Colloids and Surfaces A: Physicochem. Eng. Aspects 503 (2016) 94–100

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

An efficient strategy for preparation of polymeric Janus particles with controllable morphologies and emulsifiabilities

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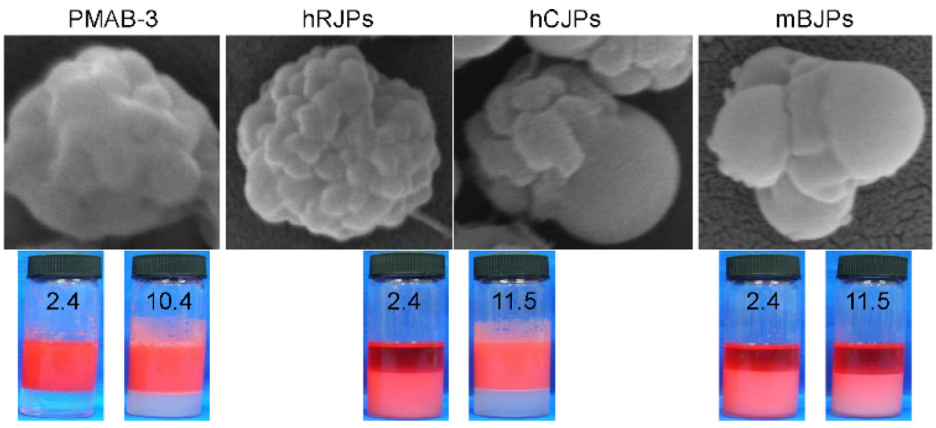
HIGHLIGHTS

- A family of polymeric JPs with high yields was synthesized via EfEP.
- Controllable morphology was achieved by simply adjusting amounts of monomers.
- Amphiphilic and double-faced particles had self-assembly behavior.
- Polymeric JPs possessed special Pickering emulsifiabilities.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 December 2015
Received in revised form 6 May 2016
Accepted 8 May 2016
Available online 11 May 2016

Keywords:
Amphiphilic Janus particles
Controllable morphology
Emulsifiability
Pickering emulsifier
Emulsifier-free emulsion polymerization

ABSTRACT

A family of polymeric Janus particles with submicron sizes of 450 ~ 700 nm has been facilely synthesized via one-step and two-step one-pot emulsifier-free emulsion polymerization (EfEP), a typical simple, time-saving and efficient method for practical production of pure polymer microparticles. The spherical, spherical bulge-like, half-raspberry, half-cauliflower and multiple-bulge morphologies in their evolution from small to large bulges are achieved by simply adjusting the amounts of hydrophilic or hydrophobic monomers based on controllable phase separation of hydrophobic copolymer. Furthermore, these amphiphilic and double-faced particles with different surface properties possess special Pickering emulsifiabilities. For example, with controlling circumstance from acidic to alkali solutions, they start from stabilizing O/W emulsion for spherical bulge-like Janus particles, phase inversion of emulsions, to W/O emulsion for multiple-bulge Janus particles. The key characteristics are without complex preparation process from masking step or multi-step polymerization, also significant strategy for preparation of structural and functional polymer microparticles, such as controllable morphologies and emulsifiabilities.

1. Introduction

During the few past decades, the development of high-performance materials from structural applications to special functions has been focused on the design and synthesis of par-

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http://dx.doi.org/10.1016/j.colsurfa.2016.05.025
0927-7757/

ticles with core-shell [1], multi-shelled [2], anisotropic [3] and Janus [4] structures, because these structured particles with specific shapes and surface reactive groups have important and potential applications in the fields of catalysts, biosensors, drug delivery and smart coatings [5–7]. Müller and coworkers [8] demonstrated that polymeric Janus micelles as supracolloidal dispersants could facilitate the dispersion of multi-walled carbon nanotubes in a variety of solvents including water. Skelhon et al. [9] reported the self-assembly of 'hard-soft' micron-sized Janus particles (JPs) into controllable structures of clusters in aqueous media. As a class of important functional materials with anisotropic structures, JPs [10], possessing spherical, cylindrical, disk-like, raspberry-like, various dumbbell-shaped or any of a variety of other shapes, can be fabricated from many strategies [11–13] typically including masking [14], block copolymer self-assembly and controlled phase separation. Amphiphilic JPs are highly efficient in the compatibilization of emulsions and immiscible polymer blends [15]. Janus polystyrene nanoparticles have also been used directly as stabilisers in the ab-initio emulsion polymerization to control polymer particle size and particle size distribution [16]. Crucially, work by Adamsa et al. [17] and Isa et al. [18] showed that the surface morphologies of amphiphilic JPs could be dominated. Ruhland et al. [19] investigated the self-assembly behavior of Janus spheres, Janus cylinders, and Janus discs at a liquid–liquid interface. The JPs with different geometries possessed different adsorption kinetics, different packing behaviors, different energy barriers, different equilibrium values for the interfacial tension. Zou et al. [20] reported structure-controllable supracolloidal helices by appropriately tuning softness of JPs, including single helices, double helices, and Bernal spirals. Obviously, the unique performances of polymeric JPs greatly depend on anisotropic shapes and asymmetric spatial distribution of compositions and functionalities [21]. To be sure, controllable design of particle shapes and properties is of great interest both from an academic and applications perspective.

