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ORIGINAL CONTRIBUTION

Preparation of micelles with azo dye and UV absorbent at their cores or coronas using non-amphiphilic block copolymers

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Abstract Micelles with azo dye and UV absorbent at their cores or coronas were prepared from non-amphiphilic random diblock copolymers by α,ω-diamine. Poly[4-(phenylazophenoxymethyl)styrene-*ran*-4-(2-hydroxybenzophenoxymethyl)styrene-*ran*-vinylphenol]-*block*-polystyrene (P(AS-*r*-HBS-*r*-VPh)-*b*-PSt) and poly(vinylphenol)-*block*-poly[4-(phenylazophenoxymethyl)styrene-*ran*-4-(2-hydroxybenzophenoxymethyl)styrene-*ran*-styrene] (PVPh-*b*-P(AS-*r*-HBS-*r*-St)) diblock copolymers were prepared by living radical polymerization mediated by 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl. The former copolymer had a molecular weight of Mn[P(AS-*r*-HBS-*r*-VPh)-*b*-PSt]=10,000-*b*-250,000 by ^{1}H NMR and a molar ratio of AS:HBS:VPh=0.01:0.01:0.98, while the latter had a molecular weight of Mn[PVPh-*b*-P(AS-*r*-HBS-*r*-St)]=10,000-*b*-111,000 and a molar ratio of AS:HBS:St=0.02:0.03:0.95. The copolymers showed no self-assembly in 1,4-dioxane because this solvent was non-selective to the copolymers. Dynamic light scattering demonstrated that the copolymers formed micelles in the solvent in the presence of α,ω-diamine. The hydrodynamic radii of the micelles slightly increased with the copolymer concentration decrease, while the aggregation numbers were almost independent of the copolymer concentration. It was found that P(AS-*r*-HBS-*r*-VPh)-*b*-PSt formed smaller micelles with a lower aggregation number than PVPh-*b*-P(AS-*r*-HBS-*r*-St) because of the steric hindrance of the AS and HBS units present at the micellar coronas.

Keywords Non-amphiphilic diblock copolymers · PVPh-*b*-P(AS-*r*-HBS-*r*-St) · P(AS-*r*-HBS-*r*-VPh)-*b*-PSt) · Micellization · α,ω-Diamine

Introduction

In recent years, non-amphiphilic copolymers consisting entirely of solvophilic moieties have attracted considerable attention in colloid chemistry because those have many advantages in molecular design. It is also able to provide a better selection of driving force [1–8]. A variety of amphiphilic copolymers can be created from one non-amphiphilic copolymer in situ by selecting it [9, 10]. In addition, it is unnecessary to take the solubility balance into account when designing the copolymers because the non-amphiphilic copolymers molecularly and entirely dissolve in solvents. The independence of the solubility balance allows us to introduce a great variety of functional groups into the copolymers. The copolymers containing functional groups produce micelles having the functional groups at the cores or coronas through micellization. We have already released publications on the preparation of micelles with functional groups at the cores and/or coronas. Examples include the micelles with UV absorbent at the coronas [11] and with azobenzene at the cores or coronas [12]. The micelles with azobenzene at the cores and UV absorbent at the coronas were expected as light stable nanospheres of the dyes [13]. A series of the micelles with the functional groups were prepared through the micellization of a non-

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amphiphilic poly(vinylphenol)-*block*-polystyrene by α,ω-diamine in a non-selective solvent [14–19]. We found that the azobenzene and UV absorbent contained in the block copolymers dominated the CMC, micellar size and aggregation number of the copolymers. This paper describes the preparation of micelles with azobenzene and UV absorbent together at the cores or coronas.

Experimental

Instrumentation ^{1}H NMR spectra were obtained with a Bruker ARX-500 NMR spectrometer. Gel permeation chromatography (GPC) was performed with a Tosoh DP-8020 dual plunger pump with a RI-8020 refractive index monitor and a CO-8020 column oven. Two polystyrene gel columns, Tosoh TSKgel α-M, were used with DMF as the eluent in the presence of LiBr at 40 °C. Light scattering experiments were performed at 20 °C with a Photal Otsuka Electronics DLS-7000 super dynamic light scattering spectrometer equipped with an LS-71 control unit, an LS-72 pump controller and an argon ion laser operating at $\lambda=488$ nm.

Materials 4-(Phenylazophenoxymethyl)styrene (AS) [12] and 4-(2-hydroxybenzophenoxymethyl)styrene (HBS) [13] were prepared as reported previously. Commercial grade styrene was washed with an aqueous alkaline solution and water and distilled over calcium hydride. 4-*tert*-Butoxystyrene (^{t}BSt) was distilled over calcium hydride. Benzoyl peroxide (BPO) was purified by precipitation of the chloroform solution into methanol. 1,4-Butanediamine (BDA), ethylenediamine (EDA), hexamethylenediamine (HMDA) and *n*-butylamine (BA) were distilled over calcium hydride. 1,4-Dioxane was purified by refluxing on sodium for several hours and distilled over sodium. 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-methoxy-TEMPO) was prepared as reported previously [20]. Poly(4-*tert*-butoxystyrene) (P^{t}BSt) was also prepared as reported previously [14]. The degree of polymerization (DP) of P^{t}BSt and the molecular weight were DP=87.3 and Mn=15400, respectively on the basis of ^{1}H NMR.

Synthesis of a P(AS-r-HBS-r-VPh)-b-PSt diblock copolymer ^{t}BSt (3.46 g, 19.7 mmol), HBS (65.7 mg, 0.199 mmol), AS (62.5 mg, 0.199 mmol), BPO (54.5 mg, 0.225 mmol) and 4-methoxy-TEMPO (54.5 mg, 0.293 mmol) were placed in an ampule. After the contents were degassed, the ampule was sealed in vacuo. The polymerization was carried out at 125 °C for 24 h. The reaction mixture was dissolved into dichloromethane and poured into methanol to precipitate a polymer. The polymer was purified by repeated reprecipitation from dichloromethane into methanol. The precipitate was then dried in vacuo for several hours to obtain a P(AS-*r*-HBS-*r*-^{t}BSt) random copolymer (2.40 g).

