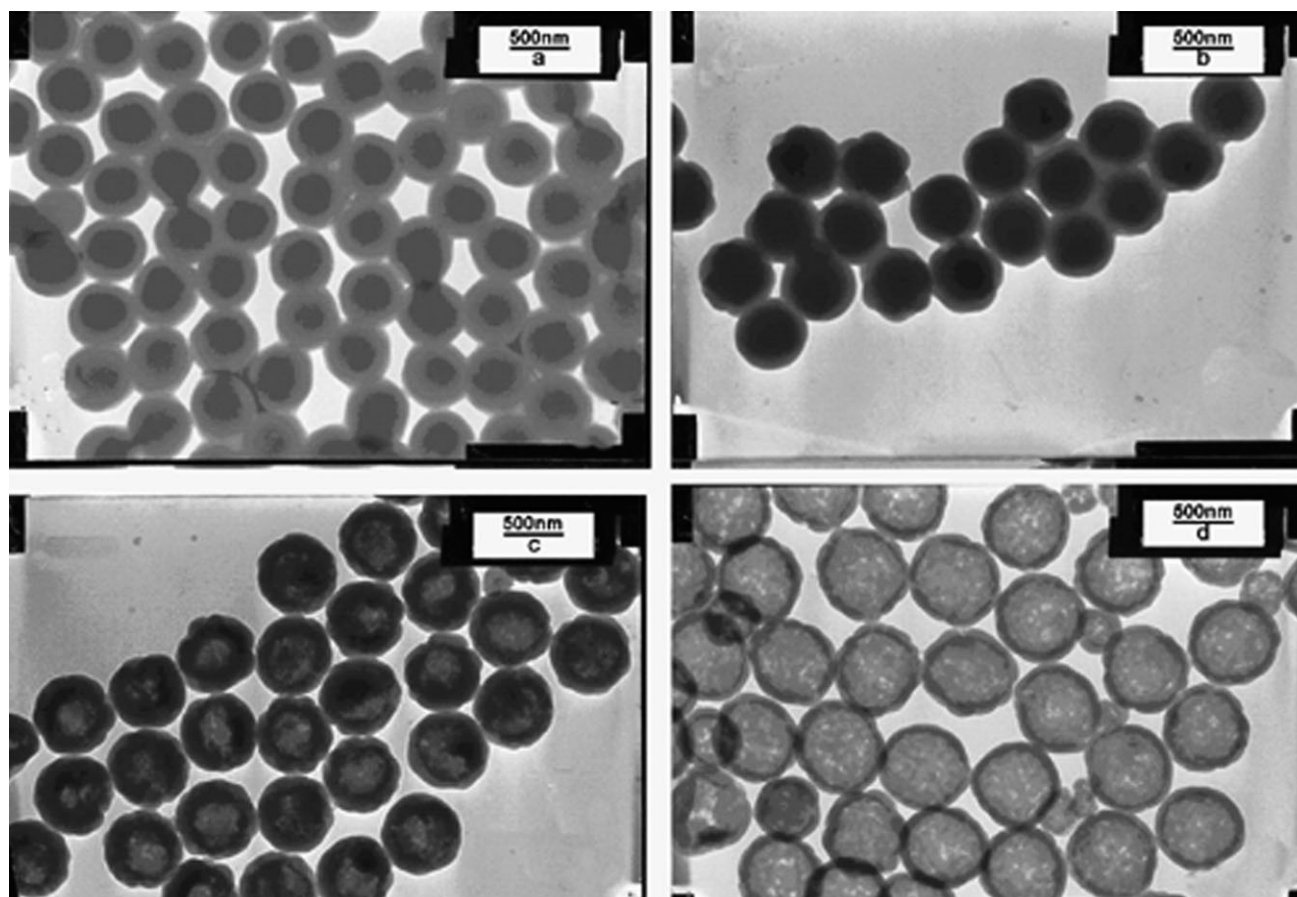


Figure 6 TEM images of hollow latex particles with different alkali-treating temperature (the core/shell monomer ratios is set at 1/4): (a) core/shell particles; (b) 65°C; (c) 75°C; (d) 85°C.

will destroy the stability of latex in high temperature, and the optimum pH value is achieved at almost equimolar $\text{NH}_4\text{OH}/\text{MAA}$ ratio.

