

Morphology and Thermoresponse Behavior of Hybrid Micelles of Polystyrene-*b*-Poly((*N*-isopropyl acrylamide)-*co*-(4-vinylbenzyl chloride)) with Prussian Blue*

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Abstract The hybrid micelles of polystyrene-*b*-poly((*N*-isopropyl acrylamide)-*co*-(4-vinylbenzyl chloride)) block copolymer (PS-*b*-P(NIPAM-*co*-VBC)) with Prussian blue (PB) in the corona were prepared by reaction of pentacyano(4-(dimethylamino)-pyridine)ferrate (Fe-DMAP)-attached PS-*b*-P(NIPAM-*co*-VBC) with FeCl₃. The formation of the PB framework inside the micelles was verified by UV-Vis, FTIR and TGA. The morphology of the hybrid micelles was studied by TEM and compared with that of the neat and Fe-DMAP-attached PS-*b*-P(NIPAM-*co*-VBC). It is found that attachment of Fe-DMAP may change the short rod-like micelles of the neat PS-*b*-P(NIPAM-*co*-VBC) into spherical ones and lead to a smaller micelle size. The morphology of the hybrid micelles may be altered or remain unchanged after formation of the PB framework, depending on the chain structure of PS-*b*-P(NIPAM-*co*-VBC) and starting concentration. The thermoresponse behavior of different micelles was studied using DLS. It is observed that attachment of Fe-DMAP can improve the hydrophilicity of the P(NIPAM-*co*-VBC) block, leading to weaker hysteresis of the micelle size during the heating and cooling cycle. However, the crosslinked PB framework in the micellar corona may result in a more evident hysteresis phenomenon and blur the two-stepwise change of the micellar size with temperature.

Keywords: Block copolymer; Thermosensitivity; Prussian blue; Micelle; Hybrid.

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-015-1656-5>.

INTRODUCTION

The self-assembly of block copolymers is known to generate a variety of different morphologies because of phase separation in the solid state and selective solvation in selective solvents and provides an effective route to different nanostructures^[1–8]. Combining of transition metals with one of the blocks is an attractive method for expanding properties of the resulting materials. Especially, the self-assembly based on block copolymers/transition metal compound hybrids is a very promising strategy for the preparation of organic-inorganic hybrid functional materials, which has attracted many researchers for decades^[9–12].

Prussian blue (PB) is a metal-organic coordination framework of Fe₄[Fe(CN)₆]₃·*n*H₂O constructed from Fe²⁺ and Fe³⁺ vertices bridged by cyanide ligands. PB and its analogues can exhibit electronic delocalization and magnetic communication between the metal centers, leading to fascinating optical, electronic and magnetic properties^[13–15]. In particular, nanostructured PBs, primarily nanoparticles, have been extensively explored for applications including electrochromic materials^[16–18], molecule-based magnets^[19], electrocatalysts^[20–22] and

* This work was financially supported by the National Natural Science Foundation of China (No. 21274130).

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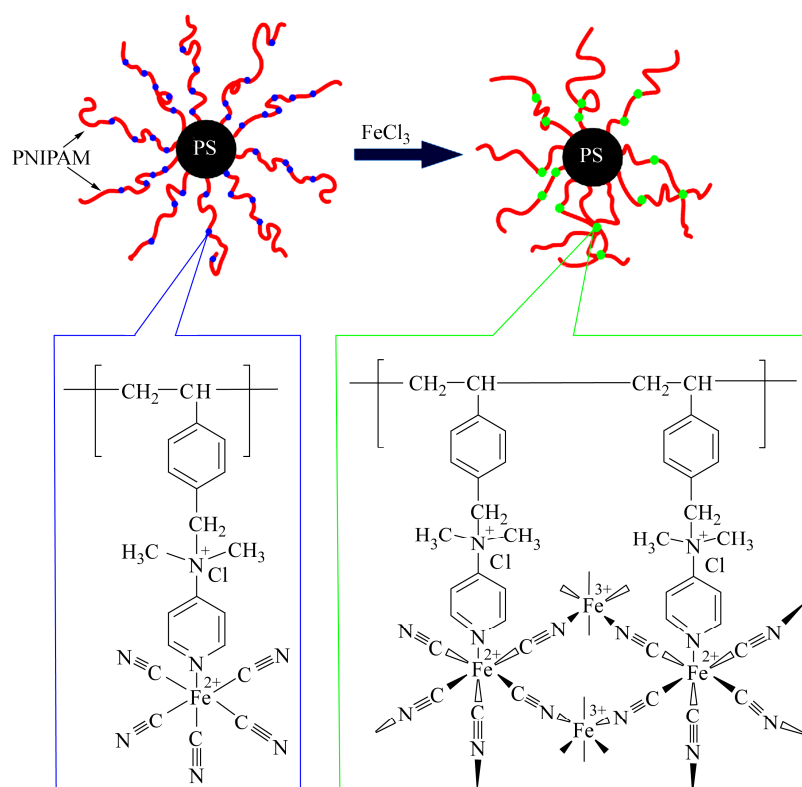
Received November 6, 2014; Revised November 27, 2014; Accepted November 27, 2014

doi: 10.1007/s10118-015-1656-5

photoswitches.

