Colloid Polym Sci (2005) 283: 521–531
DOI 10.1007/s00396-004-1179-z

ORIGINAL CONTRIBUTION

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Preparation of micelles with azobenzene at their coronas or cores from 'nonamphiphilic' diblock copolymers

Published online: 4 August 2004
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Abstract Micelles with azobenzene at the coronas or the cores were prepared by the micellization of 'nonamphiphilic' diblock copolymers through hydrogen bond cross-linking. We used 4-(phenylazophenoxymethyl)styrene (AS) as the azobenzene. A poly(vinylphenol)-*block*-poly(AS-*co*-styrene) diblock copolymer (PVPh-*b*-P(AS-*co*-St)) was prepared by combination of the nitroxide-mediated living radical polymerization and the hydrolysis. The copolymer contained ca. 1 mol% of the azobenzene units in the P(AS-*co*-St) blocks on the basis of ^{1}H NMR analysis. The PVPh-*b*-P(AS-*co*-St) copolymer showed no micellization in 1,4-dioxane, the nonselective solvent. Dynamic light scattering demonstrated that the copolymer formed micelles in the presence of 1,4-butanediamine (BDA) in this solvent. ^{1}H NMR analysis revealed that the azobenzene moieties were located at the coronas of the micelles, because the signals of the aromatic protons originating from the azobenzene had no changes in the shape and the intensity by the micellization. UV analysis supported the presence of the azobenzene at the micellar coronas. The size of the PVPh-*b*-P(AS-*co*-St) micelles was independent of the copolymer concentration. On the other hand, the aggregation number of the micelles was dependent not only on the copolymer concentration but also on the kind of the diamine. A poly(AS-*co*-vinylphenol)-*block*-polystyrene diblock copolymer (P(AS-*co*-VPh)-*b*-PSt) formed the micelles with the azobenzene at the cores of the micelles by BDA. UV analysis demonstrated that the azobenzene at the micellar cores still had the potential to function as photorefractive switching.

Keywords Micelles · Unimers · Azobenzene · Hydrodynamic radius · Aggregation number

Introduction

The forms and size of polymer particles are important and affect the performance of materials. Spherical polymer particles have a great variety of applications in many fields of coating [1, 2, 3], adhesion [4, 5], painting [6, 7], cosmetics [8, 9], electronics [10], medicine, and biochemistry [11]. There are many papers on the preparation of polymer particles having functional groups on the surface for the appropriate use of the polymer particles in these fields. Examples include the modification of the surface with amino, carbonyl, peroxy, aldehyde, glycidyl, and ammonium phosphate groups by plasma treatment [12] and by suspension and emulsion polymerizations [13, 14, 15]. The size of the polymer particles is determined by a type of polymerization. Suspension

polymerization produces polymer particles with a 10–800 μm diameter [16, 17], while dispersion polymerization gives 1–30 μm-sized microspheres [18, 19, 20]. The polymer particles prepared by these polymerizations are stabilized in the cores of the polymeric micelles. Emulsion polymerization forms stabilizer-free polymer particles with the size of 0.1–5 μm [21, 22, 23], and miniemulsion polymerization provides much smaller microspheres of 0.07–0.25 μm [24]. Still smaller polymer particles, supermicrospheres on a nanoscale cannot be prepared by these heterogeneous polymerization techniques so far, however, the supermicrospheres can be obtained by molecular aggregation.

Spherical micelles are supermicrospheres formed by molecules self-assembling. The size of the micelles is mostly dependent on the size of the structural unit. For polymer micelles consisting of block copolymers, the size of the micelles is controlled by the block length, and is at most dozens of nm [25, 26, 27, 28]. The size distribution of the micelles is mostly dominated by the molecular weight distribution of the block copolymers [29]. While polymeric micelles serve as stabilizers for microspheres in suspension and dispersion polymerizations, the micelles are important in separation technology [30, 31] and drug delivery [32, 33]. Recently, polymeric micelles have also attracted considerable attention as gene carrier [34, 35]. In spite of the fact that the polymeric micelles occupy a significant position in medicine and industry, there are few publications on the modification of the micelles. The publications concern the introduction of disulfide into micelles to interact with nucleic acids [34] and the preparation of micelles with amino groups and carboxylic acids for plastic manufacturing and textile processing [36]. The modification of polymeric micelles with functional groups and materials should expand the range of their applications.