The P(AS-*r*-HBS-*r*-^{t}BSt) copolymer (447 mg) and styrene (2.00 g, 19.2 mmol), were placed in an ampule. After the contents were degassed, the ampule was sealed in vacuo. The polymerization was carried out at 125 °C for 3 days. The reaction mixture was dissolved into dichloromethane and poured into methanol to precipitate a polymer. The polymer was purified by repeated reprecipitation from dichloromethane into methanol. The precipitate was then dried in vacuo for several hours to obtain a P(AS-*r*-HBS-*r*-^{t}BSt)-*b*-PSt block copolymer (1.71 g).

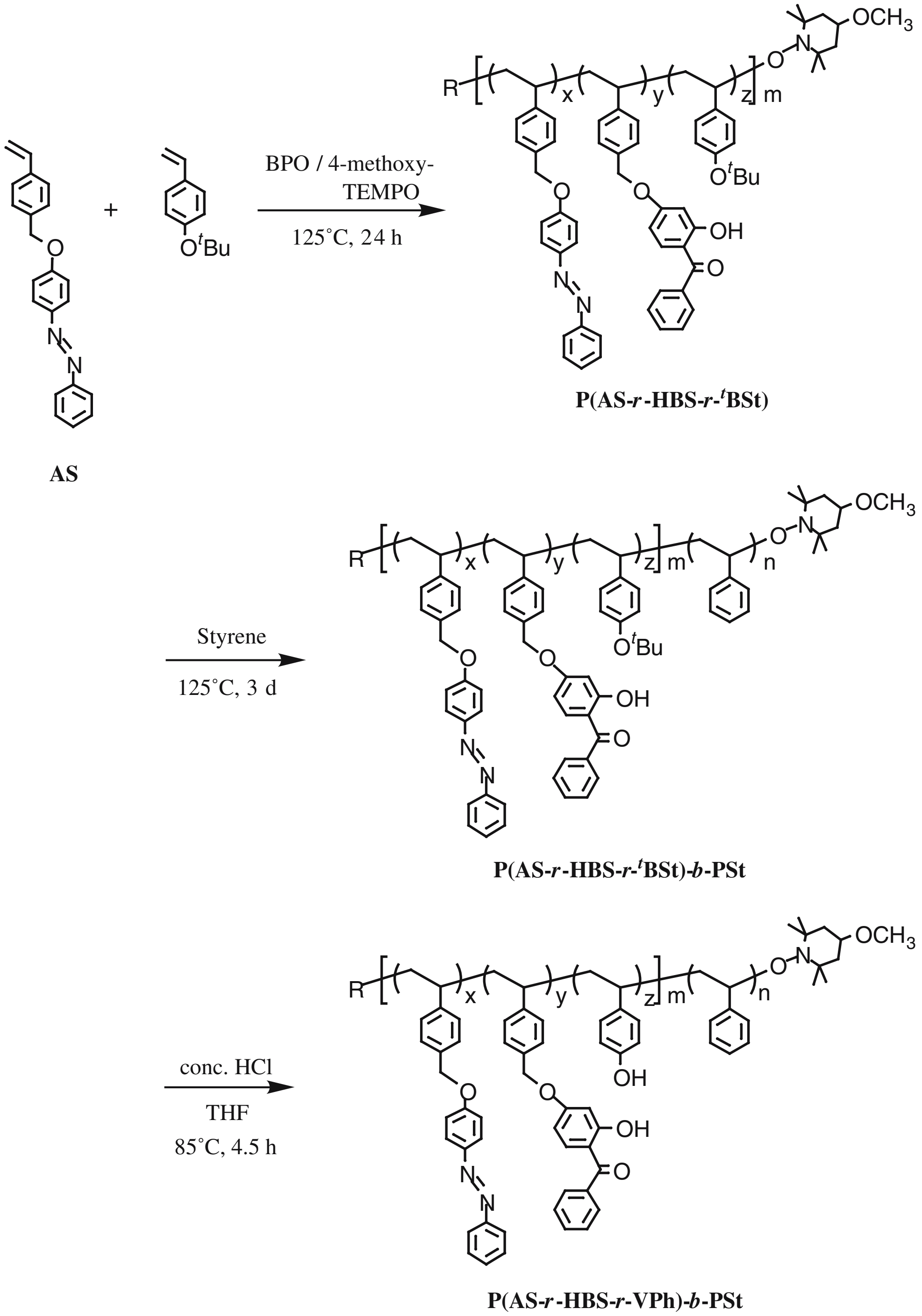
The P(AS-*r*-HBS-*r*-^{t}BSt)-*b*-PSt copolymer (500 mg) was dissolved in THF (15 ml) and concentrated HCl (1 ml) was added to the solution at room temperature. The mixture was kept at 85 °C for 4.5 h. The resulting mixture was poured into water (300 ml) to precipitate a polymer. After the polymer was dried, the product was suspended in 100 ml of methanol and stirred for 16 h at room temperature to remove P(AS-*r*-HBS-*r*-VPh). The precipitate was collected by filtration, dried in vacuo for several hours. The P(AS-*r*-HBS-*r*-VPh)-*b*-PSt diblock copolymer (430 mg) was obtained.

Synthesis of a PVPh-b-P(AS-r-HBS-r-St) diblock copolymer Styrene (1.98 g, 19.0 mmol), HBS (63 mg, 0.191 mmol), AS (63 mg, 0.191 mmol) and the P^{t}BSt prepolymer (447 mg) were placed in an ampule. After the contents were degassed, the ampule was sealed in vacuo. The polymerization was carried out at 125 °C for 4 days. The reaction mixture was dissolved into dichloromethane and poured into methanol to precipitate a polymer. The polymer was purified by repeated reprecipitation from dichloromethane into methanol. The precipitate was then dried in vacuo for several hours to obtain a P^{t}BSt-*b*-P(AS-*r*HBS-*r*-St) block copolymer (2.00 g).

The P^{t}BSt-*b*-P(AS-*r*-HBS-*r*-St) copolymer (500 mg) was dissolved in THF (15 ml) and concentrated HCl (1 ml) was added to the solution at room temperature. The mixture was kept at 85 °C for 4.5 h. The resulting mixture was poured into water (300 ml) to precipitate a polymer. After the polymer was dried, the product was suspended in 100 ml of methanol and stirred for 6 h at room temperature to remove a vinylphenol homopolymer. The precipitate was collected by filtration and dried in vacuo for several hours. The PVPh-*b*-P(AS-*r*-HBS-*r*-St) diblock copolymer (340 mg) was obtained.