Wang reported a conceptually new method for the synthesis of PB nanoshells with tunable size via miniemulsion periphery polymerization using a triblock copolymer terminated with ((dimethylamino)pyridine) ferrate as PB precursor^[23, 24]. They further synthesized monodispersed soluble PB metal-coordination nanospheres in H₂O/EtOH using pentacyanoferrate-coordinated block copolymers as templates^[25]. MacLachlan and co-workers recently synthesized worm-like PB particles from the micellar templates of bipyridinium functionalized block ionomer (BI) *via in situ* ligand exchange and the following confined metal coordination polymerization^[9]. They also used similar metal-containing BI to fabricate soluble metal organic capsules through emulsion-induced assembly and investigated the encapsulation of methylene blue inside the structure^[26].

In our previous work, we synthesized a novel Fe-containing block copolymer by quaternization of pentacyano(4-(dimethylaminopyridine))ferrate (Fe-DMAP) with the 4-vinylbenzyl chloride units in polystyrene-*b*-poly((*N*-isopropyl acrylamide)-*co*-(4-vinylbenzyl chloride)) (PS-*b*-P(NIPAM-*co*-VBC)) to yield Fe²⁺ coordinated block copolymer PS-*b*-P(NIPAM-*co*-VBC)/Fe-DMAP^[27]. Herein we further cross-link the Fe-DMAP precursor in the PS-*b*-P(NIPAM-*co*-VBC)/Fe-DMAP by addition of Fe³⁺ to form PB framework, as shown in Scheme 1. Since PS-*b*-P(NIPAM-*co*-VBC) in aqueous solution can self-assemble into micelles with hydrophilic P(NIPAM-*co*-VBC) block as corona and PS as core, the formed PB framework is dispersed in the corona of the micelles and thus water-soluble. Moreover, it is well known that PNIPAM is thermoresponsive and exhibits a lower critical solution temperature (LCST) in aqueous solution. As a result, it is interesting to study the thermoresponsive behavior of the PS-*b*-P(NIPAM-*co*-VBC)/PB hybrid micelles in aqueous solution. To our best knowledge, synthesis of the hybrid micelles of PB with thermo-responsive block copolymers and the thermo-responsive behavior of the hybrid micelles have not been reported in literature.



Scheme 1 Schematic illustration for the synthesis of PS-*b*-P(NIPAM-*co*-VBC)/PB hybrid micelles in aqueous solution

EXPERIMENTAL

Materials

FeCl₃ were purchased from Sigma-Aldrich and used without further purification. Tetrahydrofuran (THF) was refluxed with sodium flakes and distilled prior to use. Deionized water was distilled twice prior to use. Two PS-*b*-P(NIPAM-*co*-VBC) block copolymers (BCP-1 and BCP-2) and the corresponding Fe-DMAP-attached PS-*b*-P(NIPAM-*co*-VBC) (BCP-1/Fe-DMAP and BCP-2/Fe-DMAP) were synthesized according to our previous work^[27]. The fraction of VBC attached with Fe-DMAP was calculated from ¹H-NMR (see Supporting Information). 80.7% and 42.2% of the VBC units were attached with Fe-DMAP in BCP-1/Fe-DMAP and BCP-2/Fe-DMAP, respectively. The details for preparation of the block copolymers are given in supporting information. The molecular characteristics of two PS-*b*-P(NIPAM-*co*-VBC) block copolymers are listed in Table 1.

Table 1. The molecular characteristics of two PS-*b*-P(NIPAM-*co*-VBC) block copolymers

Sample	M_n^a	PDI ^b	Chemical composition ^a	f_{ps}^c
BCP-1	21060	1.14	PS ₆₅ - <i>b</i> -P(NIPAM ₁₀₁ - <i>co</i> -VBC ₁₉)	32%
BCP-2	36800	1.24	PS ₆₅ - <i>b</i> -P(NIPAM ₂₄₇ - <i>co</i> -VBC ₁₄)	19%

^a Calculated from ¹H-NMR spectra; ^b PDI = M_w/M_n , determined by GPC; ^c Volume fraction of the PS block

Preparation of BCP and BCP/Fe-DMAP Micelles

1.5 mg of PS-*b*-P(NIPAM-*co*-VBC) or BCP/Fe-DMAP was first dissolved in 12.0 mL of THF to obtain a homogeneous solution with a concentration of 0.125 mg·mL⁻¹, then 2.4 mL deionized water was slowly added to the solution under nitrogen atmosphere at a rate of 1 mL·h⁻¹. After being stirred overnight, the resulting solution was sealed in a dialysis tube (cutoff molecular weight = 3500 g mol⁻¹) and dialyzed against deionized water at 25 °C for 3 days to remove THF. The solvent THF was completely removed by exchanging with fresh water for five times. The obtained BCP/Fe-DMAP micellar solution with a final concentration of 0.06 mg·mL⁻¹ was used for characterization and preparation of the PB-containing hybrid micelles in the next step.

