

Influence of Unsaturated Acid Monomer on the Morphology of Latex Particles in the Preparation of Hollow Latex Via the Alkali Post-Treatment

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ABSTRACT: Multistage hydrophilic core/hydrophobic shell latexes containing carboxyl groups were prepared via multistep seeded emulsion copolymerization, and particles with different morphologies were obtained after alkali post-treatment. Influences of the type and content of unsaturated acid monomer on the polymerization and the particle morphology were investigated based on conductometric titration and TEM observation. Results showed that the hydrophilic core/hydrophobic shell particles could be easily formed using methacrylic acid (MAA) instead of acrylic acid. When MAA was 12.2 wt % in the core latex preparation, only fine pores existed inside the alkali-treated particles. With MAA increased from 20.0 to 30.0 wt %, the alkali-treated particle morphology evolved from porous, hollow to collapse structure. When MAA further increased to 40.0 wt %, it was difficult to prepare uniform multistage particles and distinct morphologies including solid, deficient swelling, hollow and collapse structure were coexistent in the alkali-treated particles. Moreover, the forming mechanism of different morphologies was proposed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: core-shell polymer; voids; morphology; unsaturated acid monomer; mechanism

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INTRODUCTION

Polymer particles with different morphologies or functional groups have attracted attentions of many researchers in the past few decades due to their theoretical significance and practical values.^{1–3} Void polymer particles, especially the hollow particles, have been proved to be very useful in the fields of coating, papermaking, and cosmetic because of their excellent characteristics of light scattering and low density,^{3,4} and also have potential applications in catalyst, biochemistry, and biomedicine due to the capacity of accommodating objects in hollow structure.^{5,6}

The techniques of void polymer particle preparation can be classified into two general categories: one is to obtain the void structure by post-treating polymer particles,^{7–9} and another is to encapsulate hydrocarbon or water through in-situ polymerization of monomer and followed by removing these small molecules.^{10–13} Among them, osmotic swelling was the earliest and predominant method, which was developed by Kowalski et al. and then ROPAQUE™ opaque polymer was commercialized in Rohm and Haas (Philadelphia, Pennsylvania, USA).⁷ The typical processes include the synthesis of core/shell latex particles and the expansion

of these particles through creating ions in the core under the appropriate conditions.^{3,7,14} However, the majority of the literatures about osmotic swelling technique was limited in patents due to the commercial interest in these particles. Vanderhoff et al. discussed the preparation of hollow polymer latex particles from alkali post-treating the latex particles with a soft hydrophilic core/hard hydrophobic shell.¹⁵ Okubo et al. proposed stepwise alkali/acid treatment and alkali/cooling methods to prepare sub-micron multi-hollow polymer particles by performing post-treatment on the carboxyl-containing copolymer.^{16,17}

Obviously, the unsaturated acid monomer plays an important role not only on the emulsion polymerization but also on the formation of void structure. As early as 1970s, Ceska have studied the carboxyl distribution in styrene (St)–butadiene copolymer latexes prepared in the presence of unsaturated acid monomers by neutron activation analysis and turbidimetric titration.^{18,19} Subsequently, Shoaf and Poehlein investigated the partitioning of unsaturated acid monomers between St phase and aqueous phase and the kinetic behavior of emulsion copolymerization of St with unsaturated acid monomers.^{20–22}

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Okubo et al. revealed the relationship between secondary nucleation and methacrylic acid (MAA) content in the emulsion copolymerization system of St and MAA.²³ The influences of unsaturated acid monomer content on the morphology of post-treated carboxyl-containing latex particles were also investigated.^{24–26}

In the preparation of void latex particles by osmotic swelling method, many interactional factors including ingredients, polymerization process as well as post-treatment conditions would affect the formation of void structure. Therefore, it is necessary to further understand the mechanism lies in the morphological evolution of the latex particles, though there are some researches about void latex particles have been reported. Recently, we have been engaged in the preparation of hollow polymer latex and the control of particle morphology from synthesizing multistage hydrophilic core/hydrophobic shell latex particles and performing alkali post-treatment based on the osmotic swelling principle, and some valuable results were obtained.^{27–29} In this article, with the aim of further understanding, the mechanism behind the formation of hollow morphology from aspect of unsaturated acid monomer, three-layer core/shell latex particles with hydrophilic core and hydrophobic shell were designed, and an interlayer with moderate polarity was inserted into the core and the shell to make the encapsulation of the hydrophilic core with the hydrophobic shell more effectively. Thus, the carboxyl-containing multistage core/shell latex particles were first prepared using different types and content of unsaturated acid monomers, and then the latex particles with different morphologies were obtained by the following alkali post-treatment. The influences of the unsaturated acid monomer content on the emulsion polymerization, the latex property and the particle morphology were investigated, and the forming mechanism of different particle morphologies was proposed according to the experiment results and analysis.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), acrylic acid (AA), butyl acrylate (BA), MAA, and 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 (EVB), and diethyl benzene (DEB), J&K Scientific, Beijing, China), sodium dodecyl sulfate (SDS), sodium hydroxide (NaOH), and H₂SO₄ (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.