Light scattering measurements: general procedure A PVPh-*b*-P(AS-*r*-HBS-*r*-St) diblock copolymer (10 mg, 7.16×10^{-3} mmol of the VPh unit) was dissolved in 1,4-

Fig. 1 Synthesis of the P(AS-*r*-HBS-*r*-VPh)-*b*-PSt diblock copolymer



dioxane (3 ml). Using a syringe, the resulting solution was injected through a microporous filter into a cell. The solution was subjected to light scattering measurement at 20 °C. After the measurement, 8 μL (4.14×10^{-3} mmol of BDA) of BDA solution (BDA, 45.6 mg, 0.517 mmol) in 1,4-dioxane (1 ml) was added to the copolymer solution in the cell and the mixture was shaken vigorously. The solution was allowed to stand at 20 °C for 5 min and then subjected to light scattering again. This procedure was repeated until the hydrodynamic radius of the micelles was almost constant. The hydrodynamic radius was estimated by cumulant analysis, while the distribution of the hydrodynamic radius was determined by non-negatively constrained least squares (NNLS) analysis [21]. Aggregation numbers were estimated by using the scattering intensity of the micelles and the unimers.

Results and discussion

Synthesis of P(AS-r-HBS-*r*-VPh)-*b*-PSt

The P(AS-*r*-HBS-*r*-VPh)-*b*-PSt diblock copolymer was prepared through the combination of the sequential living radical polymerization mediated by 4-methoxy-TEMPO and the hydrolysis of the ^{t}BSt units (Fig. 1). The copolymerization of AS, HBS and ^{t}BSt was performed in bulk at 125 °C for 24 h by BPO as an initiator and 4-methoxy-TEMPO as a mediator, giving a P(AS-*r*-HBS-*r*-^{t}BSt) random copolymer. Figure 2a shows the ^{1}H NMR spectrum of the P(AS-*r*-HBS-*r*-^{t}BSt) copolymer. The signal at 5.0 ppm was based on the oxybenzyl protons for the AS and HBS units. Signals of the AS units were also observed as doublet at 7.92 ppm attributed to the protons located at the *ortho* positions to the azo group. Signals of the HBS units were observed at 7.62 and 7.50 ppm. These signals originated from the aromatic protons of the phenyl group without the hydroxyl group. The former was assigned to the protons located at the *ortho* positions and the latter to those at the *meta* and *para* positions. The signal of the hydroxyl group was discerned at 12.69 ppm. In addition, the signals at 7.36 and 7.81 ppm were based on the benzoyl groups attached to the polymer head group. The molar ratio of the AS, HBS and ^{t}BSt units was estimated to be AS:HBS:^{t}BSt= 0.01:0.01:0.98 on the basis of the signal intensity at 7.62, 12.69 and 6.0–7.0 ppm, respectively. The degree of polymerization of the P(AS-*r*-HBS-*r*-^{t}BSt) copolymer was estimated on the basis of the signals for the ^{t}BSt units and the 4-methoxy-TEMPO attached to the polymer chain end. The signals of the 4-methoxy-TEMPO were discerned at 1.07, 0.90, 0.25 and 0.13 ppm for the tetramethyl protons and at 3.27 ppm for the methoxy protons. The degree of polymerization (DP) was determined as n=80.7 based on the signal intensity at 6.0–7.0 and 3.27 ppm. Therefore, the molecular weight was Mn=14,400. The molecular weight and polydispersity were estimated by GPC as Mn=9,700 and Mw/Mn=1.34 for the prepolymer based on the polystyrene standards.

The block polymerization of styrene by the P(AS-*r*-HBS-*r*-^{t}BSt) random copolymer as an initiator produced P(AS-*r*-HBS-*r*-^{t}BSt)-*b*-PSt. The P(AS-*r*-HBS-*r*-VPh)-*b*-PSt diblock copolymer was obtained by the hydrolysis of the ^{t}BSt units of the P(AS-*r*-HBS-*r*-^{t}BSt)-*b*-PSt copolymer in THF with HCl as a catalyst. Figure 2b shows the ^{1}H NMR spectrum of the P(AS-*r*-HBS-*r*-VPh)-*b*-PSt diblock copolymer. Signals originating from the VPh units were observed at 7.2–7.6 ppm attributed to the hydroxyl groups. The molecular weight of the P(AS-*r*-HBS-*r*-VPh)-*b*-PSt copolymer was estimated on the basis of the signals of these hydroxyl protons and the aromatic protons at 6.1–7.2 ppm. The molecular weight was Mn[P(AS-*r*-HBS-*r*-VPh)-*b*-PSt] =10,000-*b*-250,000. Figure 3 shows the GPC profiles of the P(AS-*r*-HBS-*r*-VPh)-*b*-PSt copolymer and the P(AS-*r*-HBS-*r*-^{t}BSt) prepolymer. The block copolymer showed a unimodal curve as is the prepolymer. The molecular weight and polydispersity were estimated by GPC as Mn=42,000 and Mw/Mn=1.88.

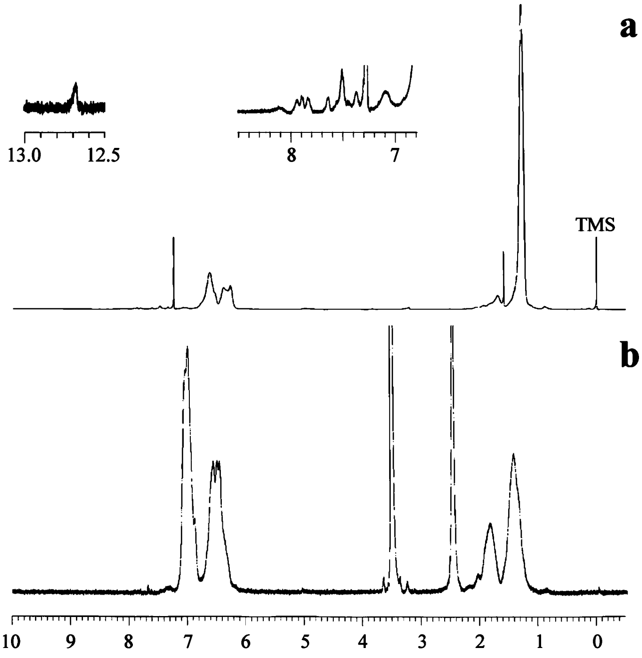


Fig. 2 ^{1}H NMR spectra of **a** P(AS-*r*-HBS-*r*-^{t}BSt) (solvent: CDCl$_3$) and **b** P(AS-*r*-HBS-*r*-VPh)-*b*-PSt (solvent: 1,4-dioxane-d_8)

