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Preparation of Bowl-Like Polymer Particles *via* Multi-Step Emulsion Polymerization and Alkali Post-Treatment

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Summary: Monodisperse P(BA-MMA-MAA-EGDMA)/P(St-MAA-DVB) core/shell latex particles were first synthesized by a four-step emulsion polymerization, and a new kind of latex particles with "bowl-like" morphology were obtained by post-treating the resultant core/shell particles under alkali condition. Results indicated that the feeding rates of the monomer mixture and initiator aqueous solution were the key parameters to obtain monodisperse core/shell latex particles in the emulsion polymerization process, and the latex particles with "bowl-like" morphology could be generated only when the treatment temperature was equal or higher than 70 °C.

Keywords: bowl-like particles; core-shell polymers; emulsion polymerization; morphology; Post-treatment

Introduction

The morphology design and control of polymer particle are very important both in theory and in application for the functional polymeric materials.[1,2] Emulsion polymerization has always been considered as one of the most important methods to synthesize spherical polymer particles from micro-size to nano-size dimension, and the particles with various anomalous shape such as multihollow, void, confetti-like, raspberry-like, snowman-like, octopus ocellatus-like and mulberry-like were also prepared using this method.[3–8]

In this work, monodisperse P(BA-MMA-MAA-EGDMA)/P(St-MAA) core/shell latex particles were first synthesized by a four-step emulsion polymerization of methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA) and styrene (St), and a new kind of latex particles with "bowl-like" morphology were obtained after alkali post-treatment, and the influences of feeding model and post-treatment temperature on the particle morphology were investigated.

Experimental Part

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), Divinyl benzene (55% content, assay isomers ethylvinylbenzene 45%, Alfa Aesar, Tianjin, China) and sodium dodecyl benzene sulfonate (SDBS) (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 as received. Distilled and deionized water was used throughout.

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Emulsion Polymerization

A typical recipes of the emulsion polymerization to synthesize P(BA-MMA-MAA-EGDMA)/P(St-MAA) core/shell latex particles were listed in Table 1. The detailed emulsion polymerization process included four steps as described below:

At first, the original P(MMA-MAA-BA) latex was prepared by batch emulsion copolymerization at 80 °C for 40 min. Then, the core latex was prepared by simultaneously dropwise adding the monomer mixture of MMA, MAA, BA and EGDMA and the aqueous solution of APS into the original latex at 80 °C within 5 h, and maintained for additional 30 min at 90 °C.

In the third step, 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 within 40 min.

In the last step, the mixture of St and MAA monomers and APS solution were dropwise added into the above system at 90 °C for 2 h to form the outer shell of the particles. After additional 30 min at 90 °C, the system was cooled down to the room temperature to obtain P(BA-MMA-MAA-EGDMA)/P(St-MAA) core/shell latex.

Table 1.
Recipes of the core/shell latex preparation *via* a four-step emulsion polymerization.

Ingredients	Core (g)		Shell (g)	
	1st step	2nd step	3rd step	4th step
MMA	0.64	15.86	7.33	0
MAA	0.03	10.02	0.84	0.68
BA	0.57	14.13	0	0
EGDMA	0	0.25	0	0
St	0	0	2.03	11.84
DVB	0	0	0	0.45
SDBS	0.01	0	0	0
APS	0.10	0.10	0.10	0.10
Water	90	10	30	10
Core latex	0	0	10.00	0

Alkali Post-Treatment

Alkali post-treatment was performed as follows: the core/shell latex was diluted to 10 wt% solid content and charged into a reactor which was immersed in a water bath with a given temperature, and its pH was adjusted to 9 with 2 wt% aqueous ammonia under stirring at around 300 rpm. After alkali treatment for 3 h, the latex was cooled down to the ambient temperature.

Characterization

Monomer conversion of each step was measured by thermal gravimetric analysis. The size and morphology of latex particles were characterized using a transmission electron microscopy (TEM, JEOL JEM-1200EX, Japan), and the bowl-like morphology of the posttreated latex particles were observed under a scanning electron microscopy (SEM, FLOTU JSM-7401F, Holland).

Results and Discussions

Synthesis of Core-Shell Particles

In the preparation of hydrophilic/hydrophobic core/shell latex particles, the mutual diffusion of the polymer chains located in the interface of the core and the shell would be unavoidable; on the other hand, the hydrophilic core containing carboxylic acid groups was very unstable and easy to coagulate in the polymerization process.[8–10] Thus, very slowly dropwise addition of the monomers should be beneficial both for the increase of the instantaneous monomer conversion to prevent the diffusion and for the stabilization of the polymerization process. Experiments showed that the core/shell latex particles could be obtained only by controlling the feeding rates of the monomers and the initiator at relatively low levels, and batch or fast feeding of monomers would induce coagulation and interrupt the formation of core/shell structure. In our experiments, a constant pressure funnel was used to dropwise adding the APS aqueous

