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A facile fabrication of amphiphilic Janus and hollow latex particles by controlling multistage emulsion polymerization

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ABSTRACT

In this paper, we found that morphology controllable compound latex particles could be prepared by controlling the multistage emulsion polymerization. Influences of the content of methacrylic acid (MAA) on preparing the hydrophilic cores and the particles were investigated with the observation of dynamic light scattering (DLS) and transmission electron microscope (TEM) results. The acorn-like latex particles were synthesized by partially encapsulated with hydrophobic polystyrene (PSt)-layer. With adding moderate polarity polymethylmethacrylate (PMMA) interlayer, the hydrophilic cores could be fully encapsulated by the hydrophobic PSt-layer, and the core–shell structure formed. After alkali treatment, the acorn-like and core–shell latex particles evolved into amphiphilic Janus and hollow latex particles, respectively. The morphology of latex particles was investigated by TEM, and the forming mechanism of amphiphilic Janus and hollow latex particles was proposed.

1. Introduction

In the past few decades, many researches were focused on the morphological control of polymer latex particles due to their theoretical significance and practical values [1,2]. Designed latex particles with morphological features and sub-micron size could significantly improve its physical and chemical properties, and enhance its application in wide range, such as functional coatings [3,4], information materials, catalyst, delivery vehicle systems [5,6] and biomedicine [7,8]. The typical morphology of polymer latex particles includes acorn-like, bowl, core–shell, hollow [9] and "Janus" particles [10]. Latex particles with different morphologies exhibit various applications. Encasing core in a shell of different compositions can be referred to core–shell particles [11]. The shell can alter the charge, functionality and reactivity of the surface, and can enhance the stability and dispersibility of the colloidal core [12]. Hollow latex particles have widely applications such as photonic crystals, delivery vehicle systems, fillers, pigments, and catalysts [13]. The particle whose chemical makeup differs between the two hemispheres was called "Janus" particles by de Gennes [14]. Janus particles have wide potential applications in many fields, such as microrheological probes, stabilization of emulsions and foams [15] and building blocks for novel 3D self-assembled structures [16]. In general, the fabrication procedure of polymer particles varied different morphologies. For example, there are two techniques for preparing hollow polymer particle: one is post-treating polymer particles [17,18]. And another is encapsulating and removing small molecules during in situ polymerization [19]. The Janus particles could be prepared by surface modification [20] or emulsion polymerization [21].

In this paper, using common monomers, we found a facile fabrication of amphiphilic Janus or hollow latex particles by controlling multistage emulsion polymerization. Firstly, using butyl acrylate (BA), methyl methacrylate (MMA) and methacrylic acid (MAA) as core monomers, the acorn-like latex particles were synthesized by encapsulating the polystyrene (PSt). Secondly, using an interlayer with moderate polarity, three-layer core–shell latex particles with hydrophilic core and hydrophobic shell were prepared. Then, using alkali post-treatment, the acorn-like and core–shell latex particles evolved to amphiphilic Janus spheres and hollow particles, separately. The morphologies of obtained latex particles were also investigated.

2. Experimental section

2.1. Materials

Butyl acrylate (BA), methyl methacrylate (MMA), methacrylic acid (MAA), and styrene (St) (Shangdong, Qilu Petrochemical Kaitai

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Industry Co.) were purified by washing, dry and distillation, and purified monomers were stored at −2 °C until used. Ethylene glycol dimethacrylate (EGDMA) (98%, Aladdin, Shanghai, China), divinyl benzene (DVB) (80% aladdin, Shanghai, China), potassium persulfate (KPS), sodium dodecyl sulfate (SDS), and octylphenol polyoxyethylene ether (OP-10) were used as received. Distilled water was used throughout. Other reagents were obtained commercially.

2.1.1. Preparation of core latex (PBMM)

The emulsion was prepared via semi-continuous emulsion polymerization in a 250 mL glass reactor equipped with a reflux condenser, a mechanical stirrer. The core monomer (MMA, MAA, BA, EGDMA) mixture and KPS (dissolved in 30 g H_2O) were simultaneously dropwise added into the reactor at 80 °C for 2.5 h. Then the reaction system maintained at this temperature for 30 min. After that, the system was cooled down to room temperature.

2.1.2. Preparation of acorn-like and Janus latex

The prepared core latex was diluted to a solid content of 10%, and the PSt-layer monomer (St, DVB) mixture and KPS (dissolved in 30 g H_2O) were simultaneously dropwise added into the reactor at 80 °C for 2.5 h, then the reaction system maintained at this temperature for 30 min, and acorn-like latex was prepared.