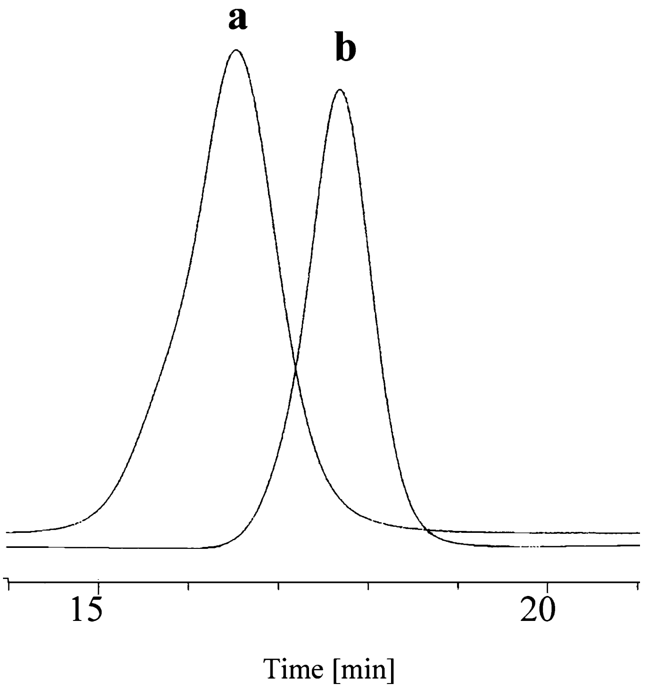
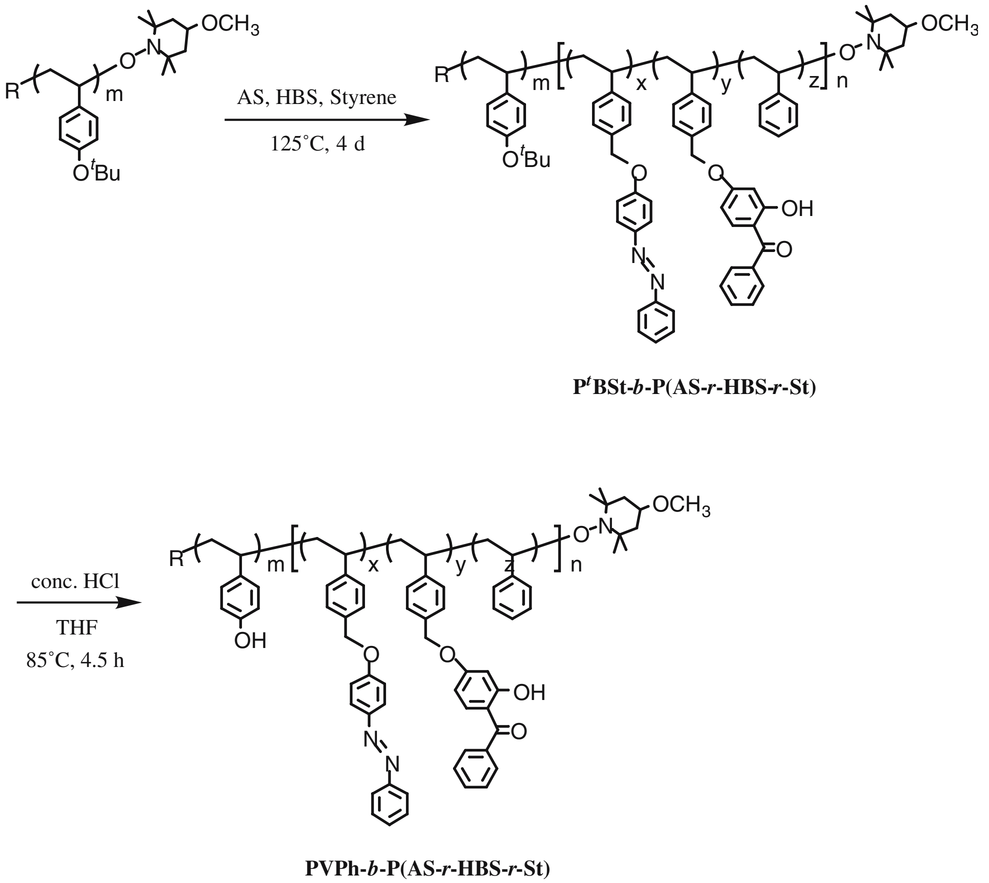


Fig. 3 GPC profiles of **a** P(AS-*r*-HBS-*r*-VPh)-*b*-PSt and **b** P(AS-*r*-HBS-*r*-^{t}BSt)

Fig. 4 Synthesis of the PVPh-*b*-P(AS-*r*-HBS-*r*-St) diblock copolymer



Synthesis of PVPh-*b*-P(AS-*r*-HBS-*r*-St)

PVPh-*b*-P(AS-*r*-HBS-*r*-St) was also obtained by living radical polymerization and hydrolysis as was the P(AS-*r*-HBS-*r*-VPh)-*b*-PSt copolymer (Fig. 4). The copolymerization of AS, BS and styrene was carried out at 125 °C for 4 days using TEMPO-terminated P^{t}BSt as an initiator. The resulting P^{t}BSt-*b*-P(AS-*r*-HBS-*r*-St) block copolymer was converted to PVPh-*b*-P(AS-*r*-HBS-*r*-St) by the HCl-catalyzed hydrolysis. Figure 5 shows the ^{1}H NMR spectrum of the PVPh-*b*-P(AS-*r*-HBS-*r*-St) diblock copolymer. A signal originating from the hydroxyl group of the benzophenone was observed at 12.63 ppm. Parts of signals for the aromatic protons of the benzophenone and azobenzene were discerned at 7.63 and 7.90 ppm, respectively. Signals of other parts of these groups observed to be at 7.34–7.56 ppm are covered with signals of the hydroxyl protons for the VPh units. The molar ratio of the respective units