Preparation of PB-containing Hybrid Micelles

The PB-containing hybrid micelles were synthesized according to the route illustrated in Scheme 1. A designed amount of FeCl₃ (molar ratio: [Fe³⁺]/[VBC] = 1) was dissolved in 0.2 mL deionized water and the FeCl₃ solution was added dropwise to the aqueous micellar solution of BCP/Fe-DMAP and a transparent dark green solution was yielded. The mixture was stirred at room temperature overnight, then centrifuged at 4500 r·min⁻¹ and filtered to remove any trace of insoluble bulk PB. The resulting solution was sealed in a dialysis tube (cutoff molecular weight = 3500 g·mol⁻¹) and dialyzed against deionized water at 25 °C for 3 days to remove excessive FeCl₃. The final solution containing the hybrid micelles can be freeze-dried to obtain the dark green solid powder or directly used for characterization.

Characterization

Dynamic light scattering (DLS) measurements were performed on a Brookhaven Instrument BI-200SM with a laser wavelength of 636 nm at 25 °C at a scattering angle of 90°. Transmission electron microscopy (TEM) observations were carried out on a JEOL JEM-1230 electron microscope at an acceleration voltage of 80 kV. TEM samples were prepared by dropping 4 μL of the micellar solution onto carbon-coated copper grids. Excessive fluid was absorbed with a piece of filter paper. Subsequently, the samples on the grid were frozen with liquid nitrogen and freeze-dried under the vacuum at -20 °C to avoid the reassembly and aggregation of the micelles during the drying process. Fourier transformation infrared (FTIR) spectra were recorded on a Vector 22 FTIR Spectrophotometer. Thermal gravity analysis (TGA) experiments were performed on a PE-PYRIS1 instrument under nitrogen atmosphere. The heating rate was 10 K·min⁻¹ and the temperature range was from room temperature to 600 °C. Ultraviolet-Visible (UV-Vis) absorption spectra were recorded on a Cary 100 UV-Vis spectrometer at room temperature. The scan range was from 350 nm to 800 nm.

RESULTS AND DISCUSSION

Characterization of PB-containing Hybrid Micelles

PB-containing hybrid micelles were prepared by adding FeCl_3 to the micellar solution of BCP/Fe-DMAP. The formation of PB framework inside the micelles was verified by UV-Vis spectrum. The UV-Vis spectra of Fe-DMAP, BCP-2/Fe-DMAP and BCP-2/PB are illustrated in Fig. 1. Fe-DMAP exhibits an absorption peak at 564 nm, which is attributed to the metal-to-ligand charge transfer. For BCP-2/Fe-DMAP, an absorption peak centered at 549 nm is observed, indicating the attachment of Fe-DMAP to the VBC groups. After reaction of BCP-2/Fe-DMAP with FeCl_3 , a strong absorption peak centered at 670 nm appears, which is ascribed to the Fe^{2+} to Fe^{3+} charge transfer in PB^[23, 28]. The shift of the UV absorption peak confirms the formation of PB framework.

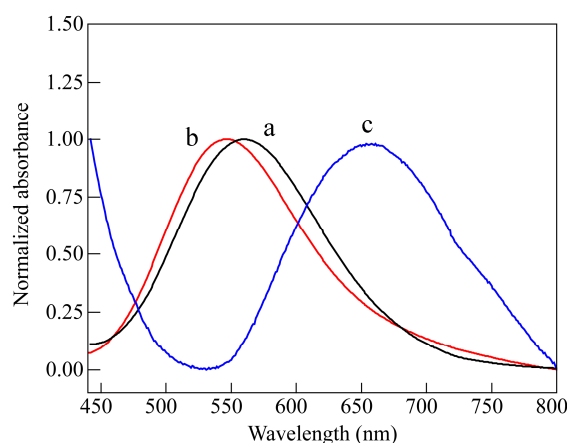


Fig. 1 UV-Vis spectra of (a) Fe-DMAP, (b) BCP/Fe-DMAP and (c) BCP/PB

The neat PS-*b*-P(NIPAM-*co*-VBC), BCP/Fe-DMAP and BCP/PB hybrids were also characterized with TGA, and the weight loss curves under N_2 atmosphere are shown in Fig. 2. Both BCP-1 and BCP-2 are completely decomposed at 600 °C because of their purely organic composition. The weight loss is 90 wt% for BCP-1/Fe-DMAP and 95 wt% for BCP-2/Fe-DMAP, respectively, which can be ascribed to the decomposition of the organic portion in the samples. For the PB-containing hybrids, the weight loss becomes smaller, as compared with that of the corresponding BCP/Fe-DMAP, which is 86 wt% and 90 wt% for BCP-1/PB and BCP-2/PB, respectively. This is due to introduction of Fe^{3+} in the hybrids and thus lower fraction of the organic component.

