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

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

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.

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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...
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 amphiphility 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 cetyltrimethylammonium 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 hydrophilic-lipophilic 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-(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 sulfate (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 (CHCl3, 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 N2 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...
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3. Results and discussion

3.1. Aggregates morphologies of P4VP-b-PAzoMA14 obtained from variable HLB values

Figs. 1 and 2 show the morphology of copolymer aggregates formed from 5 mg mL⁻¹ P4VP₁₁₅-b-PAzoMA₁₄ stabilized by 3 mg mL⁻¹ mixed emulsifier with the HLB values varying from 40 to 20. Noteworthy, it is an O/W emulsion with water as continuous phase and chloroform as disperse phase in our system. Due to the low HLB value, it is difficult to stabilize the chloroform drops in water [40] when only span 60 presented as the surfactant. A large number of precipitates appeared in the mixed solution. Microscopically, the aggregates examined by SEM gathered together. Hence, we did not investigate the aggregates in the presence of only span 60. Besides, the aggregates formed from the compound emulsifier with relatively low HLB value showed similarity. Therefore, we merely investigate the HLB value from 40 to 20. When the HLB value of the mixed emulsifier was 40, i.e. the emulsifier was composed of SDS, the emulsion droplets tended to form analogous porous microsphere with relatively integrated surface as observed by SEM (Fig. 1a) and TEM (Fig. 2a). When the HLB value decreased to 38, the microspheres were observed containing a large amount of pores of diverse sizes (Figs. 1b and 2b). Microspheres with relatively uniform pores were obtained when the HLB value was adjusted to 36 (Fig. 1c and 2c). The pore size was measured with range of 0.6–1.0 μm. When the HLB value was tuned to 30, tremella-like aggregates were observed. It looked like the inner wall of the pores had collapsed (Fig. 1d). In addition, compared with Fig. 2c, it is apparently observed that electron beam suffered less transmission with the decreasing of HLB in Fig. 2d, representing the core of aggregates as more compact. When the HLB value was 26, bowl-like aggregates with critical small size appeared in Figs. 1e and 2e. The HLB value continued to decrease to 20, the emulsion formed wrinkled aggregates with wide size distribution (Fig. 1f) and even allowed lower beam transmission, namely more compact structure (Fig. 2f). The relationship between the aggregates size and HLB values of compound emulsifiers was elucidated in Fig. 3, which illustrates that sizes of aggregates formed by emulsifiers with relative higher HLB values (> 30) were larger than that by emulsifiers with lower HLB values (< 30), and came to a smallest value when HLB value was 26.

### Table 1 Characteristics of P4VP-b-PAzoMA diblock copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ [g/mol]</th>
<th>$M_w/M_n$</th>
<th>$f_{PAzoMA}$ [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4VP₁₁₅-b-PAzoMA₁₄</td>
<td>2.67 × 10⁴</td>
<td>1.50</td>
<td>54.4</td>
</tr>
<tr>
<td>P4VP₁₆₅-b-PAzoMA₆₅</td>
<td>1.49 × 10⁴</td>
<td>1.15</td>
<td>17.9</td>
</tr>
<tr>
<td>P4VP₁₆₅-b-PAzoMA₁₃₃</td>
<td>7.17 × 10⁴</td>
<td>1.23</td>
<td>90.0</td>
</tr>
</tbody>
</table>

a Calculated by GPC in THF with calibrated PS standard at 35 °C.
b Calculated by GPC in THF with calibrated PS standard at 35 °C.
c The PAzoMA content was determined by ¹H NMR in CDCl₃.

at room temperature. The total concentration of the compound emulsifier was kept at 3 mg mL⁻¹ based on amount of water added. It is well known that the HLB value of SDS and span 60 was 40 and 4.7, respectively [38,39]. The HLB of the compound emulsifier was tuned by the compositions of span 60 and SDS as given in Eq. (1):

\[
\text{HLB} = \frac{w_1}{w_1 + w_2} \times 40 + \frac{w_2}{w_1 + w_2} \times 4.7
\]

where $w_1$, $w_2$ refer to the span 60 and SDS mass content of the mixed emulsifier, respectively. Subsequently, chloroform was allowed to be evaporated into the surrounding air at 30 °C without stirring for 24 h. Upon removal of chloroform, the organic/water interface became rough [27].