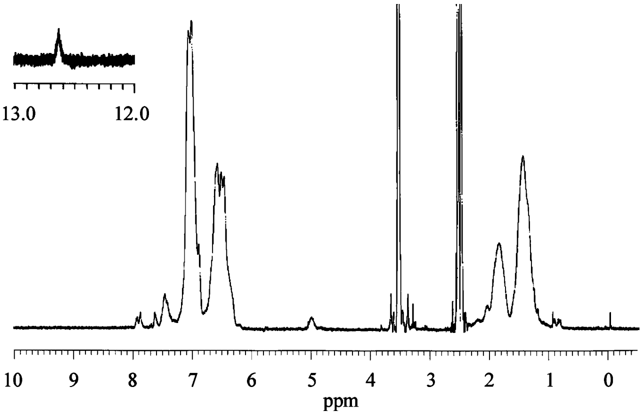


Fig. 5 ^{1}H NMR spectrum of the PVPh-*b*-P(AS-*r*-HBS-*r*-St) (solvent: 1,4-dioxane-d_8)

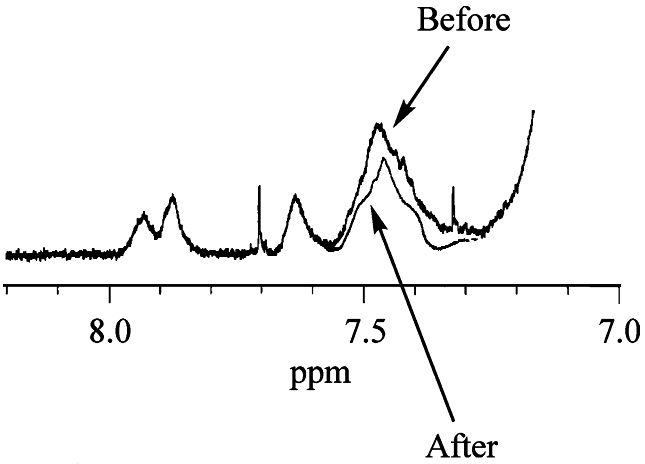


Fig. 6 ^{1}H NMR spectra of the PVPh-*b*-P(AS-*r*-HBS-*r*-St) before and after the addition of CF_3COOH (solvent: 1,4-dioxane-d_8)

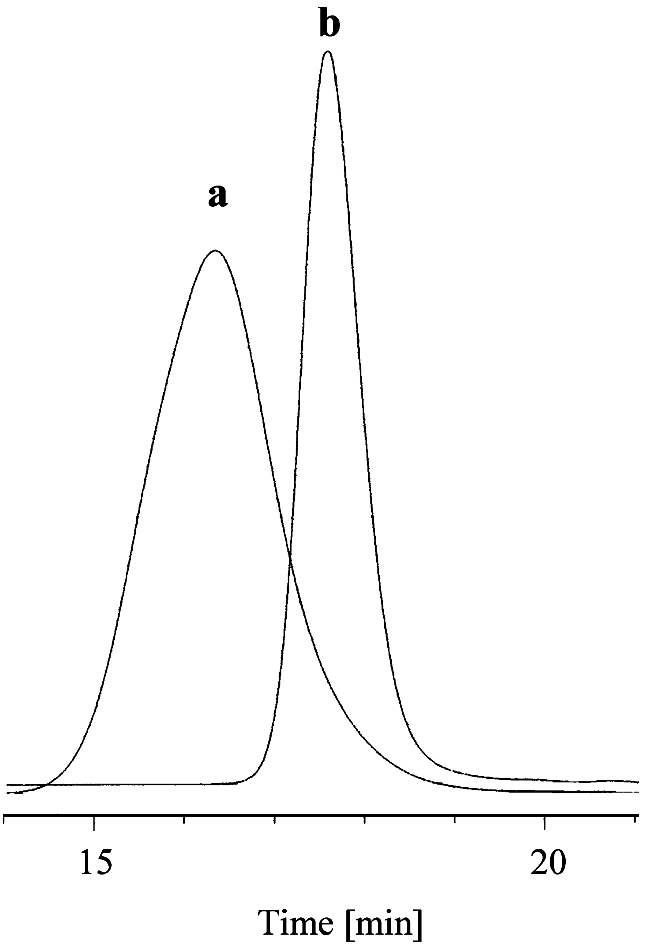


Fig. 7 GPC profiles of **a** PVPh-*b*-P(AS-*r*-HBS-*r*-St) and **b** P^{t}BSt

was estimated on the basis of the signal intensity at 7.90 ppm for the AS units, at 12.63 ppm for the HBS units, at 6.20–7.38 ppm for the St units and at 7.34–7.56 ppm for the VPh units. The signal intensity of the VPh units was determined by the difference in the intensity between the absence and presence of trifluoroacetic acid. The signals for the phenolic OH were shifted to the lower magnetic field side in the presence of trifluoroacetic acid (Fig. 6). The molar ratio was AS:HBS:St=0.02:0.03:0.95. The molecular weight of the copolymer was estimated as Mn[PVPh-*b*-P(AS-*r*-HBS-*r*-St)]=10,000-*b*-111,000 based on this ratio and the DP of the P^{t}BSt prepolymer. The GPC of the block copolymer was somewhat broadened compared with that of the prepolymer (Fig. 7). The molecular weight and polydispersity of the copolymer were estimated by GPC as Mn=38,000 and Mw/Mn=2.83.