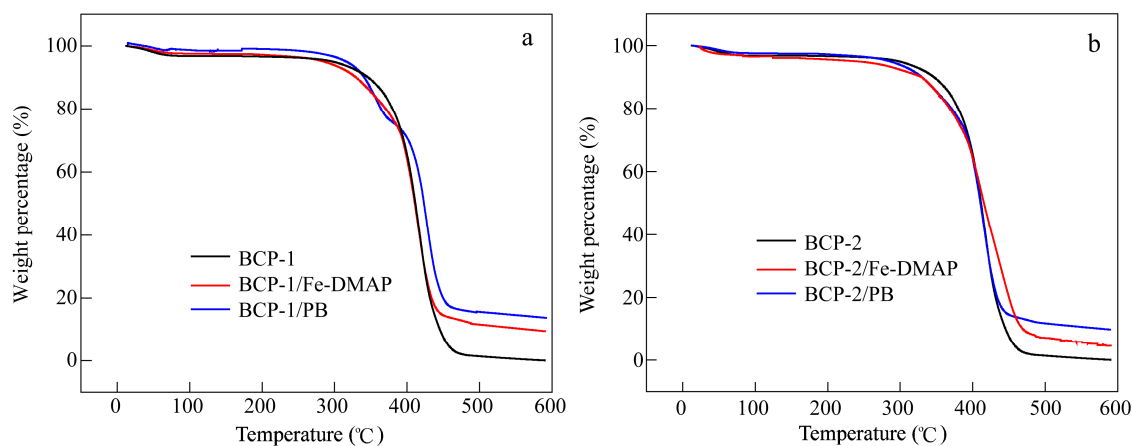


Fig. 2 TGA thermograms of BCP-1, BCP-1/Fe-DMAP and BCP-1/PB (a) and BCP-2, BCP-2/Fe-DMAP and BCP-2/PB (b)

The FTIR spectra of Fe-DMAP, BCP-2, BCP-2/Fe-DMAP and BCP-2/PB are compiled in Fig. 3. A strong absorption at 2057 cm^{-1} due to the CN stretching vibration is observed for Fe-DMAP. Such a band is absent in the neat BCP-2, but it appears again in BCP-2/Fe-DMAP, indicating the attachment of Fe-DMAP to the VBC units. By contrast, the CN stretching band shifts to 2084 cm^{-1} in BCP-2/PB, which is the characteristic of the cyanide bridge of $\text{Fe}^{2+}\text{-CN-Fe}^{3+}$ in PB^[29]. As a result, the formation of PB in the PS-*b*-P(NIPAM-*co*-VBC)/PB hybrids can be confirmed by UV, TGA and FTIR.

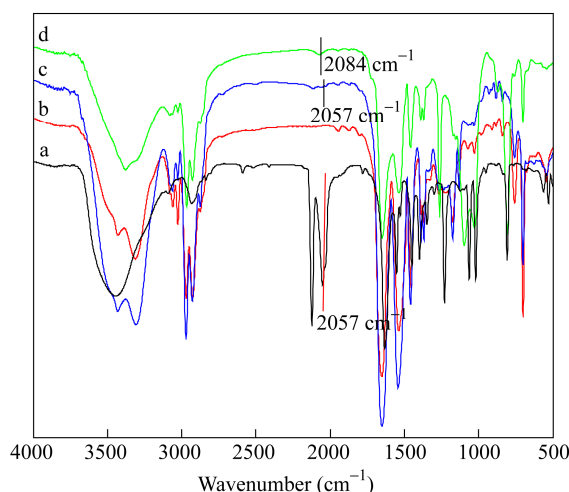


Fig. 3 FTIR spectra of Fe-DMAP (a), BCP-2 (b), BCP-2/Fe-DMAP (c) and BCP-2/PB (d)

