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Morphological evolution of multistage polymer particles in the alkali post-treatment

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ABSTRACT

Multistage carboxyl-containing polymer latex particles were synthesized by multistep emulsion copolymerization using methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA) and styrene (St) as raw materials, and the latex particles with diverse morphologies including multihollow, hollow and "bowl-like" were obtained by post-treating the multistage latex particles under alkali condition. The morphological evolution of the particles in the alkali post-treatment process was characterized with electron microscopy, and effects of alkali treatment conditions including treatment temperature, time as well as initial pH on particle morphology were investigated. Results indicated that the alkali treatment temperature and initial pH were the key parameters to control the morphology of the treated particles. When the alkali treatment temperature was below 60 °C or the initial pH was lower than 8.5, the particle morphology was almost unchanged no matter how long the treatment time was prolonged. The multihollow and hollow particles could be formed as alkali treatment temperature exceeded 60 °C in the range of initial pH from 8.8 to 9.5. While the latex particles with "bowl-like" morphology were observed when the multistage latex was alkali treated at 90 °C for 3 h with initial pH 9.8. Furthermore, extending alkali treatment time was beneficial to get the swelling equilibrium of the latex particles.

1. Introduction

The morphological control of polymer latex particles is very important both in theory and in practice for the functional polymeric materials, and many researches were focused on it in the past three decades. Recently, the preparation of sub-micron sized polymer latex particles with designed structure have been intensively investigated because of their widely applications particularly in special coatings, information materials, and biomedical and pharmaceutical fields [1–4]. The earliest hollow latex particles made by osmotic swelling mechanism were developed by Kowalski and Vogel and then commercialized as ROPAQUE™ opaque polymer in Rohm & Haas Company [5,6]. Vanderhoff et al. prepared hollow particles by drying hydrophilic/hydrophobic core/shell particles with soft alkali swelling core and hard crosslinked shell [7]. Okubo and his colleagues prepared multihollow polymer particles by stepwise alkali/acid treatment and alkali/cooling methods, respectively [8,9]. McDonald et al. investigated an approach first encapsulating a non-solvent hydrocarbon with the polymer being synthesized in an emulsion polymerization and then removing the hydrocarbon to form voided latex particles [10]. In our previous work, several kinds of latex particles with different porous morphologies were prepared, and found that many factors including ingredients, polymerization process, as well as post-treatment conditions would affect the morphology of the final particles, moreover, these factors were interactional and made the particles morphology complicated [11–16].

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In order to control the particle morphology more efficiently in the preparation of porous latex particles, it is of importance to understand the morphological evolution of the latex particles in the post-treatment process. In this paper, P(BA-MMA-MAA-EGDMA)/PSt multistage latex particles were first synthesized by multistep emulsion copolymerization of methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA) and styrene (St), and then post-treated with alkali under different conditions. The morphological evolution of the particles in the post-treatment process was characterized with transmission electron microscopy (TEM) and scanning electron microscopy (SEM), and the influences of post-treatment temperature, time and initial pH on the particle morphology were investigated.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), 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) and sodium dodecyl sulfate (SDS) (A. P. grade, 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. Ammonia (25 wt%, A. P. grade, Beihua Fine Chemical Products Co. Ltd., Beijing, China) was used in alkali treatment process as received. Distilled and deionized water was used throughout.

2.2. Synthesis of multistage polymer latex

P(BA-MMA-MAA-EGDMA)/PSt multistage polymer latex particles were synthesized by multistep emulsion copolymerization in a four-necked 250 ml round-bottom flask equipped with an inlet of nitrogen gas, a reflux condenser, a glass stirrer and a pressure-equalizing funnel, and typical recipes were listed in Table 1. The synthetic route included sequential three steps of core, intermediate layer and shell preparations as below.

P(MMA-MAA-BA-EGDMA) core latex was prepared via semi-continuous emulsion polymerization. At first, 5 wt% of the mixture of MMA, MAA, BA and EGDMA, 90 g H_2O and 0.10 g APS was charged into the reactor, and polymerized at 80 °C for 40 min. Then, the residual monomer mixture and aqueous solution of APS (0.30 g APS dissolved in 10 ml water) were simultaneously dropwise added into the reactor at 80 °C for 4.5 h, then the reaction system was heated to 90 °C, and maintained at this temperature for 30 min. After that, the system was cooled down to room temperature.