Many synthesis methods, including seed dispersion/emulsion polymerization [22], swelling polymerization [23], microfluidic technique [24,25], phase separation of binary blends [26,27] and self-assembly of colloids [28], have been developed for controllable morphologies [29] of polymer particles. However, most of methods or techniques have drawbacks from complex instruments, tedious processes to time-consuming swelling state [30], which leads to low yields. Comparing with the above methods for polymeric JPs, emulsifier-free emulsion polymerization (EfEP) is highly advantageous in streamlining processes because of its simpleness and high yield in the aqueous phase, especially for the synthesis of amphiphilic polymer particles. It could also effectively avoid the effect of residual emulsifiers on performances of polymer materials. However, as we know, there are few papers about synthesis of controllable morphologies and amphiphilicities of polymeric JPs. Although Niu et al. [31] reported that EfEP could endow anisotropic polymer particles with controllable morphologies based on non-directional phase separation, it is not suitable to synthesize amphiphilic JPs. Therefore, efficient synthesis of polymeric JPs with controllable morphologies and emulsifiabilities is still a great challenge so far. Our group has focused on the study of special polymer materials prepared by radical copolymerization of simple and efficient methods [32]. We observed the influence of emulsifiers on shape and size of synthetic particles in the emulsion copolymerization of same monomers [4,33]. And the half-cauliflower amphiphilic Janus particles with pH-switchable emulsifiabilities could be synthesized by one-pot facile methods. In this work, a family of amphiphilic Janus-type particles was synthesized by controllable phase separation in the simple one-step and one-pot EfEP. Surprisingly, their characterizations showed that the morphologies from smooth, bulge-like, raspberry, cauliflower to multiple-bulge surfaces and different emulsifiabilities could be adjusted by only changing the amounts of monomers. Due to preparation process without swelling process, volatile organic solvents and emulsifiers, this is the simplest way to synthesize amphiphilic JPs up to now, which is very important for synthetic polymers with various morphologies and properties by adjusting function monomers via EfEP.

Table 1
Recipe [a] for the synthesis of controllable double-faced particles in the second step polymerization.

Sample	Hydrophobicmonomers		KPS solution (mL)
	St (g)	BA (g)	
hRJPs	2.5	0.5	12
hCJPs	5.0	1.0	24
mBJPs	10.0	2.0	48

[a] PMAB-2 latex as seeds.

2. Experimental section

2.1. Materials

Methacrylic acid (MAA, 98.0%), methyl methacrylate (MMA, ≥99.5%), butyl acrylate (BA, ≥99.0%), styrene (St, ≥98.0%) and toluene (≥99.5%) were purchased from Tianjin kaixin chemical industry co., LTD. China. Potassium persulfate (KPS, AR), sodium hydroxide (NaOH, AR), hydrochloric acid (HCl, AR) and the above reagents were used as received. Distilled water (pH = 7.04) was used throughout.

2.2. Preparation of amphiphilic seed particles

The amphiphilic seed particles (PMAB) of copolymerization of MAA, MMA and BA were prepared by one-step EfEP. 40 mL of distilled water was first added into a round-bottom flask, and heated to 80 °C. 6 mL of KPS solution (3 mg/mL) was quickly added into the flask. After constant stirring for 20 min, the comonomer mixture and 14 mL of KPS solution were simultaneously dropwise at constant feeding rates (10 drops/minute) added into mixture. Then, the reaction system was kept for 2 h until copolymerization was complete. Here, we could adjust the components of comonomer mixture to prepare spherical PMAB-1, spherical PMAB-2 and spherical bulge-like PMAB-3 particles in the presences of MAA/MMA amounts (1.2 g/2.8 g, 1.5 g/2.5 g and 1.8 g/2.2 g, respectively) and 2.0 g of BA.

2.3. Preparation of controllable double-faced particles

The controllable double-faced microparticles were simply prepared by one-pot EfEP. The PMAB-2 latex was directly used as seeds. The half of KPS solution (2.5 mg/mL) was quickly introduced into the PMAB-2 latex. Then residual KPS solution and hydrophobic monomers (Table 1) were slowly dropwise added into the seed latex. Finally, the half-raspberry JPs (hRJPs), half-cauliflower JPs (hCJPs) and multiple-bulge JPs (mBJPs) were prepared until the copolymerization was finished for another 2 h.

2.4. Preparation of polymeric films

The aqueous latex containing 0.3 wt% of colloidal particles was first homogeneously dropped on the clean glass. And the polymeric film was prepared by horizontal hot air drying (80 °C) for 2 h. The other film was prepared by vertical deposition method as follows. The same latex was added into a glass vial, then clean glass was vertically placed in the vial. After standing for 72 h, the glass was