As an example of the modification of polymeric micelles, we describe here the preparation of micelles having azobenzene as the pendant group at the coronas or the cores. The polymeric micelles with the azobenzene moieties are expected as supermicrospheres with azobenzene useful for dye stuffs for DVD-R [37, 38]. A few papers have been published on the micelles of low molecular weight compounds containing azobenzene [39, 40, 41], while there is only one paper on polymeric micelles with azobenzene [42]. The micelles were formed from amphiphilic random copolymers with azobenzene at the polymer chain end. We applied the method of micelle formation of 'nonamphiphilic' block copolymers to the synthesis of the micelles with azobenzene at the coronas and the cores. While amphiphilic copolymers have solvophobic and solvophilic parts in the molecules, the nonamphiphilic copolymers consist entirely of solvophilic polymer blocks. Hence, the nonamphiphilic copolymers show no self-assembly, however, the copolymers aggregate into micelles by external stimuli or in the presence of additives. The nonamphiphilic copolymers have advantages over amphiphilic copolymers in designing copolymers, because it is unnecessary to take the solubility of the copolymers into account when designing copolymers. We have already published papers on the micelle formation of a nonamphiphilic poly(vinylphenol)-*block*-polystyrene diblock copolymer using α,ω-diamines through hydrogen bond cross-linking [43, 44, 45]. Azobenzene located at the micellar cores of nonamphiphilic copolymers should retain the mobility, because the micellar cores are composed of solvophilic polymer blocks. This paper describes the preparation of the micelles having azobenzene at the coronas or the cores through the micellization of nonamphiphilic diblock copolymers.

Experimental

Instrumentation Gel permeation chromatography (GPC) was performed with a Tosoh DP-8020 dual plunger pump with a RI-8020 refractive index monitor and with a CO-8020 column oven. Two polystyrene gel columns, Tosoh TSKgel α-M, were used with DMF as the eluent at 40 °C. UV spectra were recorded with Shimadzu UV-2200 UV-VIS recording spectrophotometer. ^{1}H NMR spectra were obtained with a Bruker ARX-500 NMR spectrometer. Light scattering experiments were performed at 20 °C at an angle of 90°, with a Photal Otsuka Electronics DLS-7000 super dynamic light scattering spectrometer equipped with LS-71 control unit, an LS-72 pump controller, and an argon ion laser operating at $\lambda = 488$ nm.

Materials 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-methoxy-TEMPO) was prepared as reported previously [46]. Benzoyl peroxide (BPO) was precipitated from chloroform, and crystallized in methanol at 0 °C. 4-*tert*-Butoxystyrene (^{t}BSt) was supplied from Hokko Chemical Industry Co. Ltd. ^{t}BSt and commercial grade styrene were washed with aqueous alkaline solution and water, and distilled over calcium hydride. Ethylenediamine (EDA), 1,4-butanediamine (BDA), hexamethylenediamine (HMDA), and *n*-butylamine were distilled over calcium hydride. DMF was purified by standing stirred over calcium hydride for several hours, and distilled over calcium hydride. 1,4-Dioxane was purified by refluxing on sodium for several hours, and distilled over sodium. Extrapure 4-phenylazophenol, potassium carbonate, and trifluoroacetic acid were used without further purification. P^{t}BSt prepolymer was prepared as reported previously [47]. The degree of polymerization (DP) of the prepolymer and the molecular weight were DP = 87.3 and Mn = 15400, respectively on the basis of ^{1}H NMR.