In the intermediate layer preparation, a certain amount of the core latex was first diluted with water to a solid content of 10 wt%, and the seeded emulsion copolymerization of MAA, St and MMA onto the core particles was carried out at 80 °C by constant feeding the monomer mixture and APS aqueous solution simultaneously into the diluted core latex for 40 min.

At last, the system was heated to 90 °C, and St and APS aqueous solution were simultaneously dropwise added into the system using 2 h to form the outer shell of the particles. After additional 30 min at 90 °C, the system was cooled down to room temperature to obtain the multistage polymer latex particles.

2.3. Alkali post-treatment

A certain amount of the resultant multistage polymer latex was charged into a reactor which was immersed in a water bath at a given temperature, and the initial pH of the latex was accurately adjusted to 8.3–10.0 with 2 wt% aqueous ammonia under stirring at around 300 rpm. After treatment for a certain time, the latex was cooled down to ambient temperature.

2.4. Characterization

Monomer conversion of each polymerization step was measured by gravimetric analysis. The size (D_p) and morphology of the latex particles were characterized using transmission electron microscopy (TEM, JEOL JEM-2100EX, Japan) and scanning electron microscopy (SEM, FLOTU JSM-7401F, Holland).

Characterization of the dried number-average diameter of the alkali post-treated particles (D_t) was a little complicated because of their irregular morphologies in most conditions. So, D_t were estimated by using an approximate method as follows: three diameters of each particle from three different directions were first measured, namely

Table 1
Recipes of the multistage latex preparation via multistep emulsion polymerizations.

Ingredients	Core preparation (g)	Intermediate preparation (g)	Shell preparation (g)
MMA	16.50	7.33	0
MAA	10.05	0.84	0
BA	14.6	0	0
EGDMA	0.25	0	0
St	0	2.03	11.84
SDS	0.01	0	0
APS	0.40	0.10	0.10
H_2O	100	35	10
Core latex	0	10.00	0

from the direction to obtain the largest particle diameter ($D_{\max}$), from the direction to obtain the smallest particle diameter ($D_{\min}$) and from the direction between the above two to obtain the middle diameter (D_{mid}), and an equivalent diameter (D_{equ}) of individual particle was then calculated by the equation

$$D_{\text{equ}} = (D_{\max} + D_{\min} + D_{\text{mid}})/3$$

Finally, D_t was obtained by averaging D_{equ} of at least thirty particles in number.

3. Results and discussion

3.1. Preparation of multistage polymer latex

In the preparation of porous latex by osmotic swelling mechanism, since the neutralization of carboxyl groups inside the particles and the following hydration are essential to form porous structure [11,17,18], certain amount of carboxyl groups inside the untreated original polymer latex particles is necessary. In conventional emulsion polymerization, because of their hydrophilicity, carboxyl groups thermodynamically tend to localize towards the surface and the outer layer of the latex particles, which means the level of carboxyl groups inside the particles is often relatively low [19]. On the other hand, the shell of the porous particles must be strong enough to maintain their porous structure. In order to obtain the original latex particles with required the amount of carboxyl groups and the shell strength, the original core/shell latex particles with carboxyl-riched polyacrylics core and polystyrene-riched shell are often prepared via seeded polymerization [20–23]. From the viewpoint of thermodynamics, the hydrophilic core polymer is easily migrated towards the shell in the seeded emulsion polymerization, and as a result, the core and shell polymer chains interpenetrate with each other to form undesirable particles with blurry core/shell interface, sea-island structure or even inverted core/shell morphologies based on the recipes and polymerization conditions [23,24]. For the purpose of preventing the core and shell polymers from the interpenetration, small amount of crosslinker with two polymerizable double bonds and an intermediate layer with moderate polarity were introduced into the core and the core/shell particles, respectively, and the multistage latex particles with the polar gradient of high in the core to low in the shell were prepared via multistep seeded emulsion polymerization.

In the latex preparation, each step of emulsion polymerization could be performed smoothly and the monomer conversions reached 99.9%, 99.5% and 99.4% for the core, intermediate layer and shell preparations, respectively. The morphologies of core, core/intermediate and multistage polymer latex particles were shown in Fig. 1. The original core diameter was 236 nm, and the particle size increased to 350 nm after intermediate layer preparation. The diameter of final multistage particles was 455 nm, which was close to its theoretical value of 460 nm assuming that all of the polymerized intermediate and shell monomers were uniformly covered on the cores. These manifested that monodisperse core, core/intermediate as well as core/intermediate/shell multistage particles were obtained and the hydrophilic core was successfully encapsulated by the outer layer polymer.