Synthesis of Multistage Core/Shell Latex

The multistage core/shell latexes were synthesized by multistep seeded emulsion polymerization using different types and content of unsaturated acid monomer under a nitrogen atmosphere in a four-necked 250-mL round-bottom flask equipped with an inlet of nitrogen gas, a reflux condenser, an electric mechanical

Table I. Typical Recipes of the Multistage Core/Shell Latex Prepared Via Multistep Emulsion Polymerizations

Ingredients	Core (g)	Interlayer (g)	Shell (g)
MMA	16.50	3.66	0
MAA/AA	Variable	0.42	0
BA	14.70	0	0
EGDMA	0.25	0	0
St	0	1.02	11.84
DVB	0	0	0.45
SDS	0.025	0	0
APS	0.40	0.05	0.10
H ₂ O	100	30	10
Core latex ^a	0	10.00	0

^aCore latex represented the emulsion prepared according to core recipe.

stirrer, and a thermometer. The stirring speed was fixed at around 300 rpm throughout the process, and the typical recipes were listed in Table I. The synthetic route included three sequential steps of core, interlayer, and shell preparations as below.

Carboxyl-containing core latexes were prepared via semi-continuous emulsion polymerization as follows. About 90 g of H₂O, 0.10 g of APS, 0.025 g of SDS, and 5 wt % of the mixture of MMA, MAA or AA, BA, and EGDMA were charged into the reactor, and the polymerization was carried out at 80°C for 40 min. Then, the residual monomer mixture and aqueous solution of APS (0.30 g of APS dissolved in 10 mL of water) were simultaneously dropwise added into the reactor at 80°C within 4.5 h, and then the reaction system was heated to 90°C, and maintained at this temperature for 30 min. Then, the system was cooled down to room temperature.

In the interlayer preparation, 10 g of the core latex was first diluted with 25 g of H₂O, and then the seeded emulsion copolymerization of MAA or AA, St, and MMA onto the core particles was carried out at 80°C by constant feeding the monomer mixture and APS aqueous solution (0.05 g of APS dissolved in 5 mL of water) simultaneously into the diluted core latex within 40 min.

At last, St and DVB, as well as APS aqueous solution (0.10 g of APS dissolved in 10 mL of water) were simultaneously dropwise added into the system at 90°C within 2 h to form the outer shell of the particles. After additional 30 min, the system was cooled down to room temperature to obtain the multistage core/shell latex.

Alkali Post-Treatment

A certain amount of the multistage core/shell latex was charged into a reactor which was immersed in a water bath at 85°C, and the initial pH of the latex, which represented the pH value of emulsion at the time of just finishing the introduction of NaOH aqueous solution, was regulated to 9.3 with 5 wt % NaOH aqueous solution. After 3 h of treatment, the emulsion was cooled down to ambient temperature.

Table II. Influence of Unsaturated Acid Monomer Type on the Property of Core Latexes

Core latex	Conversion (%)	$D_{\text{core}}^{\text{TEM}}$ (nm)	SF_a (mmol/g)	E_a (mmol/g)	PE_a (%)
P(MMA-BA-MAA-EGDMA)	99.42	140	1.074	1.746	61.9
P(MMA-BA-AA-EGDMA)	99.84	136	1.828	1.507	45.2

Characterization

Monomer conversion was measured by gravimetric analysis. The hydrodynamic diameter (D_p^{DLS}), polydispersity index, and zeta potential (ζ) of the latex particles were measured on Zetasizer 3000HS (Malvern, UK). The number-average diameter (D_p^{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 to do TEM observation were prepared as follows: the latex was first diluted with water to solid content about 1 wt %, and then mounted on carbon-coated copper grids and dried overnight at room temperature. The volume expansion (ΔV) of the particles after alkali post-treatment was calculated as below:

$$\Delta V = ((D_{\text{al}}^{\text{TEM}}/D_{\text{cis}}^{\text{TEM}})^3 - 1) \times 100\%$$

where, $D_{\text{cis}}^{\text{TEM}}$ and $D_{\text{al}}^{\text{TEM}}$ denoted the diameters of the dried particles before and after the alkali post-treatment, respectively.