2.4. Characterization

2.4.1. Transmission electron microscopy (TEM)

The morphologies of emulsion droplets were characterized by TEM (JEM-2100F, JEOL) operated at an accelerated voltage of 200 kV. Drops of the suspension were placed on a copper grid coated with carbon film and then dried at room temperature. The samples were sputtered by Au to enhance conductivity of samples before observation.

2.4.2. Scanning electron microscope (SEM)

The surface profiles of the resulting aggregates were examined by field-emission scanning electron microscope SEM (S-4800, HITACHI) operated at an accelerated voltage of 15 kV. Drops of suspension were placed on a silicon wafer and then dried at room temperature. The samples were sputtered with Au to study the formation and distinction of shape-changing aggregates via emulsion and solvent evaporation, optical
microscope was utilized to monitor the evolution of the emulsion droplets containing 5 mg mL\(^{-1}\) P4VP\(_{115}\)-b-P\(_{34}\) and 3 mg mL\(^{-1}\) mixed emulsifier with HLB values of 38, 30, 26, 20 respectively (Fig. 4). Limited by the resolution and focusing delay of the optical microscope, only the significant deformation could be observed.

It was clearly observed that optical micrographs of the as-formed emulsion droplets with mixed emulsifiers of different HLB values looked rather similar, namely, emulsion droplets were all much bigger than 10 \(\mu\)m with little swimming drops of water of slightly different size on them (Fig. 4a, e, i). After almost 15 min, upon continuous removal of CHCl\(_3\), it showed that emulsion droplets with mixed emulsifier of different HLB values showed enlarging roughness, the distortion of their shapes, as well as the size decrease with time elapsing in Fig. 4. The process is under the synergistic action of mixed emulsifier and amphiphilic copolymer, which can reduce the interfacial tension between the disperse phase oil and the continuous phase water.

Figure 1  SEM images of shape-changing aggregates from emulsions containing 5 mg mL\(^{-1}\) P4VP\(_{115}\)-b-P\(_{34}\) and 3 mg mL\(^{-1}\) mixed emulsifier with different HLB values at (a) 40; (b) 38; (c) 36; (d) 30; (e) 26; (f) 20.

Figure 2  Bright field TEM images of shape-changing aggregates formed from emulsions containing 5 mg mL\(^{-1}\) P4VP\(_{115}\)-b-P\(_{34}\) and 3 mg mL\(^{-1}\) mixed emulsifier with different HLB values at (a) 40; (b) 38; (c) 36; (d) 30; (e) 26; (f) 20.
However, great changes and obvious differences occurred with various HLB values. As shown in Fig. 4a–d, spherical emulsion droplets contracted, deformed (Fig. 4b) and then recovered to relative smaller spheres when the HLB value was 38. At the HLB value of 30, emulsion droplets shrank into the core swiftly within 14 s before the morphology fixed, resulting in a tremela-like aggregates (Fig. 4a–d). When the HLB value turned down to 20, emulsion droplets shrank into the core before the morphology fixed for almost 26 s, leaving the formation of wrinkled aggregates (Fig. 4p). Particularly, the final aggregates were fairly small with the HLB value of 26. According to Fig. 4i and l, the aggregates would disintegrate into some small aggregates at the later stage of CHCl3 evaporation.

On the basis of the discussion above, a mechanism of the formation of various aggregates was speculated. Here, emulsifiers were used to stabilize the CHCl3 droplets containing P4VP-b-PAzoMA to avoid the gathering of the aggregates. The evaporation of CHCl3 resulted in a prominent shrinkage in size of the droplets and an increase of polymer concentration accordingly. If there was only the single surfactant SDS, water molecules would diffuse into the droplets after CHCl3 evaporation.

![Figure 3](image)

**Figure 3** The plot of relationship between the HLB value and the diameter of aggregates formed from emulsions containing 5 mg mL\(^{-1}\) P4VP\(_{115}\)-b-PAzoMA\(_{34}\) and 3 mg mL\(^{-1}\) mixed emulsifier. Error bars represent standard deviation.