Synthesis of 4-(phenylazophenoxymethyl)styrene (AS) A solution of 4-phenylazophenol (3.25 g, 16.4 mmol) in DMF (20 mL) was added at 0 °C to a suspension of K_2CO_3 (2.72 g, 19.7 mmol) in DMF (20 mL). The mixture was stirred at room temperature for 20 min. A solution of 4-chloromethylstyrene (3.00 g, 19.7 mmol) in DMF (10 mL) was added to the mixture at 0 °C. After the mixture was stirred at room temperature for 28 h, ether (100 mL) was poured into it. The ether layer was washed with water, concentrated by evaporation, and dried in vacuo for several hours. The crude product (3.86 g) was obtained. The product was purified by recrystallization from benzene to obtain AS of 2.21 g. ^{1}H NMR ($CDCl_3$): δ 5.16 (2H, s, methylene, C H_2), 5.27 (1H, d, $J = 12$ Hz, vinyl C H), 5.76 (1H, d, $J = 18$ Hz, vinyl C H), 6.73 (1H, dd, $J = 12$, 18 Hz, vinyl C H), 7.18 (2H, d, $J = 8$ Hz, aromatic O-C = C H), 7.4–7.5 (7H, m, aromatic CH_2 = CH-C_6H_4, N = N-C = CH-C H = C H), 7.87 (2H, d, $J = 8$ Hz, aromatic, O-C = CH-C H), 7.92 (2H, d, $J = 9$ Hz, aromatic, N = N-C = C H). Mass (M + 1): 315.15.

Synthesis of a PVPh-b-P(AS-co-St) diblock copolymer P^{t}BSt prepolymer (Mn = 15400 determined by ^{1}H NMR, Mw/Mn = 1.27, 447 mg), AS (60 mg, 0.191 mmol), and St (2.00 g, 19.2 mmol) were placed in an ampoule. After the contents were degassed, the ampoule was sealed in vacuo. The polymerization was carried out at 125 °C for eight 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 the P^{t}BSt-*b*-P(AS-*co*-St) random block copolymer (2.01 g).

P^{t}BSt-*b*-P(AS-*co*-St) (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 300 mL of methanol, and stirred for 6 h at room temperature to remove a VPh homopolymer. The precipitate was collected by filtration, dried in vacuo for several hours. The PVPh-*b*-P(AS-*co*-St) random diblock copolymer (390 mg) was obtained.

Synthesis of a P(AS-co-VPh)-b-PSt diblock copolymer ^{t}BSt (6.93 g, 39.3 mmol), AS (125 mg, 0.398 mmol), 4-methoxy-TEMPO (109 mg, 0.586 mmol), and BPO (109 mg, 0.450 mmol) were placed in an ampoule. After the contents were degassed, the ampoule 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 resulting polymer was dried in vacuo for several hours to obtain a P(AS-*co*-^{t}BSt) random copolymer (4.68 g).

The P(AS-*co*-^{t}BSt) copolymer (447 mg) and St (2.00 g, 19.2 mmol) were placed in an ampoule. After the contents were degassed, the ampoule was sealed in vacuo. The polymerization was carried out at 125 °C for 45 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-*co*-^{t}BSt)-*b*-PSt block copolymer (1.90 g).

P(AS-*co*-^{t}BSt)-*b*-PSt (500 mg) thus obtained was dissolved in THF (15 mL), and conc. HCl (1 mL) was added to the solution at room temperature. The mixture was kept at 85 °C for 5.5 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 13 h at room temperature to remove P(AS-*co*-VPh). The precipitate was collected by filtration, dried in vacuo for several hours. The P(AS-*co*-VPh)-*b*-PSt diblock copolymer (400 mg) was obtained.

Light scattering measurements: general procedure PVPh-*b*-P(AS-*co*-St) (10 mg) was dissolved in 1,4-dioxane (3 mL) and 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, 6 μL of BDA solution (BDA, 122 mg, 1.38 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 [48]. Aggregation numbers were estimated by using scattering intensity of the micelles and the unimers.

Results and discussion

Preparation of micelles with azobenzene at the coronas

The PVPh-*b*-PSt diblock copolymer with the azobenzene in the PSt blocks was prepared through the radical copolymerization of AS and St by a P^{t}BSt prepolymer as an initiator. The P^{t}BSt prepolymer was prepared by the living radical polymerization by BPO as an initiator and 4-methoxy-TEMPO as a mediator. The resulting P^{t}BSt-*b*-P(AS-*co*-St) diblock copolymer was hydrolyzed with hydrochloric acid to convert PVPh-*b*-P(AS-*co*-St)