Micelle formation of the diblock copolymers

The micellization of the P(AS-*r*-HBS-*r*-VPh)-*b*-PSt and PVPh-*b*-P(AS-*r*-HBS-*r*-St) diblock copolymers was explored in 1,4-dioxane. The copolymers showed no self-assembly in this solvent because the solvent is non-selective to the copolymers. Light scattering studies demonstrated that the block copolymers formed micelles in 1,4-dioxane in the presence of α,ω-diamine. Figure 8 shows the variability in hydrodynamic radius (R_H) and relative scattering intensity (I/I_0) of the PVPh-*b*-P(AS-*r*-HBS-*r*-St) copolymer during micellization by BDA, HMDA, EDA and BA. The hydrodynamic radius and relative scattering intensity of the copolymer increased as a result of increase in the diamine/VPh ratio. There was a negligible difference among BDA and HMDA in the transition from the unimers to the micelles suggesting a similar effect on the critical micelle concentration (CMC). The copolymer showed higher CMC in the presence of EDA compared with BDA and HMDA. EDA is less effective for micellization based on the fact that a stable five-membered ring is formed through the intramolecular hydrogen bonding. On the other hand, the copolymer formed no micelles by *n*-butylamine, so that the hydrodynamic radius and scattering intensity of the copolymer was immutable during micellization. No micellization by the monoamine indicates that micellization occurred through the hydrogen bond cross-linking between the PVPh blocks via diamine (Fig. 9). The scattering intensity was regarded as the apparent aggregation number (N_{agg}) estimated approximate-

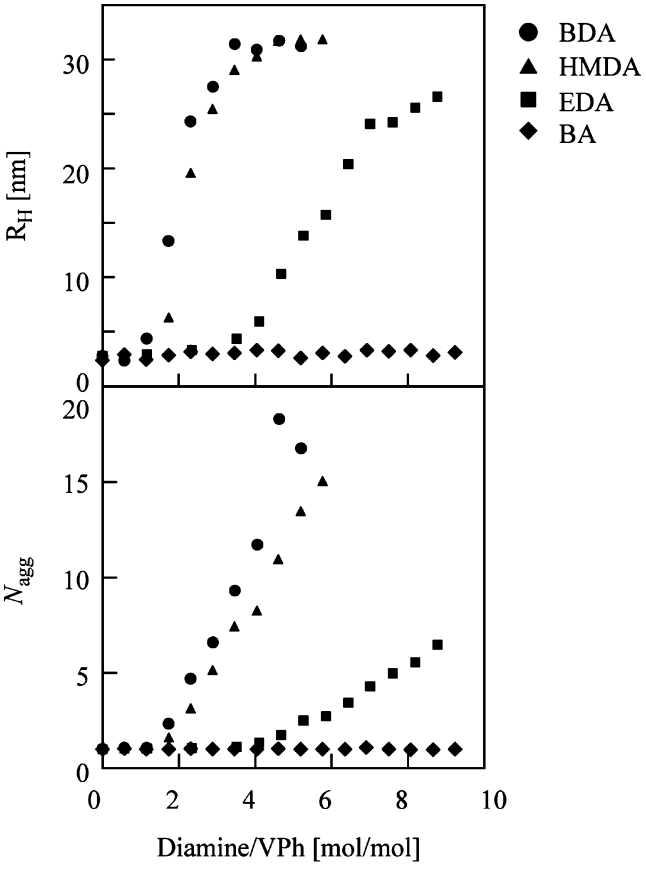


Fig. 8 The micellization of PVPh-*b*-P(AS-*r*-HBS-*r*-St) by BDA through hydrogen bond cross-linking

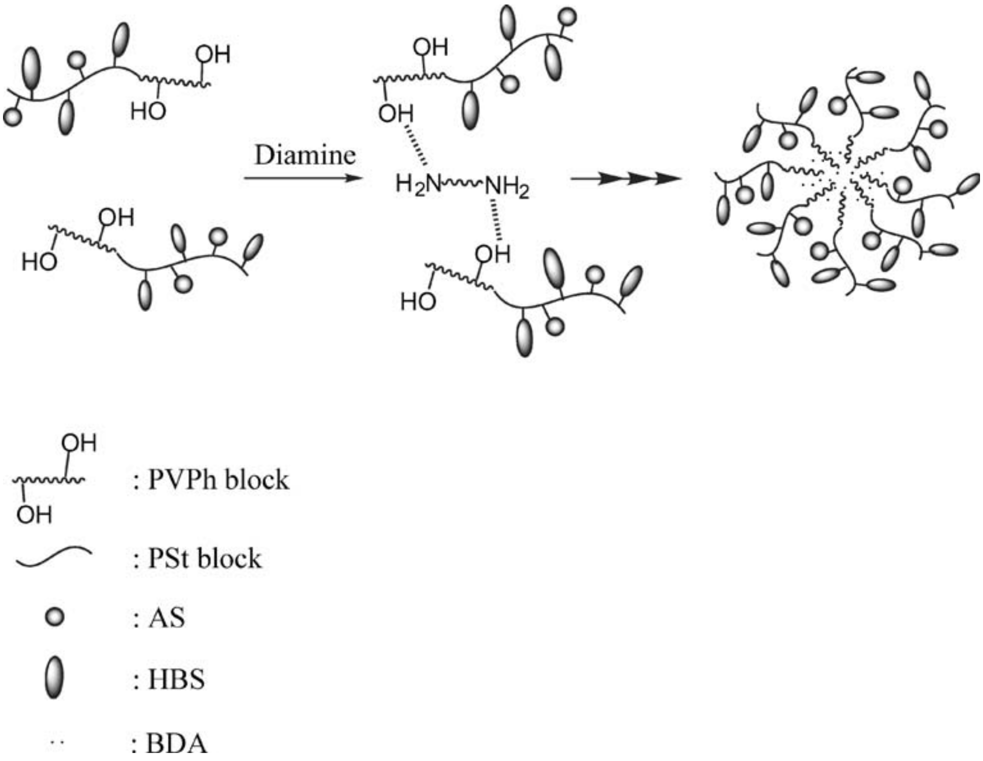


Fig. 9 Variations in the hydrodynamic radius and aggregation number of the PVPh-*b*-P(AS-*r*-HBS-*r*-St) copolymer vs the BDA/VPh ratio through micellization ([copolymer]=3.33 g/L) (20 °C, θ=90°)