![Figure 4](image)

**Figure 4** Optical micrographs showing the evolution of the emulsion droplets containing 5 mg mL\(^{-1}\) P4VP\(_{115}\)-b-PAzoMA\(_{34}\) and 3 mg mL\(^{-1}\) mixed emulsifier with different HLB values during chloroform evaporation. The HLB values were (a–d) 38; (e–h) 30; (i–l) 26; (m–p) 20. The time elapse for the images was at (a) 5 min; (b) 15 min 23 s; (c) 15 min 40 s; (d) 17 min; (e) 5 min; (f) 15 min; (g) 16 min 39 s; (h) 16 min 53 s; (i) 5 min; (j) 14 min; (k) 15 min 32 s; (l) 16 min; (m) 5 min; (n) 17 min 19 s; (o) 17 min 31 s; (p) 17 min 55 s.

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evaporation, subsequently the hydrophilic P4VP block and some emulsifiers extended toward water while the hydrophobic PAzoMA block formed the core. This process effectively reduced the interfacial energy between water and emulsion droplets and developed porous complex micelles. Therefore the W/O surfactant with relatively low HLB value span 60 affects the formation of P4VP-b-PAzoMA aggregates in two ways. (1) It reduced the amount of water molecules permeated from the continuous water phase into the emulsion droplets by enhancing the thickness and viscosity of the surfactant lamellae with increasing of its ratio in the oil phase \[41,42\]. As a result, the aggregates suffered the transition from porous microsphere to tremela-like and wrinkled aggregates with the decreasing of HLB value. Meanwhile, noteworthy shrinkage of aggregates was observed as fewer holes were formed inside the droplets owing to the impediment of water permeation, which resulted in smaller size and transmission in bright field TEM images. As discussed in 3.1, the aggregates became larger when the HLB value of compound emulsifier was greater than 30. (2) It exerted significant influence on the stability of W/O/W double emulsion \[43–45\] constructed by CHCl3 droplets and interior water permeated during the course of CHCl3 evaporation. As a W/O surfactant with low HLB value, span 60 impaired the stability of dispersed CHCl3 droplets containing polymers in the continuous water phase. As illustrated in Figs. 1e and 2e, the aggregates were disintegrated when adjusting the HLB value to 26. It can be embodied in Fig. 1f that the aggregates showed a wide particle size distribution, which was another manifestation of low emulsion stability. Whereas, for the water-in-oil system constructed by CHCl3 droplets as the continuous phase and permeated water as the dispersed phase, water droplets have better stability and became homo-dispersed by relatively higher weight ratio of span 60, inducing homo-dispersed pores in aggregates. In addition, as shown in Fig. 1a–c, small but homogenous pores can be obtained by reducing the HLB value of compounded emulsifier from 40 to 36.

3.3. Aggregates formed from P4VP-b-PAzoMA at various concentrations

Fig. 5 showed the SEM images of aggregates with copolymer concentration changing from 15 to 2.5 mg mL\(^{-1}\) while the HLB values were 38 and 20. At the HLB value of 38, pores in the aggregates formed from 15 mg mL\(^{-1}\) P4VP\(_{115}\)-b-PAzoMA\(_{34}\) were large and uneven (Fig. 5a). Subsequently, when polymer concentration decreased to 10 mg mL\(^{-1}\), several
relatively smaller pores appeared except for the large pores. On further decrease in the polymer concentration to 2.5 mg mL\(^{-1}\), the pores became extremely uniform and tiny (Fig. 5c). When the HLB value was decreased to 20, pores in the aggregates turned smaller and disappeared along with wrinkled surface (Fig. 5d–f). This changing trend should be attributed to the following explanation. Firstly, the solution viscosity increases at a higher concentration, which induces more difficult movement of polymer chain. Additionally, there are more azobene moieties in higher concentration tending to form stronger \(g\)-\(g\) stacking which limits the segments movement\(^{[46]}\). When the concentration was relatively high, movement of polymer chains is difficult and the aggregate structure could be immobilized as sphere shaped emulsified droplets during the evaporation process. When the concentration was low, segment moves easily and the structure collapsed and wrinkled after CHCl\(_3\) evaporation.

Besides, when polymer concentrations were 15 mg mL\(^{-1}\), 10 mg mL\(^{-1}\), or 2.5 mg mL\(^{-1}\), wrinkled aggregates appeared with mixed emulsifier HLB values changed from 38 to 20 (Fig. 5), which was similar to the aggregate structure transformation when polymer concentration was 5 mg mL\(^{-1}\).