3.2. Morphological evolution of the multistage polymer particles

Carboxyl-containing latex particles with different ingredients and different morphologies have been synthesized and applied to prepare porous latex particles by alkali post-treatment, and found that besides the ingredients and polymerization processes, the post-treatment temperature, time and initial pH were the top three factors to affect the treated particle morphology, and a little change of them would lead to the change of the final particle structure [12,25,26]. Here, the influences of these top three factors on the morphological evolution of the multistage polymer particles in the alkali post-treatment were investigated.

3.2.1. Alkali treatment temperature

In the post-treatment process, the segment mobility of shell polymer must be released to allow alkali and water molecules penetrate into the particles to neutralize carboxyl groups and swell the particles. Theoretically, the post-treatment temperature must be controlled at least above the actual glass transmission temperature (T_g) of the shell polymer in the system. However, because of the water plasticization, it is believed that the actual T_g of the shell polymer in the system must be much lower than that of the polymer in its dried state and is very difficult to

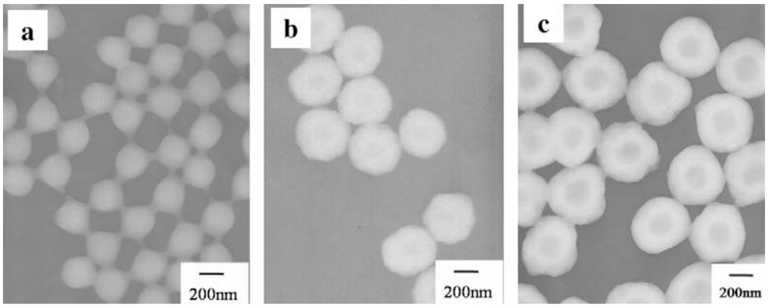

Fig. 1. TEM photos of (a) P(BA-MAA-MMA-EGDMA) core, (b) P(BA-MAA-MMA-EGDMA)/P(MMA-MAA-St) core/intermediate and (c) multistage polymer latex particles.

Table 2
Influence of alkali treatment temperature on particles morphology.

T (°C)	50	60	70	80	90	100
D_t (nm)	412	488	482	565	578	618
Void	No	No	Yes	Yes	Yes	Yes

determine. In reference to the post-treatment temperature, it has been suggested that an optimum post-treatment temperature should be equal to or above T_g of the shell polymer [5,27,28]. Whereas, it has also been stated that in some cases hollows can be formed even at temperature below the T_g of the shell polymer [5,29]. Therefore, it should be investigated case by case for different latex systems.

To investigate the effect of treatment temperature on the particle morphology, the alkali treatment of the multistage polymer latex was carried out at different temperature for 3 h with an initial pH of 10.0, and the results were shown in Table 2 and Fig. 2. When the treatment temperature was below 60 °C, no any visible porous structure was identified in the treated particles though the diameter of the treated particles was slightly increased in comparison to the untreated ones. The porous structure began to be observed when the temperature was higher than 60 °C, and both the diameters of the treated particles (D_t) and the pore size tended to increase with the increase of temperature. In order to understand more about the particle morphology, the appearance of the same latex particles treated at 90 °C was observed under SEM (Fig. 3). By comparing Fig. 2d with Fig. 3, one can see that the voided structure on the TEM photographs is not from the hollow morphology, but from the "bowl-like" morphology.

During alkali treatment process, carboxyl groups on the chains of the shell polymer were neutralized to carboxylate groups. Since the hydrophilicity of polymer chains with $-COO^-$ is better than that of polymer chains with $-COOH$, and $-COO^-$ will be hydrated with water molecules, the actual T_g of the shell polymer in such system is much lower than that of the polymer in its dried state. The experiment results indicated that the actual T_g of the shell polymer must be between 60 and 70 °C. Once alkali post-treatment temperature was above this actual T_g, the segments of the shell polymer were defrozen, so the alkali molecule could penetrate through the shell into the particles to neutralize the core polymer to form carboxylate-containing polyelectrolyte inside, and then the subsequent imbibing of water into the interior due to osmotic pressure would lead to the particle expansion and the voided structure formation.