Morphologies of BCP, BCP/Fe-DMAP and BCP/PB Micelles

The micellar morphologies of the PS-*b*-P(NIPAM-*co*-VBC), BCP/Fe-DMAP and BCP/PB were characterized with TEM. The TEM images for the BCP-1, BCP-1/Fe-DMAP and BCP-1/PB micelles at 25 °C are shown in Fig. 4. Mixed micelles with different morphologies were observed for PS₆₅-*b*-P(NIPAM₁₀₁-*co*-VBC₁₉) (Fig. 4a). Most of the micelles are short rod-like with a mean diameter about 29 nm, and the minority of the micelles are spherical with a diameter about 32 nm. After attachment of Fe-DMAP to BCP-1, most of the micelles become spherical (Fig. 4b). The mean diameter of the micelles is ~22 nm. This shows that coordination of Fe^{2+} may alter the micellar morphology of BCP-1, which can be interpreted in terms of the hydrophilicity of the P(NIPAM-*co*-VBC) block before and after attachment of Fe-DMAP. In the P(NIPAM-*co*-VBC) block, the randomly distributed VBC units are hydrophobic and thus tend to be located at the interface between the PS core and the P(NIPAM-*co*-VBC) corona, resulting in looped conformation of the P(NIPAM-*co*-VBC) block. This indeed shortens the length of the corona-forming block, and reduces the repulsion force among the corona-forming blocks, thus rod-like micelles with an interface of small curvature (as compared with spherical micelles) are formed. On the other hand, Fe-DMAP is water-soluble and the VBC units may become hydrophilic after attachment of Fe-DMAP. Therefore, the Fe-DMAP-attached P(NIPAM-*co*-VBC) block may recover its full length in the corona, and the repulsion force among the corona-forming blocks becomes larger, leading to formation of spherical micelles. Moreover, due to enhancement in hydrophilicity of the corona-forming block, the diameter of the BCP-1/Fe-DMAP micelles decreases slightly as well. When the attached Fe-DMAP is further cross-linked with FeCl_3 to form PB framework, the micellar morphology basically remains unchanged (Fig. 4c), as compared with that of the BCP-1/Fe-DMAP micelles. Sometimes crosslinking among different micelles may also occur. It should be pointed out that, although the PB framework is formed in the corona of the BCP-1/PB hybrid micelles, the PB particles cannot be clearly identified by TEM due to the small micellar size and thus the finely dispersed PB particles. However, in the TEM images, the BCP-1/PB hybrid micelles do exhibit significantly better contrast than the BCP-1/Fe-DMAP micelles. The BCP-1/Fe-DMAP micelles are also decomposed more easily upon irradiation of electron beam during TEM observation. These observations are

consistent with the presence of metal-crosslinked PB framework, since it is well-known that crosslinking can improve the stability of polymers under the electron beam^[9, 30, 31].

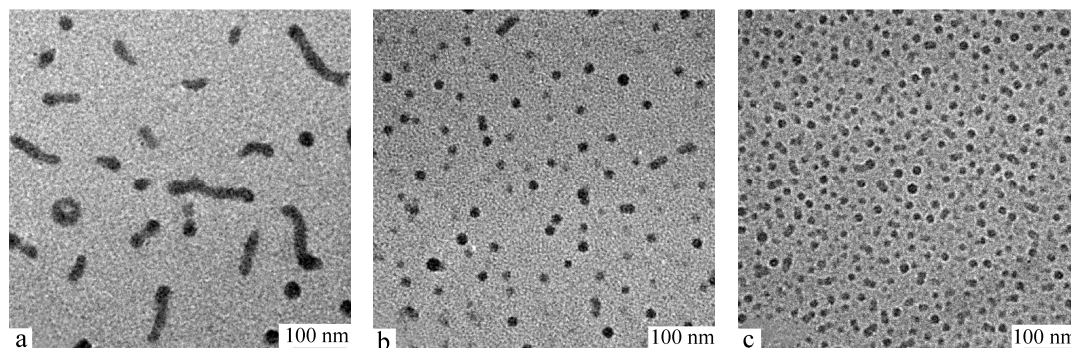


Fig. 4 TEM images of the micelles of BCP-1 (a), BCP-1/Fe-DMAP (b) and BCP-1/PB (c)

The starting concentration of BCP-2 and BCP-2/Fe-DMAP in THF for preparation of the micelles is $0.125 \text{ mg} \cdot \text{mL}^{-1}$.

The TEM images of the BCP-2, BCP-2/Fe-DMAP and BCP-2/PB micelles are illustrated in Fig. 5. Like BCP-1, mixed short rod-like and spherical micelles are again observed for the neat $\text{PS}_{65}\text{-}b\text{-P}(\text{NIPAM}_{247}\text{-}co\text{-VBC}_{14})$ (BCP-2) (Fig. 5a). The mean diameter of the rod-like micelles is about $\sim 27 \text{ nm}$. As compared with the micelles of BCP-1, the length of the rod-like micelles of BCP-2 is a little shorter, possibly due to the longer $\text{P}(\text{NIPAM}\text{-}co\text{-VBC})$ block. Similarly, attachment of Fe-DMAP to BCP-2 induces a rod-to-sphere transformation of the micellar morphology (Fig. 5b). The spherical micelles of BCP-2/Fe-DMAP have a wide size distribution, ranging from 15 nm to 50 nm . After formation of PB framework in the corona of the BCP-2 micelles, most of the micelles remain to be spherical, but the size of the micelles becomes slightly larger and there is tendency of aggregation for the micelles (Fig. 5c). Some ring-like micelles with a thickness about 18 nm are formed as well, which may be attributed to crosslinking of different spherical micelles. The contrast of the TEM image for BCP-2/PB hybrid micelles is improved due to crosslinking, with respect to that of BCP-2/Fe-DMAP.

