Journal of Saudi Chemical Society (2016) **xxx**, xxx–xxx

King Saud University

**Journal of Saudi Chemical Society**

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

# Tuning the morphology of amphiphilic copolymer aggregates by compound emulsifier via emulsion–solvent evaporation

**Xiaomei Gao [1], Fei Gao [1], Lingzhi Chen, Yuan Yao *, Tao Chen, Shaoliang Lin ***

*Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China*

Received 18 April 2016; revised 16 May 2016; accepted 16 May 2016

**KEYWORDS**

Emulsion-solvent evaporation;
Compound emulsifier;
HLB value;
Aggregate structure

**Abstract** A series of poly(4-vinylpyridine)-*b*-poly{6-[4-(4-butyloxyphenylazo)phenoxy]hexyl methacrylate} (P4VP-*b*-PAzoMA) were employed to fabricate aggregates via the emulsion–solvent evaporation method. The emulsion was stabilized by compound emulsifier composed of SDS and span60. By tuning the ratio of two emulsifiers, P4VP-*b*-PAzoMA could self-assemble into various morphologies including porous microspheres, tremella-like aggregates, bowl-like aggregates and wrinkled microspheres. The transformation of the morphologies could be ascribed to three major aspects: the stability of emulsified chloroform droplets, the permeation of water into chloroform and the dispersity of the interior water droplets with regard to different HLB values. Besides, the morphology could even be tuned by changing the block ratio and the concentration of P4VP-*b*-PAzoMA, and the HLB dependent morphology changing was also proved within other block ratio or different concentration. The study uncovers a convenient and effective technique to manipulate the morphology of amphiphilic copolymer aggregates.

## 1. Introduction

Amphiphilic block copolymer (BCP) can self-assemble into various regular morphologies [1–9] including spheres, cylinders, bicontinuous structures, lamellae, vesicles, and complex or hierarchical assemblies that received increasing concern in drug delivery [10,11], growing templates [12–14], nanophotonics [15], optical nanoimaging [16] due to their structural and chemical diversity. Conventional fabrication procedure of BCP micelles involves dissolution in a good solvent for both blocks followed by addition of a selective solvent (typically water) for the corona block [8]. The aggregate structure mainly

---

* Corresponding authors.
E-mail addresses: yaoyuan@ecust.edu.cn (Y. Yao), slin@ecust.edu.cn (S. Lin).

[1] These authors contributed equally to this work.

Peer review under responsibility of King Saud University.

**Production and hosting by Elsevier**

http://dx.doi.org/10.1016/j.jscs.2016.05.007
1319-6103

depends on the composition and molecular weight of the copolymer, which requires synthesizing a number of new polymers for tuning the aggregate morphologies.

Recently, an alternative convenient route to form polymeric micelles based on the interfacial instabilities in shrinking emulsion droplets was developed to tune the aggregate structure of amphiphilic block copolymer. In this "emulsion-solvent evaporation" method [17–26], the copolymer was dissolved in a volatile water-immiscible solvent and then dispersed in aqueous phase in the presence of surfactant, followed by slow removal of the solvent from the droplets by diffusion through the aqueous phase and evaporation to obtain the final copolymer aggregates. On account of increasing content of copolymer within the droplets, self-assembly behavior takes place by virtue of the interfacial instabilities. Investigations by Zhu et al. provided plenty and informative insights in this field including the fabrication of ordered fantastic morphologies, efficient encapsulation of hydrophobic materials (especially nanoparticles) into the core of assemblies, etc. [27–29]. They successfully fabricated spherical and cylindrical aggregates from polystyrene-*b*-poly (ethylene oxide) (PS-*b*-PEO) chloroform solution through the interfacial instability of emulsion droplets and loaded iron oxide nanoparticles in the micelles [29]. Su et al. [21,30] had studied the micelle formation via the emulsion-solvent evaporation process of PS-*b*-PEO in the presence of poly(acrylic acid) (PAA) and investigated the effect of solvent evaporation rate on the micelle morphology. The aggregates fabricated from more volatile solvent dichloromethane were cylindrical micelles, while vesicles were prepared in 1,2-dichloromethane with slower evaporation rate. In our previous work [31], photo responsive block copolymer was employed to fabricate porous microsphere through the above-mentioned procedure. The pore size and diameter of the microsphere were controlled by tailoring the concentration of polymer and surfactant. The necessity of amphiphilicity of polymer for the formation of porous sphere was also proved.