The distribution of carboxyl groups in the latex was determined by conductometric titration as follows.³⁰ One gram of the original latex was diluted with 100 g of water and its solid content

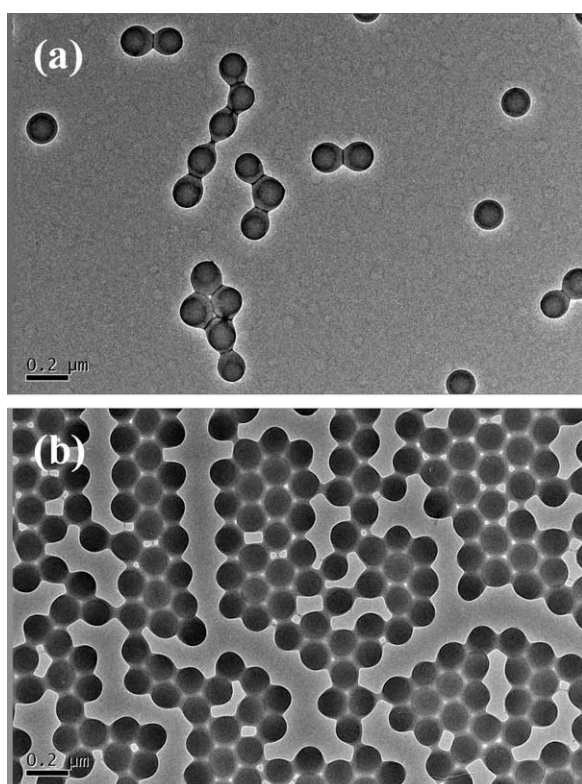


Figure 1. TEM photos of the core latex particles prepared with 24.4 wt % of unsaturated acid monomer: (a) P(MMA-BA-MAA-EGDMA) and (b) P(MMA-BA-AA-EGDMA).

was measured by gravimetric method. The pH value of the diluted latex was first adjusted to 11.5 ± 0.02 using 0.385 mol/L NaOH aqueous solution, and then the latex was titrated with 0.102 mol/L H_2SO_4 aqueous solution, and its conductance (σ) was recorded using a DDS-307 conductometer (Leici, Shanghai, China). The conductometric titration curve was plotted with the σ value of latex versus the amount of H_2SO_4 aqueous solution. The amount of $-\text{COOH}$ bound on the particle surface and free in aqueous phase corresponding to per gram polymer (SF_a) was calculated directly from the conductometric titration curve, and the amount of $-\text{COOH}$ embedded inside the particles corresponding to per gram polymer (E_a) was obtained from the difference between the initial charge of unsaturated acid monomer (M_a) and SF_a , and the percentage of $-\text{COOH}$ embedded inside the particles (PE_a) was calculated as below:

$$PE_a = E_a / (E_a + SF_a) \times 100\%$$

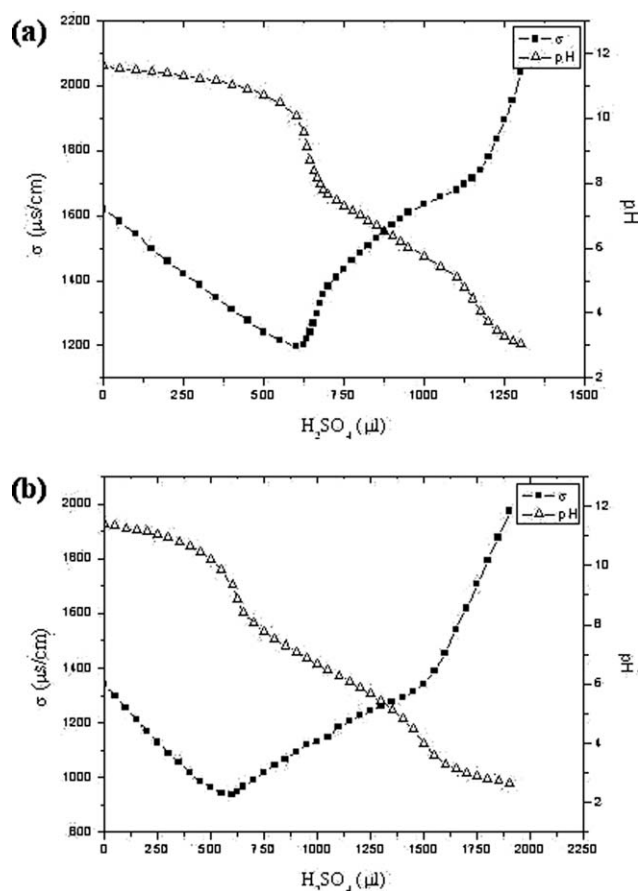


Figure 2. The conductometric titration curves of (a) P(MMA-BA-MAA-EGDMA) and (b) P(MMA-BA-AA-EGDMA) latexes. (■) The conductivity of the solution and (Δ) the pH of the solution.