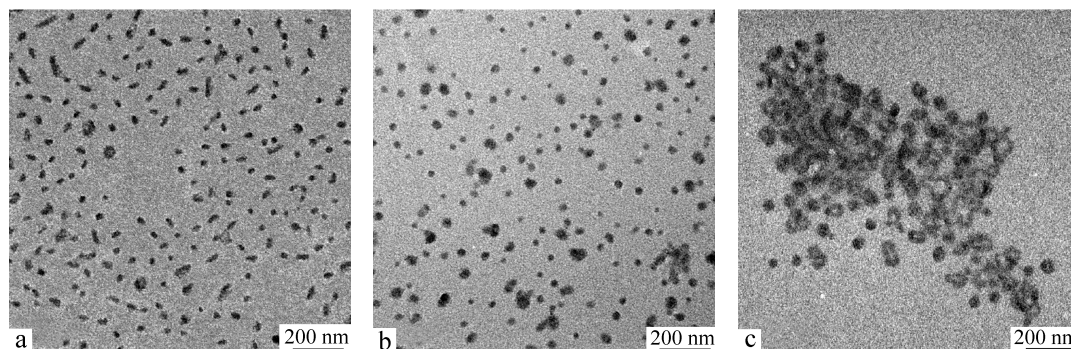


Fig. 5 TEM images of the micelles of BCP-2 (a), BCP-2/Fe-DMAP (b) and BCP-2/PB (c)

The starting concentration of BCP-2 and BCP-2/Fe-DMAP in THF for preparation of the micelles is $0.125 \text{ mg} \cdot \text{mL}^{-1}$.

We also examined the effect of the starting concentration of the BCP-2/Fe-DMAP in the THF solution on the final morphology of the BCP-2/PB hybrid micelles. The BCP-2/Fe-DMAP micelles were prepared at a higher starting concentration, *i.e.* $0.5 \text{ mg} \cdot \text{mL}^{-1}$. The TEM images of the BCP-2/Fe-DMAP and BCP-2/PB micelles prepared from this starting concentration are shown in Fig. 6. For the purpose of comparison, the TEM image of the BCP-2 micelles is presented as well. One can see from Fig. 6(a) that, at a higher starting concentration, the micellar size of the neat BCP-2 becomes evidently larger and aggregation of the micelles occurs. By contrast, the BCP-2/Fe-DMAP micelles have a smaller size than those of the neat BCP-2 due to the enhanced solubility of the $\text{P}(\text{NIPAM}\text{-}co\text{-VBC})$ block after attachment of Fe-DMAP (Fig. 6b). However, some

aggregated micelles with large sizes are still observed for BCP-2/Fe-DMAP. A high starting concentration also leads to more severe crosslinking of different micelles of BCP-2/PB, thus more ring-like micelles are formed (Fig. 6c).

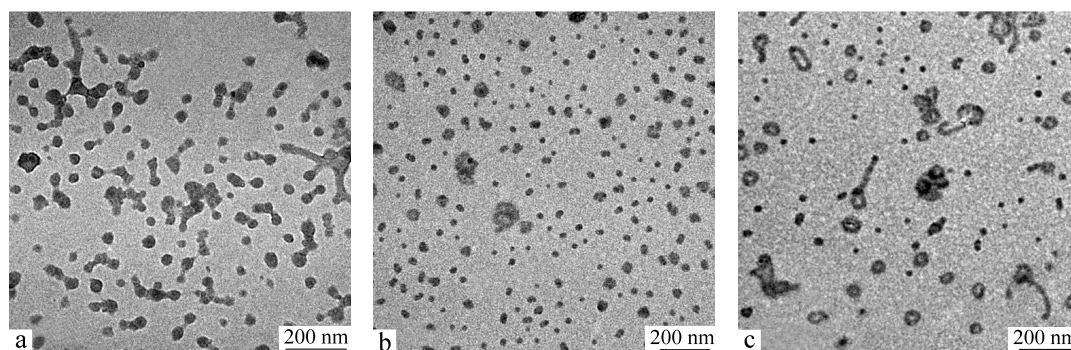


Fig. 6 TEM images of the micelles of BCP-2 (a), BCP-2/Fe-DMAP (b) and BCP-2/PB (c)

The starting concentration of BCP-2 and BCP-2/Fe-DMAP in THF for preparation of the micelles is $0.5 \text{ mg} \cdot \text{mL}^{-1}$.

Thermoresponsive Behavior of BCP, BCP/Fe-DMAP and BCP/PB Micelles

Since PNIPAM can exhibit a LCST phase diagram in aqueous solutions^[32, 33], we compared the thermoresponsive behaviors of the micelles of the neat PS-*b*-P(NIPAM-*co*-VBC), BCP/Fe-DMAP and BCP/PB. Figure 7 shows the variations of the average apparent hydrodynamic radius (R_h) with temperature during a heating-cooling cycle for the micellar solutions of the neat BCP-1, BCP-1/Fe-DMAP and BCP-1/PB prepared from the starting concentration of $0.125 \text{ mg} \cdot \text{mL}^{-1}$ in THF. It is observed that the micelles of all samples exhibit some common characteristics. Firstly, R_h of the micelles decreases as temperature increases. This is due to the collapse of PNIPAM above the LCST. The smaller size at high temperatures also shows that no aggregation occurs in a short time and the micelles with collapsed corona are temporarily stable in the aqueous solution at elevated temperatures, as reported in literature^[34]. Secondly, the variation of the micellar size is basically reversible during the heating-cooling cycle.