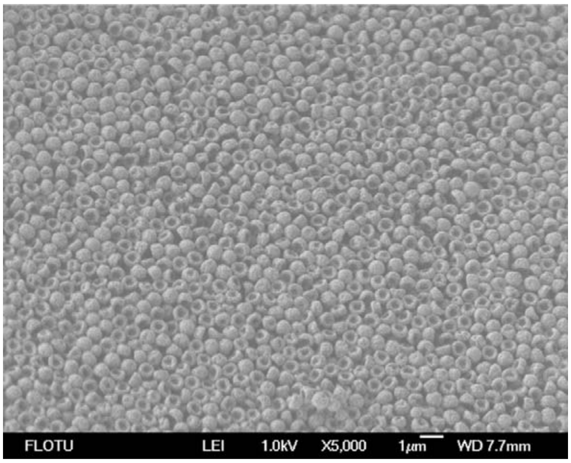

Fig. 3. SEM photo of the alkali-treated multistage polymer latex particles with initial pH 10.0 for 3 h at 90 °C.

3.2.2. Alkali treatment time

As indicated above, the mobility of polymer chain segments and the penetration of alkali and water molecules are necessary for the change of particle morphology in the post-treatment process. It is well known that the movement of polymer chain segments is a relaxation process, that is to say the time for the movement of polymer chain segments can be shortened by increasing the temperature. In addition, considering molecules have different penetrating speed at different temperature, osmotic equilibrium also needs a certain time to achieve at a given temperature. No doubt, the alkali treatment time and temperature are not independent factors affecting the particle morphology.

Here, the multistage polymer latex with initial pH of 10.0 was separately treated at 60 and 80 °C for different time, and TEM photos of the treated particles were shown in Figs. 4, 5, 2a and c, respectively. When the alkali treatment was performed at 60 °C, the voided structure ap-

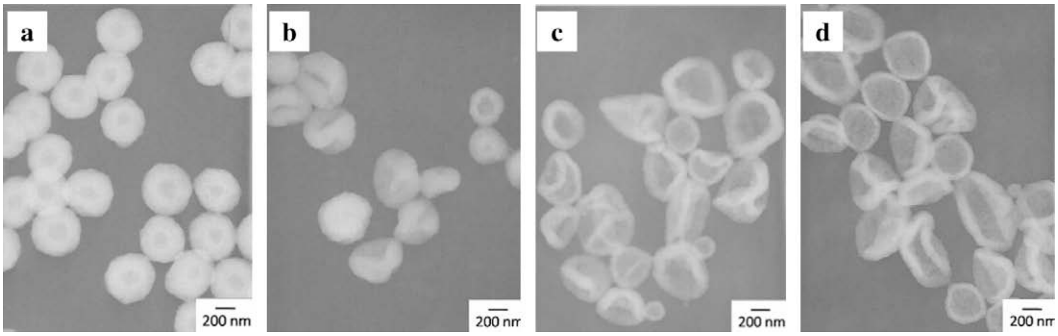

Fig. 2. TEM photos of the alkali-treated multistage polymer latex particles obtained with initial pH 10.0 for 3 h at different treatment temperature (°C): (a) 60; (b) 70; (c) 80; (d) 90.

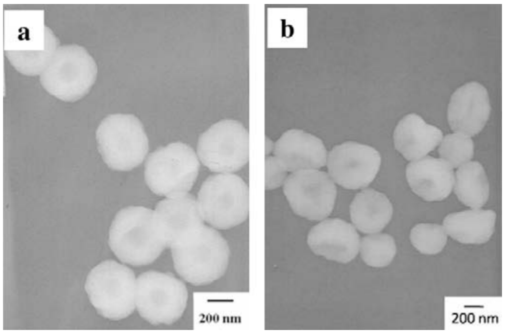

Fig. 4. TEM photo of alkali-treated multistage polymer particles obtained with initial pH 10.0 at 60 °C for (a) 1 h; (b) 5 h.

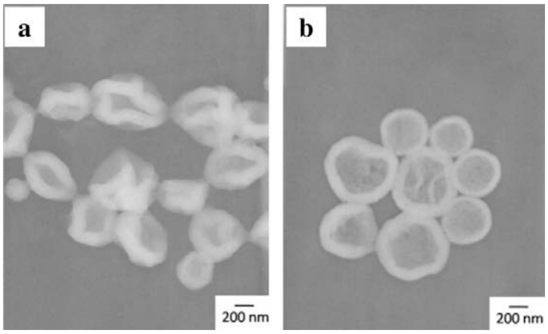

Fig. 5. TEM photos of the alkali-treated multistage polymer latex particles obtained with initial pH 10.0 at 80 °C for different time: (a) 1 h and (b) 5 h.

peared until the treatment time reached 5 h (Fig. 4b). However, as the treatment temperature increased to 80 °C, the "bowl-like" morphology which displayed voided structure on TEM photograph was observed clearly even though the treatment time was less than 1 h (Fig. 5a).