Based on the complementary investigation about the relationship between the polymer concentration, HLB value and the aggregates morphology, the phase diagram of the aggregates as a function of polymer concentration \((c_p)\) and HLB value of mixed emulsifiers is shown in Fig. 6. The overall morphology is wrinkled aggregates at low polymer concentrations and HLB values. For \(c_p = 10\)–15 mg mL\(^{-1}\), HLB value = 20–28, or \(c_p = 2.5\) mg mL\(^{-1}\), HLB value = 26–32, wrinkled aggregates with pores can be generated. The transformation from tremella-like aggregates to other morphological aggregates takes place around HLB value = 30. The effect of polymer concentrations on the overall morphology is insignificant for HLB ≥ 36, with porous microspheres being observed over the entire range of polymer concentration. It is found that the aggregates morphology was influenced by HLB value of mixed emulsifier as well as the polymer concentration.

### 3.4. Aggregates formed from P4VP-b-PAzoMA with various block ratios

As amphiphilic copolymers are similar to macromolecule surfactants, a series of experiments were made to investigate the effect of block length and weight ratio on morphology of aggregates in different HLB values (Fig. 7). The concentration of the polymers and mixed emulsifier was fixed at 5 mg mL\(^{-1}\) and 3 mg mL\(^{-1}\), respectively. The characterization of P4VP-b-PAzoMA copolymers was shown in Table 1.

It is illustrated in Figs. 1a and 7a,d that the decrease of mass ration and chain length of P4VP resulted in larger pores on the aggregates at a fixed HLB value of 40. By comparison between Figs. 1b and 7b, similar variation tendency could be summarized when HLB value of mixed emulsifier was kept at 36. As shown in Fig. 7a–c, the pore size of P4VP\(_{68}\)-b-PAzoMA\(_{153}\) microspheres turned smaller with the decreasing of HLB value of mixed emulsifier, and the pore wall collapsed worse, which was similar to the polymer P4VP\(_{115}\)-b-PAzoMA\(_{6}\) that discussed above. Particularly, as for polymer P4V\(_{115}\)-b-PAzoMA\(_{6}\), significant difference in the morphology of resulting aggregates has been found. For the HLB value of 40, the obtained aggregates were porous microspheres (Fig. 7d). When the HLB value decreased to 36, wrinkled aggregates were fabricated (Fig. 7e). However, there was no obvious morphology change with continuous decrease in HLB value even to 20 (Fig. 7f). This phenomenon could be ascribed to low hydrophobic block content of this copolymer, resulting in nearly deficient amphiphility, which is one of the

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Figure 7  SEM images of shaping-changing aggregates from emulsions consisting of (a–c) P4VP\(_{68}\)-b-PAzoMA\(_{153}\), (d–f) P4VP\(_{115}\)-b-PAzoMA\(_{6}\) at concentration of 5 mg mL\(^{-1}\) and 3 mg mL\(^{-1}\) mixed emulsifier of variable HLB values, which were (a, d) 40; (b, e) 36; (c, f) 20.
prerequisites of the formation of porous microspheres [31]. According to the discussions, it is indicated that the HLB value depended morphology transformation is versatile and effective to tune the morphology of P4VP-b-PAzOMA regardless of the block ratio.

4. Conclusion

In summary, we demonstrated a convenient and effective method for producing P4VP-b-PAzOMA aggregates with various morphologies by compounded emulsifier comprising of SDS and span60 via the emulsion-solvent evaporation method. The morphology variation on aggregates (such as porous microspheres, tremella-like, bowl-like and wrinkled aggregates) was observed with the decreasing of HLB value of the emulsifier. The morphology transformation was attributed to the stability of emulsified CHCl3 droplets, the permeation of water into CHCl3 and the dispersity of the interior water droplets with regard to different HLB values. In addition, the morphology could also be tailored by varying the block weight ratios and concentration of P4VP-b-PAzOMA. This study is anticipated to provide a simple and effective technique to tune the microstructures of amphiphilic copolymer.

Acknowledgements

This work was supported by National Natural Science Foundation of China (51573046 and 51573088). Support from Projects of Shanghai Municipality (14SG29) and Fundamental Research Funds for the Central Universities (NCET-12-0857, B14018 and WD1213002) is also appreciated.

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