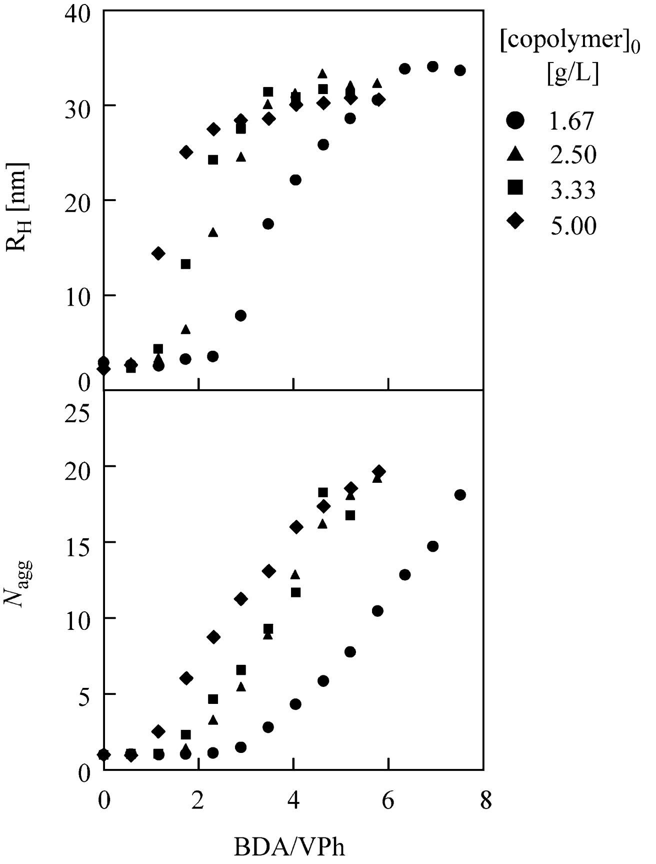


Fig. 10 Variations in the hydrodynamic radius and the aggregation number of the PVPh-*b*-P(AS-*r*-HBS-*r*-St) copolymer at the four different copolymer concentrations (20 °C, θ=90°)

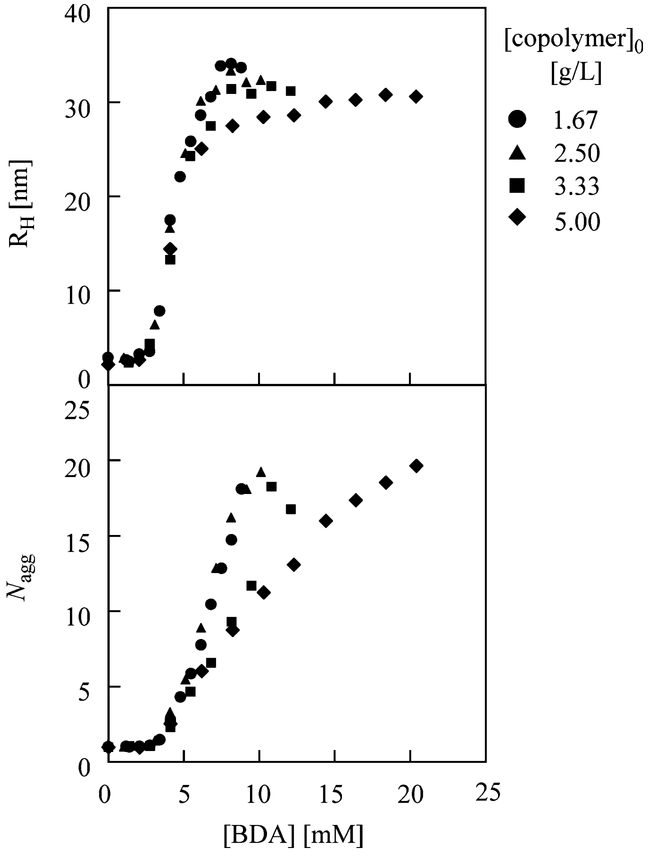


Fig. 11 Plots of the hydrodynamic radius and the aggregation number of the PVPh-*b*-P(AS-*r*-HBS-*r*-St) copolymer vs the BDA concentration (20 °C, θ=90°)

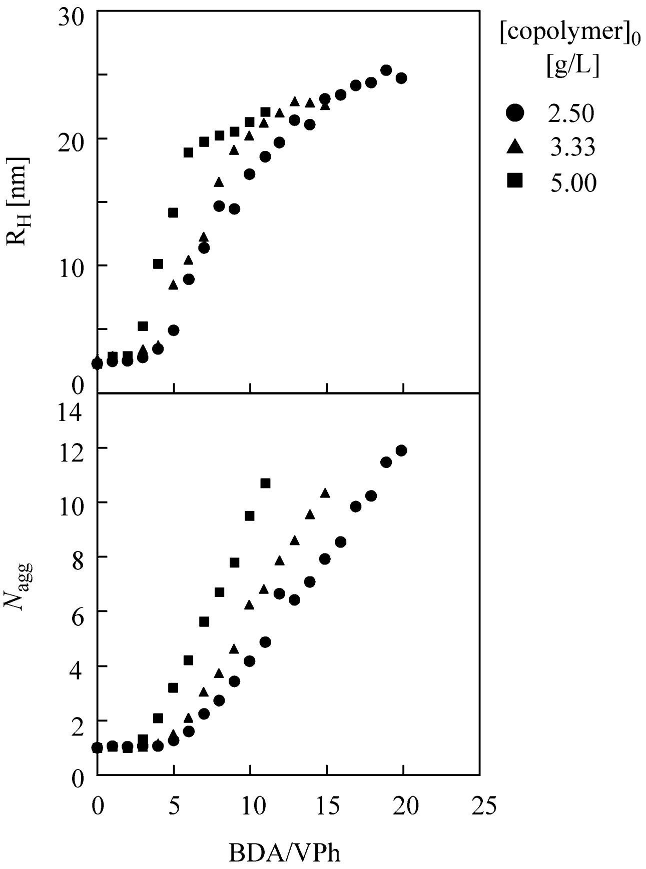


Fig. 12 Variations in the hydrodynamic radius and the aggregation number of the P(AS-*r*-HBS-*r*-VPh)-*b*-PSt copolymer at the different copolymer concentrations (20 °C, θ=90°)