For the PS₆₅-*b*-P(NIPAM₁₀₁-*co*-VBC₁₉) (BCP-1) micelles, a two-stepwise decrease in R_h upon heating is observed. There is a large decrease of R_h between 25 °C and 35 °C, then R_h decreases slowly in the range of 35–43 °C. Such a phenomenon is also observed for the micelles of PS-*b*-PNIPAM in our previous work^[34] and for PNIPAM grafted on gold and SiO₂ nanoparticles^[35–37]. It is believed that the PNIPAM segments in the inner region, *i.e.* near the surface of the nanoparticles or near the interface between the core and corona of the micelles, have a lower LCST due to the more stretched conformation. By contrast, the conformation of the PNIPAM segments is less stretched in the outer region far from the surface of the nanoparticles or from the interface of the micelles, and the phase transition of the PNIPAM segments in this region occurs at a higher temperature. Comparing the thermoresponsive behaviors of the micelles of PS₆₅-*b*-PNIPAM₁₀₈ and PS₆₅-*b*-P(NIPAM₁₀₁-*co*-VBC₁₉) (BCP-1), which have a similar chain structure, one can see that the first step decrease of R_h occurs in the same temperature range (25–35 °C) for both samples. The second step decrease of R_h for the BCP-1 micelles takes place at 35–43 °C, but it happens at 45–60 °C for the PS₆₅-*b*-PNIPAM₁₀₈ micelles^[34]. This indicates that the PNIPAM segments in the outer region of BCP-1 micelles may be more stretched than those in the PS₆₅-*b*-PNIPAM₁₀₈ micelles, which is in accordance with the looped conformation of PNIPAM chains due to the presence of the hydrophobic VBC units in BCP-1, as mentioned in the previous section.

On the other hand, it is observed that R_h of the BCP-1 micelles upon heating is smaller than that during cooling process at the same temperature. Such a hysteresis phenomenon is widely reported for PNIPAM homopolymer and block copolymers^[33, 38–42]. This can be attributed to the different rates of dehydration of the swollen PNIPAM chains upon heating and hydration of the collapsed PNIPAM chains upon cooling^[43]. For PNIPAM-containing BCP micelles, the PNIPAM chains in the inner region of the corona tends to dehydrate

quickly due to the crowded conformation, leading to a fast decrease of R_h in the initial period of heating. By contrast, in the initial period of cooling the PNIPAM chains in the outer region of the corona can be easily hydrated and thus an obvious increase in R_h is observed. More severe hysteresis is observed for the BCP-1 micelles, as compared with the PS₆₅-*b*-PNIPAM₁₀₈ micelles^[34]. This indicates that random enchainment of hydrophobic units in the PNIPAM chain may intensify hysteresis. After attachment of Fe-DMAP to the VBC units in BCP-1, the curves for the variation of R_h with temperature during heating and cooling are nearly overlapped (Fig. 7b), showing that the hysteresis becomes weaker. This can be ascribed to the enhanced solubility of the P(NIPAM-*co*-VBC) block after attachment of Fe-DMAP. In addition, the second step change of the micellar size in a wider temperature range (25–50 °C) and it accounts for the majority of decrease in R_h for BCP-1/Fe-DMAP. This implies that, the PNIPAM segments in the outer region of BCP-1/Fe-DMAP micellar corona are less crowded than those in the BCP-1 micelles. When the PB framework is formed in the micellar corona, the temperature range for change of R_h is altered as well, which is similar to that of BCP-1. An “inverse S” type change of R_h with temperature is observed for BCP-1/PB hybrid micelles and the two-stepwise change in R_h can hardly be recognized (Fig. 7c). This shows that crosslinking may result in a similar LCST for the PNIPAM segments in the inner and outer regions of the micellar corona. Crosslinking also lowers the mobility of the PNIPAM segments, which leads to more obvious hysteresis between the curves of the dependence of R_h on temperature during the heating and cooling cycle.