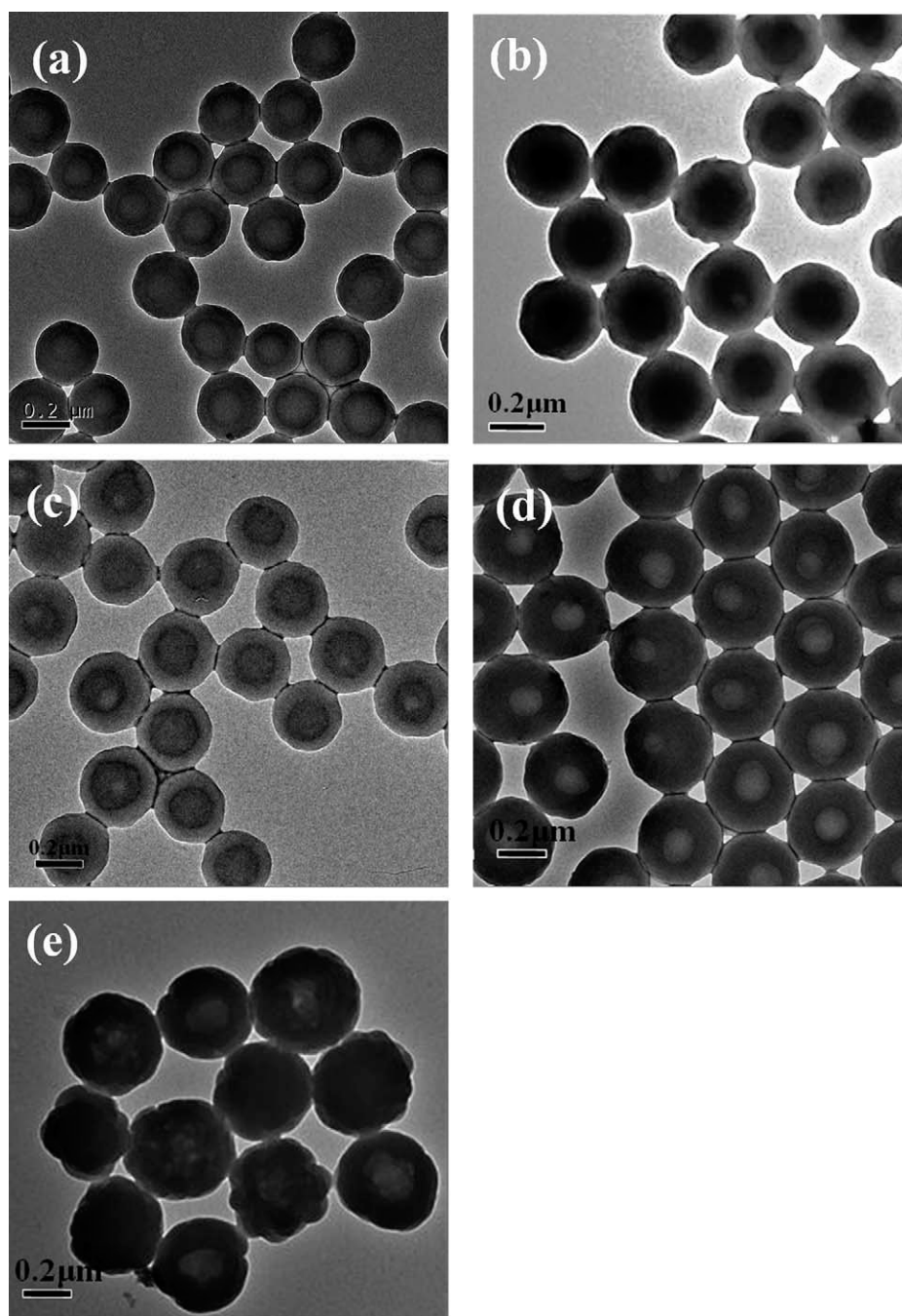


Figure 3. TEM photos of P(MMA-BA-MAA-EGDMA)/P(MMA-St-MAA)/P(St-DVB) core/shell latex particles prepared with different content (wt %) of MAA in the core latex preparation: (a) 12.2, (b) 20.0, (c) 24.4, (d) 30.0, and (e) 40.0.

Table III. Influence of MAA Content on the P(MMA-BA-MAA-EGDMA) Core Latex Particles

No.	MAA (g)	MAA content (wt % to core monomers)	D_{core}^{TEM} (nm)	D_{core}^{DLS} (nm)	Polydispersity index	ζ (mV)
MC1	4.32	12.2	142	160.7	0.0160	-41.9
MC2	7.78	20.0	125	187.9	0.0311	-43.7
MC3	10.05	24.4	140	165.9	0.0130	-46.9
MC4	13.33	30.0	135	221.0	0.0142	-52.7
MC5	20.73	40.0	142	178.1	0.0105	-45.7

Table IV. Influence of MAA Content in the Core Latex Preparation on the P(MMA-BA-MAA-EGDMA)/P(MMA-St-MAA)/P(St-DVB) Core/Shell Latex Particles

No.	MAA content in core monomers (wt %)	D_{cis}^{TEM} (nm)	D_{cis}^{Theory} (nm)	D_{cis}^{DLS} (nm)	Polydispersity index
MC1IS	12.2	280	277.3	303.5	0.0239
MC2IS	20.0	312	239.8	374.6	0.0300
MC3IS	24.4	326	265.2	382.0	0.0194
MC4IS	30.0	404	252.0	458.2	0.0265
MC5IS	40.0	375	257.6	421.2	0.0422

RESULTS AND DISCUSSION

Effect of Unsaturated Acid Monomer Type in the Core Latex Preparation

The carboxyl distribution and surface polarity of the resultant latex particles varied with the type of the unsaturated acid comonomer because of their different hydrophilic properties.^{18,19} Here, two kinds of unsaturated acid monomers, MAA and AA, were employed with the same content of 24.4 wt % to the monomers in the preparation of P(MMA-BA-MAA-EGDMA) and P(MMA-BA-AA-EGDMA) core latexes, and results were given in Table II and Figure 1. Regardless of using MAA or AA, the monomer conversion was higher than 99.4% and the D_{core}^{TEM} of the core latex particles was close to each other.

Previous investigation suggested that the amount of $-COOH$ embedded inside the particles is essential of forming hollow structure,^{3,24,28} and the conductometric titration is an effective way to measure the density of acidic groups on the particles surface.^{30,31} Therefore, the conductometric titration was employed to determine the carboxyl distribution, and the conductometric titration curves of the core latexes were shown in Figure 2, which were accordance with the typical conductometric titration curve of carboxyl groups.³⁰ It could be calculated from the inflexion of the curve that the values of SF_a in the P(MMA-BA-MAA-EGDMA) and P(MMA-BA-AA-EGDMA) latexes were 1.074 and 1.828 mmol/g, and the values of E_a were 1.746 and 1.507 mmol/g, respectively. It is clear that, in comparison with using AA, embedded percentage of $-COOH$ (PE_a) was considerably greater when using MAA as unsaturated acid monomer. This difference attributed to the more hydrophobic nature of MAA, which allowed it to diffuse more into the latex particles.

When using the P(MMA-BA-MAA-EGDMA) core latex as seed, the following seeded emulsion polymerization processes performed smoothly and the monomer conversions of the interlayer and shell preparation both reached higher than 99.4%.