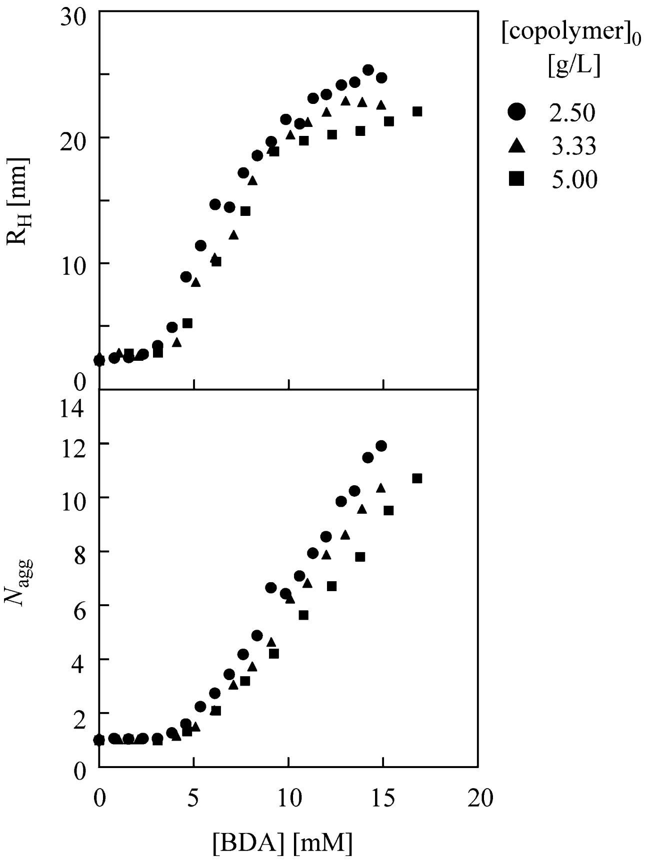


Fig. 13 Plots of the hydrodynamic radius and aggregation number of the P(AS-*r*-HBS-*r*-VPh)-*b*-PSt copolymer vs the BDA concentration (20 °C, θ=90°)

ly. This is because the copolymer concentration was constant during micellization and the interaction between the phenolic OH and the amino groups accompanying no aggregation had no effect in the scattering intensity [15].

Figure 10 shows the micellization of the PVPh-*b*-P(AS-*r*-HBS-*r*-St) copolymer by BDA at four different copolymer concentrations: 1.67, 2.50, 3.33 and 5.00 g/L. As the copolymer concentration decreased, the transition from unimers to micelles was shifted to a higher side of the BDA/VPh ratio. The copolymer at a lower concentration needed more BDA to form micelles. The hydrodynamic radius at complete micellization slightly increased with the decrease in copolymer concentration, while the aggregation number was almost independent of the copolymer concentration. Plotting the hydrodynamic radius and aggregation number of the copolymer vs the BDA concentration instead of the BDA/VPh ratio showed that the transition occurred at almost identical BDA concentrations (Fig. 11). This is implied that the CMC was determined by the diamine concentration, independent of the copolymer concentration.

The P(AS-*r*-HBS-*r*-VPh)-*b*-PSt diblock copolymer showed the same tendency of micellization regarding the

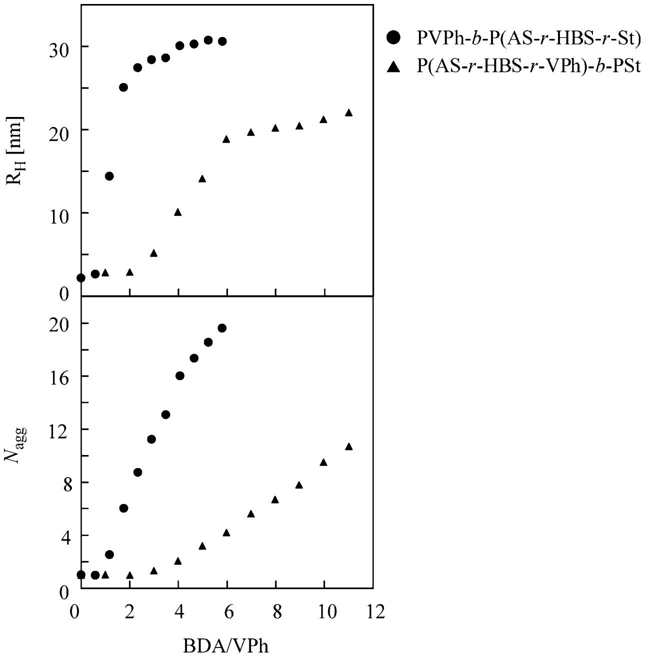


Fig. 14 Difference in the micellization by BDA between P(AS-*r*-HBS-*r*-VPh)-*b*-PSt and PVPh-*b*-P(AS-*r*-HBS-*r*-St) ([copolymer]=5.00 g/L) (20 °C, θ=90°)

copolymer concentration as the PVPh-*b*-P(AS-*r*-HBS-*r*-St) copolymer (Figs. 12 and 13). However, the P(AS-*r*-HBS-*r*-VPh)-*b*-PSt copolymer formed smaller micelles than PVPh-*b*-P(AS-*r*-HBS-*r*-St), in spite of the fact that the former had higher molecular weight of the corona blocks (Fig. 14). The formation of larger micelles by PVPh-*b*-P(AS-*r*-HBS-*r*-St) may be based on the steric hindrance of the AS and HBS units contained in the corona blocks. The P(AS-*r*-HBS-*r*-VPh)-*b*-PSt copolymer also produced micelles with a lower aggregation number than PVPh-*b*-P(AS-*r*-HBS-*r*-St). The steric hindrance of the AS and HBS units in the core blocks should prevent the VPh units from interacting with diamine and from aggregating into micelles. The difficulty in aggregation of the P(AS-*r*-HBS-*r*-VPh)-*b*-PSt copolymer was also reflected in the higher CMC.

Conclusion

We attained the preparation of micelles having the azo dye and UV absorbent at the cores or coronas through the micellization of the non-amphiphilic random block copolymers obtained by the TEMPO-mediated living radical polymerization. The copolymers showed no self-assembly in 1,4-dioxane. The copolymers, however, formed micelles in the non-selective solvent in the presence of α,ω-diamine. The copolymer at lower copolymer concentration needed more BDA to form micelles. The hydrodynamic radius of the micelles slightly increased with the decrease in copolymer concentration, while the aggregation number was almost independent of the copolymer concentration. The P(AS-*r*-HBS-*r*-VPh)-*b*-PSt diblock copolymer formed smaller micelles than PVPh-*b*-P(AS-*r*-HBS-*r*-St). The presence of the azobenzene and UV absorbent at the corona blocks should expand the corona blocks. The presence of these compounds at the cores prevented the VPh units from interacting with diamine and from aggregating into micelles resulting in the higher CMC and lower aggregation number of the micelles.

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