Acorn-like latex emulsion was diluted to a solid content of 2%, and charged into a reactor at 90 °C. The pH was adjusted to 10 with aqueous ammonia. After the treatments for 2 h, the emulsion was rapidly cooled to room temperature, and the Janus latex was prepared. The typical recipes are listed in Table 1.

2.1.3. Preparation of core–shell latex with interlayer and hollow latex

The prepared core latex was diluted to a solid content of 10%, and the interlayer monomer (MMA, MAA) mixture and KPS (dissolved in 10 g H_2O) were simultaneously dropwise added into the reactor at 80 °C for 1.5 h. Then, the reaction system maintained at this temperature for 30 min. After completion of the interlayer monomer, the shell monomer (St, DVB) mixture and KPS (dissolved in 30 g H_2O) were simultaneously dropwise added into the reactor at 80 °C for 2.5 h. Then, the reaction system maintained at this temperature for 30 min, and the core–shell latex emulsion was prepared.

Core–shell emulsion was diluted to a solid content of 2%, and charged into a reactor at 90 °C. The pH was adjusted to 10 with aqueous ammonia. After the treatments for 2 h, the emulsion was rapidly cooled to room temperature and the hollow latex was prepared. The typical recipes are listed in Table 2.

2.1.4. Characterization

The final conversions were measured by the gravimetric method. The average particle size and polydispersity index of the emulsion particles were measured by dynamic light scattering (DLS) (Nano series, Malvern Instruments Ltd., UK) at 25 °C, and the samples were highly diluted (<0.01%) to prevent multiple scattering before tested. The micrographs of latex particles were observed by JEM-1230 transmission electron microscope (TEM) from JEOL, at 200 kV.

Table 1
Recipe for synthesis of core–shell copolymer latex.

Components	Core preparation (g)	PSt-layer (g)
MMA	7.40	0
BA	9.50	0
MAA	2.0	0
KPS	0.20	0.16
EGDMA	0.50	0
St	0	15.2
DVB	0	0.8
SDS/OP-10	0.20/0.20	0.16/0.16
H_2O	50	0
Core emulsion (10%solids)	0	40

Table 2
Recipe for synthesis of core–shell copolymer latex with interlayer.

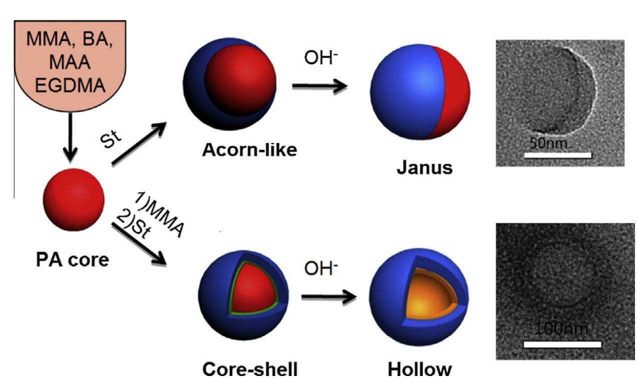
Components	Interlayer preparation (g)	Shell preparation
MMA	3.50	0
MAA	0.5	0
KPS	0.04	0.16
St	0	15.2
DVB	0	0.8
SDS/OP-10	0.04/0.04	0.16/0.16
H_2O	30	0
Core emulsion (10%solids)	20	0

3. Results and discussion

With controlling multistage emulsion polymerization and varying monomers ratio, we found that an amphiphilic Janus or hollow latex particles could be prepared easily. Scheme 1 shows the process of latex particles preparation in different conditions. Firstly, the core latex was prepared using BA, MMA and MAA as core monomers. In the core latex (PBMM), EGDMA was employed as crosslinking agent. Secondly, the acorn-like latex was particles prepared by encapsulating PSt-layer using St and DVB. After alkali post-treatment, amphiphilic Janus latex particles were obtained. Thirdly, the core–shell latex particles were successfully synthesized by using PMMA as the interlayer between the core and PSt-layer. And the hollow structure formed with alkali post-treatment. Here, we used MAA as unsaturated acid because the carboxyl groups of MAA could embed in the core latex particles more effectively, which was also favorable for encapsulating of the shell [22]. It was found that small amount of the crosslinking agent, EGDMA and DVB, could crosslink the core and shell polymer chain to prevent the diffusing of shell polymer chain which increased the encapsulation efficiency of the shell polymerization [23].

3.1. Preparation and morphology of core latex particles

The influence of MAA content on preparation of core latex particles (PBMM) was investigated. The results are shown in Table 3. It was found that the conversion got to 99.0% if MAA content was from 10.0% to 30.7%. However, some coagulation generated when the MAA content was more than 30.7%. The particle size increased with increasing of MAA content. The reason is that it would increase superfluous MAA oligomer and carboxyl-enriched poly-



Scheme 1. Preparation of the latex particles for with different morphological features.