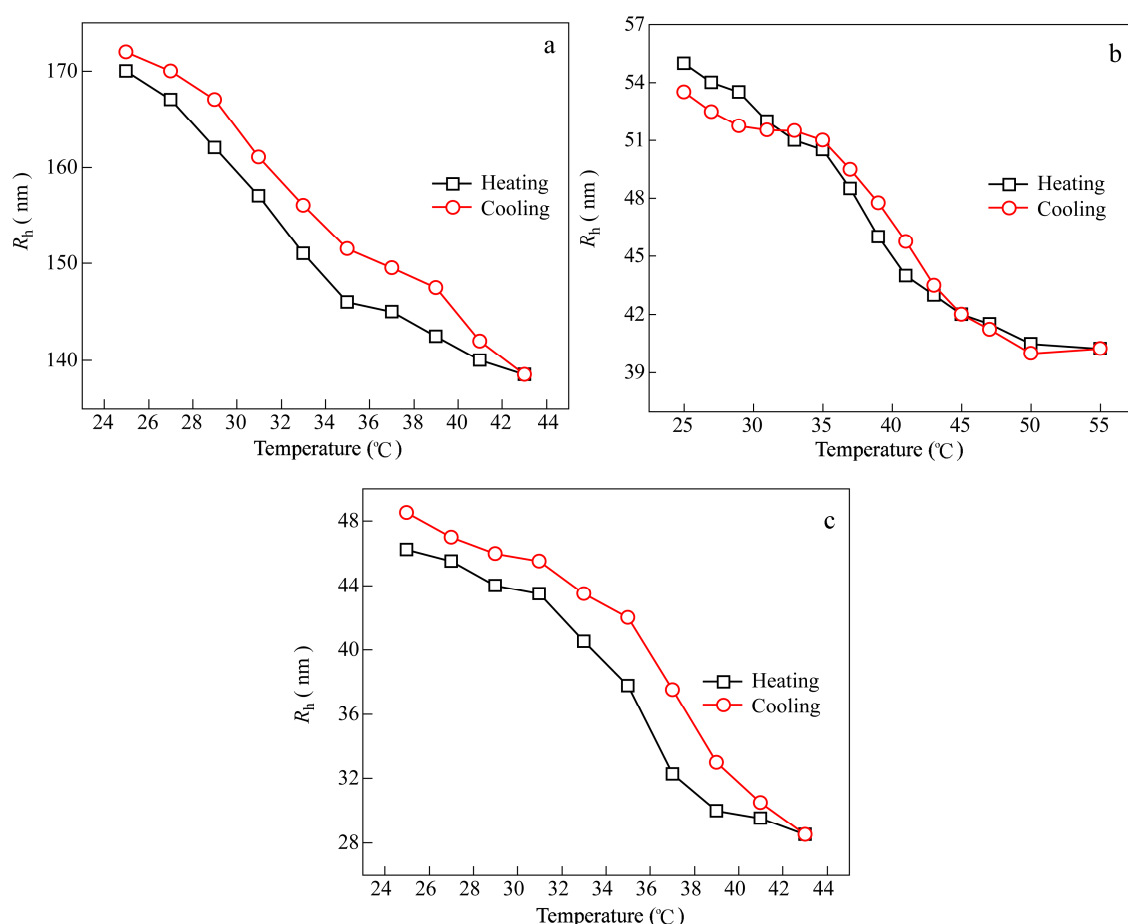


Fig. 7 Variation of R_h with temperature for the micelles of BCP-1 (a), BCP-1/Fe-DMAP (b) and BCP-1/PB (c)

When the P(NIPAM-*co*-VBC) block becomes longer and the content of VBC is lower, the hysteresis in micellar size during the heating and cooling cycle will become less pronounced (Fig. S3). The longer P(NIPAM-*co*-VBC) block also leads to the more stretched PNIPAM segments in the inner region of the micellar corona, and thus a lower temperature range for the first step change of R_h in the micelles of BCP-2 and BCP-2/Fe-DMAP. Like the thermoresponsive behavior of BCP-1/Fe-DMAP and BCP-1/PB micelles, BCP-2/Fe-DMAP exhibits the weakest hysteresis in micellar size due to improved hydrophilicity of the corona-forming block, and the hysteresis is the strongest for the BCP-2/PB hybrid micelles because of the existence of crosslinked PB framework.

CONCLUSIONS

The UV-Vis, FTIR and TGA characterizations reveal that the PB framework is formed in the corona of the PS-*b*-P(NIPAM-*co*-VBC)/PB hybrid micelles. The neat PS-*b*-P(NIPAM-*co*-VBC) block copolymers used in the present work tend to form mixed short rod-like and spherical micelles. Attachment of Fe-DMAP can improve the hydrophilicity of the P(NIPAM-*co*-VBC) block, leading to formation of spherical micelles and a smaller micellar size. The crosslinked PB framework may solidify the micellar structure. However, crosslinking can also occur among different micelles, which depends on the chain structure of PS-*b*-P(NIPAM-*co*-VBC) and solution concentration, thus the micellar morphology may be altered. Both the micelles of PS-*b*-P(NIPAM-*co*-VBC) and PS-*b*-P(NIPAM-*co*-VBC)/Fe-DMAP exhibit a two-stepwise decrease in size upon heating, but an “inverse S” type change is observed for the PS-*b*-P(NIPAM-*co*-VBC)/PB hybrid micelles. The hydrophilicity of the corona-forming block can be enhanced by attachment of Fe-DMAP, thus the hysteresis in micellar size during the heating and cooling cycle is not so pronounced for the PS-*b*-P(NIPAM-*co*-VBC)/Fe-DMAP micelles. By contrast, formation of the crosslinking PB framework in the corona may reduce the mobility of the PNIPAM segments, thus more obvious hysteresis is observed for the PS-*b*-P(NIPAM-*co*-VBC)/PB micelles.

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