These results suggested that at a relatively low temperature, the mobility of the polymer chain segments decreased, and more time must be needed for the polymer chains to reach their corresponding equilibrium state. When the temperature was below 60 °C, the polymer chain segments were frozen and as a result, the particle morphology was almost unchanged no matter how long the latex was treated for. Furthermore, above the segments frozen temperature, there always was a minimum treatment time to make the particle morphology change obviously, and this minimum treatment time decreased rapidly with the increase of treatment temperature.

3.2.3. Initial pH

Alkali amount used in the alkali post-treatment is also important for the morphological evolution of the multistage polymer latex particles. During the post-treatment process, since the carboxyl groups of polymer chains were neutralized to carboxylates, the hydrophilicity of the polymer chains increased and as a result, the mobility of polymer chains towards particle surface also increased, which was beneficial for the particle expansion and morphology change. Because a volatile alkali, aqueous ammonia, was utilized in this study, the level of alkali amount was expressed by initial pH of the latex system, and the relationship between the initial pH and the morphology of the alkali-treated multistage polymer latex particles was investigated under the same conditions of 90 °C and 3 h.

Results showed that no visible porous structure was observed in the treated particles at an initial pH of 8.5 (Fig. 6a). When the pH varied from 8.8 to 9.5, multihollow and hollow morphology could be easily identified under TEM (Fig. 6b and c). Moreover, the distinct "bowl-like" morphology appeared when the pH increased to 9.8 (Fig. 6d). This is because that the hydrophilicity of polymer chains at relatively low pH 8.5 cannot provide enough driving force for the migration of polymer chains. As the pH increased to 8.8, some of the polymer chains could move to the particle surface because of their enhanced mobility, leaving some small pores inside the particle to form multihollow morphology. Along with the pH increased continuously, more and more small pores were generated in the alkali-treated particles, and these small pores preferred to aggregate to decrease the potential energy by reducing interfacial area, resulting in the formation of hollow structure. When the pH value was higher than 9.8, overfull polymer chains would transfer towards the particle surface and dissolve gradually into aqueous phase. In fact, similar phenomena have been observed and discussed in our previous report [30]. In this case, the pressure which the hollow particles suffered would induce the shell deformation during particles drying process, so "bowl-like" structure was observed in TEM photo.

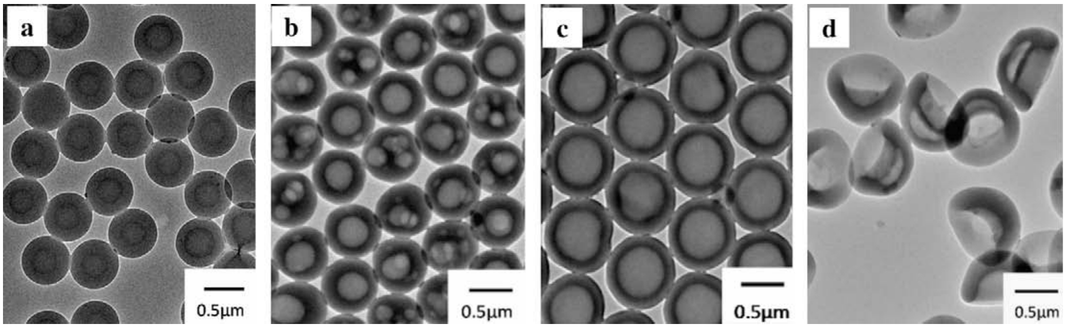

Fig. 6. TEM photos of the alkali-treated multistage polymer latex obtained at 90 °C for 3 h with different initial pH: (a) 8.5; (b) 8.8; (c) 9.5; (d) 9.8.

4. Conclusion

In this study, monodisperse P(BA-MAA-MMA-EGDMA)/PSt multistage polymer latex particles were prepared via multistep emulsion copolymerizations, and porous latex particles with different morphologies were obtained by alkali post-treatment. It was found that the morphology of the particles evolved from multihollow, hollow to "bowl-like" as alkali treatment conditions changed in the post-treatment process. There was a lowest post-treatment temperature and initial pH to make the particle morphology change, and when the temperature exceeded 60 °C and the pH reached 8.8, multihollow morphology appeared, and along with the number of the small pores inside particles increased, these small pores inclined to aggregate to form one hollow structure, and finally the "bowl-like" morphology was generated by the deformation of the shell at 90 °C with initial pH 9.8. In addition, the particle morphology changed more clearly as alkali treatment time prolonged.

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