Accordingly, self-assembly behavior via this "emulsion-solvent evaporation" method is closely associated with (1) the interfacial force between the BCP droplet and the aqueous phase, and (2) the stretching/bending penalty of BCP chains induced by the spatial confinement effect [32–34]. By the modulation of interfacial interaction using a mixture of cetyltrimethyl ammonium bromide (CTAB) and polyvinyl alcohol (PVA), Kim et al. [35] fabricated colloidal patchy particles with a variety of three-dimensional shapes including snowmen, dumbbells, triangles, tetrahedral and raspberry via the evaporation-induced assembly of polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer (BCP) in an oil-in-water emulsion. Hawker et al. [36] demonstrated the control of polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) particle shape by tuning the surface interaction via mixed surfactant system. Onion-, ellipsoids- and reverse onion-like structure were obtained by using surfactant CTAB, CTAB mixing with hydroxyl group terminated CTAB (HO-CTAB), and HO-CTAB, respectively. However, the effect of hydrophile-lipophile balance (HLB) value, which is the characteristic of emulsifying capacity on the self-assembly of copolymer, has not been systematically investigated in consideration that it influences the interface between the emulsion droplet and aqueous phase and exerts significant impacts on the final morphologies.

Herein, we report a study of surfactant mediated emulsion-solvent evaporation in regard to the effect of HLB value. In this work, a series of poly(4-vinylpyridine)-*b*-poly{6-[4-(4-butyloxyphenylazo) phenoxy]hexyl methacrylate} (P4VP-*b*-PAzoMA) copolymers were dispersed in oil-in-water emulsion with different HLB values by tuning the ratio of typical O/W surfactant sodium dodecyl sulfonate (SDS, HLB value = 40) and typical W/O surfactant sorbitan monostearate (span60, HLB value = 4.7). The variation of compound emulsifier's HLB values was found to greatly influence the morphology of copolymer aggregates. Porous microspheres, tremella-like aggregates, bowl-like aggregates and wrinkled microspheres appeared gradually with the decrease of HLB values of the compound emulsifier. To elucidate the thermodynamic formation mechanism of various structures, the evolution of the emulsion droplets was monitored by an optical microscope. Moreover, the influences of block ratio and concentration on the morphology of P4VP-*b*-PAzoMA aggregates were also investigated. Meanwhile, the HLB value-dependent morphology changing has been even observed under other block ratio in different concentration.

## 2. Experimental

### 2.1. Materials

SDS, a typical W/O surfactant, of 96% purity was purchased from Shanghai Lingfeng chemical reagent co., Ltd. Span60, a typical O/W surfactant, was purchased from Shanghai Titan technology co., Ltd. Chloroform ($CHCl_3$, AR) was purchased from Shanghai Chemical Reagent co., Ltd. Deionized water was obtained from Millipore water purification system. All the materials were used as received without further purification.

### 2.2. Synthesis of diblock copolymer P4VP-b-PAzoMA

The RAFT polymerization of P4VP-*b*-PAzoMA was conducted as reported in our previous work [37]. The chain transfer agent P4VP (P4VP-CTA) was first synthesized by using 4-cyano-4-(phenyl-carbonothioylthio) pentanoic acid (CPPA) as the chain transfer agent. In a typical protocol, the monomer AzoMA (1.2 g, 3 mmol), P4VP-CTA macro agent (142.8 mg, 0.02 mmol) and azobisisobutyronitrile (AIBN) (0.82 mg, 0.005 mmol) were dissolved in 5 mL tetrahydrofuran (THF). The reaction mixture was sealed in a 25 mL round-bottomed flask and purged with $N_2$ for 20 min before immersing into the oil bath at 70 °C for 24 h. Here, three different diblock copolymers (Scheme 1) with distinctive block efficiencies were synthesized (Table 1).

### 2.3. Sample preparation

Firstly, definite amounts of P4VP-*b*-PAzoMA copolymer and span 60 were dissolved in chloroform to a desired concentration. SDS of certain concentration was dissolved in deionized water. O/W emulsion with mixed emulsifier was generated by mixing chloroform solution with tenfold premium in volume aqueous phase through vigorous stirring at the speed of 500 r/min with 3 min. All the above experiments were carried out

Please cite this article in press as: X. Gao et al., Tuning the morphology of amphiphilic copolymer aggregates by compound emulsifier via emulsion–solvent evaporation, Journal of Saudi Chemical Society (2016), http://dx.doi.org/10.1016/j.jscs.2016.05.007