The storage stability of the resultant core/shell latexes were more than 3 months at room temperature, and the monodisperse multistage core/shell latex particles could be identified clearly under the TEM observation [Figure 3(c)]. On the contrary, there were a mass of coagulation appeared during the interlayer and shell preparation processes when the P(MMA-BA-AA-EGDMA) core latex was used as seed to perform the seeded emulsion polymerization. These might be predominantly ascribed to the different distribution of carboxyl groups in different latex systems. According to the results of conductometric titration, when AA was employed instead of MAA, the carboxyl groups embedded in the core latex particles (E_a) decreased while the carboxyl groups on the particle surface and free in water phase (SF_a) increased, which inevitable resulted in the difficulty of encapsulating such more hydrophilic seeds P(MMA-BA-AA-EGDMA) and the high possibility of coagulation during the seeded emulsion polymerization. Therefore, MAA was employed as unsaturated acid monomer in the following investigation.

Effect of MAA Content in the Core Latex Preparation on the Emulsion Polymerization

As MAA content varied from 12.2 to 40.0 wt % in the core latex preparation, the core preparation process performed smoothly and all the monomer conversion of the core latex preparation were higher than 99.0%. Furthermore, there was no obvious change in the diameter of core latex particles. Only the zeta potential of the latexes (ζ) was dependent on the content of MAA (Table III). The absolute value of ζ increased with the MAA content increased from 12.2 to 30 wt %. When the content of MAA increased from 30 to 40 wt %, local electrolyte concentration was excessive and more ions with opposite charge probably diffused towards the surface of latex particles to get electric neutralization, which caused the compression of electric double layers and the increase of ζ from -52.7 to -45.7 mV, and as a result, the stability of the emulsion system decreased and some coagulation was generated.

Table V. Influence of MAA Content in the Core Latex Preparation on the Alkali-Treated Particles

No.	MAA content in core monomers (wt %)	D_{al}^{TEM} (nm)	D_{al}^{DLS} (nm)	Polydispersity index	ΔV (%)
AP1	12.2	280	360.7	0.0291	0
AP2	20.0	493	638.8	0.0364	294.5
AP3	24.4	510	621.5	0.0221	282.9
AP4	30.0	498	652.0	0.0428	87.3
AP5	40.0	528	666.3	0.288	179.1