TEM images in Figure 6 show the structure of hollow latex particles with different alkali-treating temperature for 4 h at pH of 10. The glass transition temperature (T_g) of the shell polymer in this experiment is 85°C determined by DSC. When the alkali-treating temperature was set at 65°C , as shown in Figure 6(b), the size of the particle only increased from 488 to 542 nm after alkalization treatment, and almost no hollow structure can be seen. As the alkali-treating temperature was increased to 75°C , the size of particles increased to 581 nm, while the hollow ratio was 6.9%, as shown in Figure 6(c). Only when the alkali-treating temperature was increased to 85°C , the hollow ratio and expansion ratio got a wide-range increase with hollow ratio 42.7% and expansion ratio 164.3%, as seen in Figure 6(d). But the hollow and expansion ratio was almost no change at 90°C compared with the result of 85°C .

The alkali must diffuse through shell polymer to core followed by neutralization and the shell polymer with glassy state would prevent this process taking place. The T_g of the shell polymer is determined to be 85°C , and if the alkali-treating temperature is below 85°C , the movement of polymers chain in shell is restricted, and the hydrophilic chain with carboxyl in core can not move to outside effectively. So, the core/shell particles can not be alkalized, swelled, and formed into hollow structure with high expansion ratio. Because the dispersion medium is water, the neutralization should be carried out at the temperature equal to the T_g of the shell polymer or above it by a little.

The effect of alkalization treatment time on the hollow structure was also investigated. Figure 7 shows the hollow particles characteristics with time

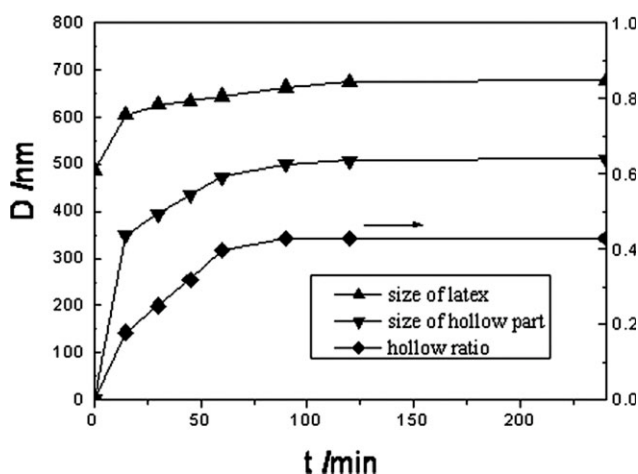


Figure 7 Hollow particles characteristics at different alkalization time.

for alkalization treatment carried out at 85°C . The size of swelling core/shell particles increased with alkalization time and at the same time the hollow and expansion ratio increased with the same trend. It suggests that the increase of size will reach final ratio of expansion after alkalization treatment for 120 min at 85°C . When the alkalization treatment time was more than 240 min, the integrated shape of the hollow polymer particles would be destroyed, and the stability of the hollow latex is damaged followed by the thickening of the dispersion system. Therefore, to keep integrated morphology and stability of the latex, the optimal alkalization treatment time should keep in 120–180 min at 85°C .

CONCLUSIONS

The performed work has investigated the uniform hollow particle latex preparation process according to the seeded emulsion polymerization with carboxylated copolymer as core latex, followed by step-wise treatment with ammonia. The results show that it is possible to control the structure of hollow polymer particles by optimization of preparation techniques. And the effects of the various factors on the performances of the resulting hollow particles were clarified. During the whole polymerization process, the feeding rate of monomer mixture, emulsifier content, crosslinking agent content, and ratio of the monomers during the core and shell polymer preparation are the main factors that affect the formation of specific morphology of the hollow particles. To obtain the uniform hollow latex particles with large size, the starved feeding technique should be adopted, and the optimum emulsifier content should be 0.8 to 1.1 wt % during the preparation of the core/shell polymer latex. The application of crosslinking agent is necessary in the formation of shell copolymers and the optimum content of DAM is 0.5 to 1.0 wt %. The hollow latex particles obtained with core/shell monomer ratio of 1 : 7 are monodisperse and keep a more preferable balance between the rigidity of the shell polymers and hollow percentages. The neutralization should be carried out at the temperature equal to or above the T_g of the shell polymer.

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