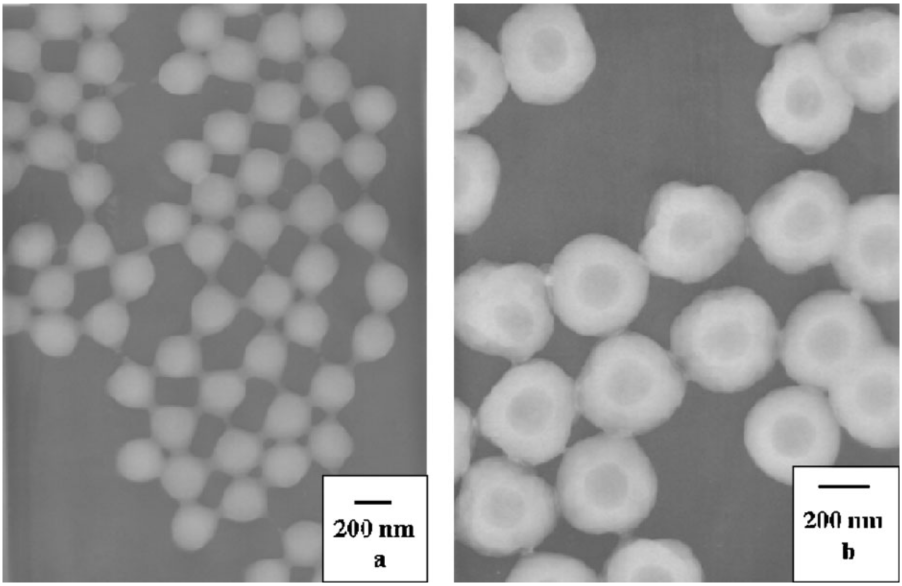

Figure 1.
TEM photos of (a) the P(BA-MAA-MMA-EGDMA) core and (b) the P(BA-MAA-MMA-EGDMA)/P(St-MAA) core/shell latex particles.

solution, and a peristaltic pump was employed to control the dropwise adding rate of the monomer mixture. When the rotation rate of the pump head was setted as 0.001 rpm, the feeding rate of the monomer mixture was approximately 0.14 ml/min, which means the feeding time of the monomer mixture was about 5 h. In this way, the polymerization could be performed smoothly and there was no coagulation formed, and monomer conversions in the core and the core/shell latex preparation reached above 99.4%

The morphologies of the core and the core/shell latex particles were shown in Figure 1. It manifested that well monodisperse core and core/shell particles could be obtained *via* the four-step emulsion polymerization by controlling the feeding rates of the monomers and initiator aqueous solution. The diameters of the core and the core/shell particles were 236 nm and 500 nm, respectively, which also indicated that the core particles were successfully encapsulated by the shell polymer.

Morphology after Alkali Post-Treatment

It has been reported that the morphology of the latex particle was strongly affected by the treatment temperature.[9,11,12] In order to investigate the effect of treatment temperature on particle morphology, the initial pH of the latex was first adjusted to 9 with aqueous ammonia and the system was treated for 3 h separately at the temperatures of 60 °C, 70 °C and 80 °C. Results showed that the latex particles remained their initial spherality at 60 °C, and when the temperature was increased to 70 °C and 80 °C, anomalous particles appeared under TEM observation (Figure 2a). In order to confirm the detailed particle morphology, SEM was employed to characterize the anomalous appearance of the particles. It is clear in Figure 2b that the concave structure appeared on the surface of each sphere and as a result, the morphology of the particle looked like a bowl. This bowl-like morphology might be resulted from the deformation and collapse of the particles during post-treatment and characterization, and the research of the detailed forming mechanism is still in process.

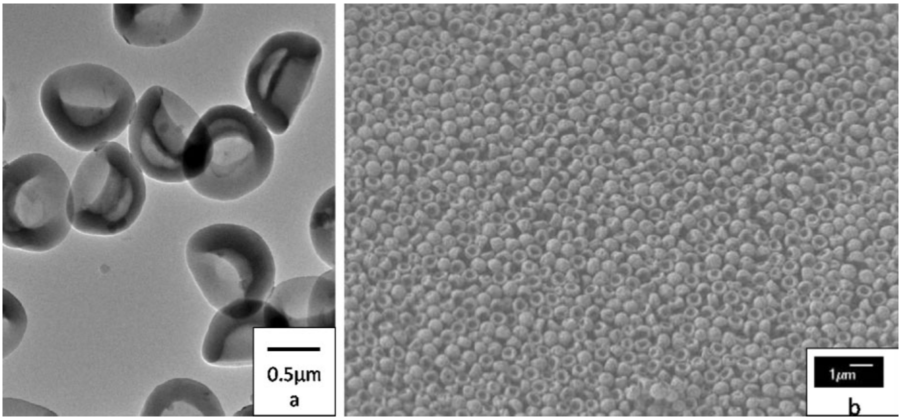

Figure 2.
(a) TEM and (b) SEM photo of the alkali-treated P(BA-MAA-MMA-EGDMA)/P(St-MAA) latex particles at 70 °C.

Conclusion

Monodisperse sub-micron sized P(BA-MAA-MMA-EGDMA)/P(St-MAA) core/shell latex particles were prepared *via* a four-step emulsion polymerization by controlling the feeding rates of the monomer mixture and the initiator aqueous solution; the ''bowl-like'' latex particles could be generated after alkali treating the core/shell latex particles at equal or higher than 70 °C with initial pH 9 for 3 h.

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