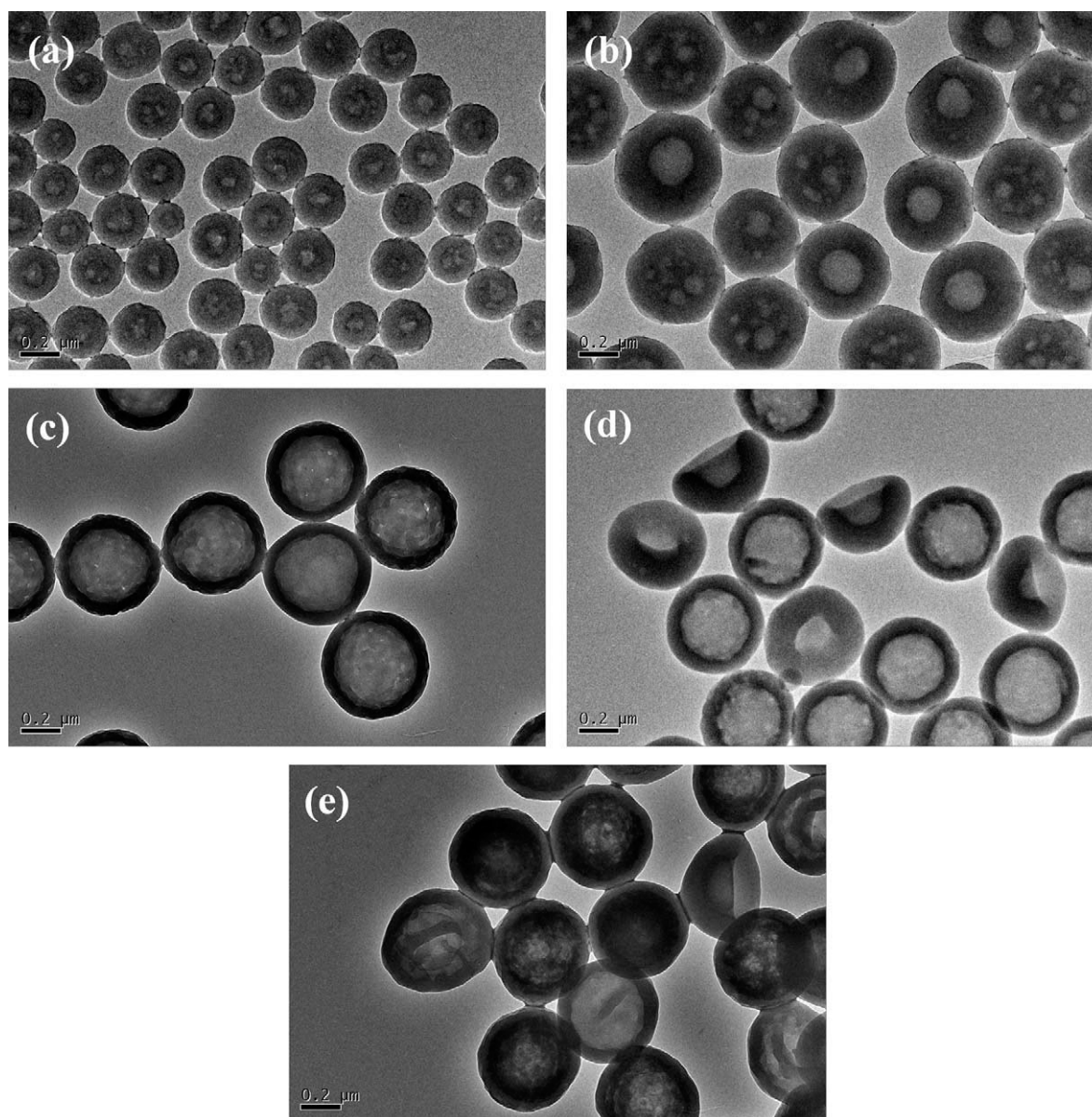


Figure 4. TEM photos of the alkali-treated particles prepared with different content (wt %) of MAA in the core latex preparation: (a) 12.2, (b) 20.0, (c) 24.4, (d) 30.0, and (e) 40.0.

Using the P(MMA-BA-MAA-EGDMA) core latex particles as seed, multistage core/shell latexes were synthesized by seeded emulsion polymerization and the results were listed in Table IV. It was found that the diameter of the dried core/interlayer/shell particles ($D_{\text{cis}}^{\text{TEM}}$) was bigger than its theoretical value ($D_{\text{cis}}^{\text{Theory}}$) which was calculated based on $D_{\text{core}}^{\text{TEM}}$ by assuming all of the monomers polymerized onto the core particles, and $D_{\text{cis}}^{\text{TEM}}$ first increased from 280 to 404 nm with the content of MAA increased from 12.2 to 30 wt % in the core latex preparation, and then decreased to 375 nm when the content of MAA further reached 40 wt %.

It is notable that because of the carboxylic hydration, carboxyl-containing core particles could retain a significant amount of water during the shell preparation,¹⁴ which would lead to the

difference between $D_{\text{cis}}^{\text{TEM}}$ and $D_{\text{cis}}^{\text{Theory}}$. Moreover, this hydration would intensify as MAA content increased, so $D_{\text{cis}}^{\text{TEM}}$ increased with the content of MAA increasing from 12.2 to 30.0 wt %, even some small pores could be observed by water evaporation during the TEM characterization for those particles obtained at high MAA content (24.4 and 30.0 wt %) [Figure 3(c,d)]. When the content of MAA reached 40.0 wt % in the core latex preparation, the size distribution of the resultant core/shell latex became broad (Table IV), and two kinds of particles with solid and hollow structure coexisted in the resultant core/shell latex [Figure 3(e)]. This is because that the hydrophilicity of the core particles prepared with MAA content 40.0 wt % was too strong to be encapsulated by the hydrophobic shell. According to homogeneous nucleation, in the following soap-free seeded emulsion polymerization of hydrophobic St and DVB, a majority of

the monomers would first polymerize and precipitate in water phase to form new colloidal particles by secondary nucleation, and then, these small colloidal particles would grow and aggregate to form the new latex particles without or with little amount of carboxyl groups, alternatively, be absorbed on the surface of the seed particles to generate core/shell latex particles. When the content of MAA was 40 wt % in the core preparation, the possibility of heterocoagulation decreased because of the great difference of polarity between the core latex and the small secondary particles, implying that the probability of homogeneous nucleation increased. It was believed that at a high concentration of MAA, monomer and/or polymer segments containing carboxyl groups free in the aqueous have more opportunity to participate in the homogeneous nucleation and as a result, new particles with little amount of carboxyl groups were generated. In the TEM observation, the new latex particles without or with little amount of carboxyl groups presented solid structure, while the core/shell latex particles containing carboxyl groups in the core showed hollow structure, as shown in Figure 3(e). Additionally, the difference between $D_{\text{cis}}^{\text{DLS}}$ and $D_{\text{cis}}^{\text{TEM}}$ was connected to the considerable hydration of carboxyl groups.

Effect of MAA Content in the Core Latex Preparation on the Morphology of Alkali-Treated Particles

It has been demonstrated that when the core/shell latex particles with embedded carboxyl groups were heated in an alkali aqueous phase at an appropriate temperature to unfreeze the shell polymer chain segments, the alkali molecule would neutralize the carboxyl groups in the polymer chains to form carboxylate polyelectrolyte, and the subsequent imbibing of water into the interior of the particles due to the osmotic pressure would lead to the volume expansion and void formation of the particles.^{3,15,16,29} Apparently, the amount of carboxylic monomer employed in the polymerization would determine the amount of carboxylate ions in the emulsion system and have a crucial effect on the final morphology of the alkali-treated particle.

The alkali post-treatment on the P(MMA-BA-MAA-EGDMA)/P(MMA-St-MAA)/P(St-DVB) core/shell latex particles with different content of MAA in the core latex preparation were performed, and the property as well as morphology of the alkali-treated latex particles were listed in Table V and Figure 4. After alkali post-treatment, the value of $D_{\text{al}}^{\text{DLS}}$ was much bigger than that of $D_{\text{al}}^{\text{TEM}}$ due to strong hydration and electrostatic repulsion of carboxylate groups, and the volume of particles expanded clearly except those prepared using 12.2 wt % of MAA. At low MAA content (12.2 wt %), the ionized polymer chains generated by the neutralization were insufficient, and the osmotic pressure was not enough for driving the particles to an effective expansion; so there was no obvious change in the particle size and only several small pores were found in the alkali-treated particles [Figure 4(a)]. When MAA content was 20 wt %, the particles absorbed more water and resulted in more water pools during the alkali post-treatment process, and even in some of particles, small water pools aggregated into a large one to decrease the interfacial free energy through decreasing the interfacial area [Figure 4(b)]. Much more water would be absorbed and the number of water pools would increase dramatically as the content of MAA reached 24.4 wt %, accordingly

all of the water pools aggregated into one hollow to get low interfacial free energy [Figure 4(c)]. With the further increase of MAA content, the increasing of ionized polymer chains promoted the osmotic swelling and as a result, the excess volume expansion of the latex particles would lead to the shell deformation during the drying process, thereupon some collapsed particles were observed in the samples with high MAA content over 30 wt %. It was worth pointing out that besides the collapsed particles, some deficient swollen particles also appeared in the alkali post-treated latex prepared using 40 wt % of MAA [Figure 4(e)], which resulted from the latex particles with two different morphologies prepared in the seeded emulsion polymerization stage [Figure 3(e)]. As mentioned above, since the hydrophilicity of the core particles prepared with 40 wt % of MAA was too strong to be encapsulated, two kinds of latex particles, the new latex particles without or with little amount of carboxyl groups and the core/shell latex particles containing carboxyl groups, were formed in the seeded emulsion polymerization, and after underwent alkali post-treatment, the former presented solid and deficient swelling structure, while the latter turned into hollow and collapse structure [Figure 4(e)].

CONCLUSION

The multistage core/shell latexes containing carboxyl groups were first synthesized via multistep seeded emulsion copolymerization, and then the particles with different porous morphologies were obtained by the following alkali post-treatment. The stability of the polymerization and the property of the resultant latex particles were significantly influenced by the type and content of the unsaturated acid monomer used in the core latex preparation. In comparison to AA, MAA was beneficial to form hydrophilic core/hydrophobic shell latex particles. As the content of MAA in the core latex preparation increased, both the diameter of the core/shell particles and that of the alkali-treated particles first increased and then decreased, and the alkali-treated particles underwent different morphologies from fine porous, porous, hollow to collapse structure. When the MAA content in the core latex preparation reached 40.0 wt %, two kinds of particles with solid and hollow structure coexisted in the core/shell latex, and after alkali post-treatment, the particles with morphologies including solid, deficient swelling, hollow, and collapse structure were formed.

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