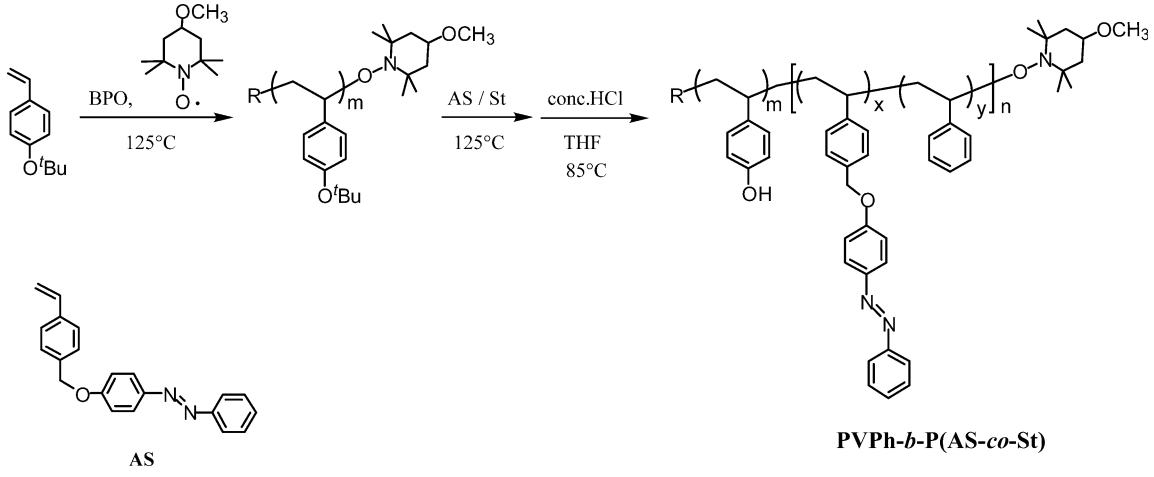
(Fig. 1). Figure 2 shows the ^{1}H NMR spectra of the P^{t}BSt-*b*-P(AS-*co*-St) and PVPh-*b*-P(AS-*co*-St) copolymers. A signal based on the *tert*-butyl groups at 1.25 ppm was absent in the spectrum of PVPh-*b*-P(AS-*co*-St), indicating that all the ^{t}BSt units were converted to the VPh units. The small signals at 0.85 and 0.94 ppm observed in this spectrum are assigned to the tetramethyl protons of 4-methoxy-TEMPO attached to the chain end of the copolymer. The proton signals at 4.7–5.1 ppm are attributed to the benzyl group bonded to the 4-phenylazophenoxy moiety. The doublets discerned at 7.90 and 7.43 ppm are based on the aromatic protons of the azobenzene. The signals at 7.90 ppm originate from the protons located at the *ortho* positions to the azo group, while those at 7.43 ppm from the protons at the *meta* and *para* positions of the phenyl group. Signals of the hydroxyl protons of the VPh units were overlapped with the signals at 7.43 ppm, and were shifted to a lower side of the magnetic field by the addition of CF_3COOH (Fig. 3). The unit ratio of the AS to St in the P(AS-*co*-St) blocks was estimated as AS/St = 0.011/0.989, using the signal intensities at 7.2–7.6 ppm before and after the addition of CF_3COOH. The molecular weight of the PVPh-*b*-P(AS-*co*-St) copolymer was estimated as Mn = 10490-*b*-95000, on the basis of this AS/St ratio, the DP of the P^{t}BSt prepolymer, and the signal intensities at 6.2–7.3 and 7.90 ppm.

Figure 4 shows GPC profiles of the PVPh-*b*-P(AS-*co*-St) copolymer and the P^{t}BSt prepolymer. The molecular weight distributions of PVPh-*b*-P(AS-*co*-St) and the prepolymer were estimated to be Mw/Mn = 2.18 and 1.27, respectively. The curve of the block copolymer was somewhat broadened at a lower molecular weight side. This broadening should be caused by adsorption of the PVPh blocks on PSt gels in the columns with DMF as the eluent. Thin layer chromatography using methanol as the eluent revealed that the block copolymer contained no homopolymer of VPh.

The PVPh-*b*-P(AS-*co*-St) diblock copolymer formed no micelles in 1,4-dioxane, because the PVPh and P(AS-*co*-St) blocks are solvophilic to 1,4-dioxane. Dynamic light scattering studies demonstrated that this nonamphiphilic PVPh-*b*-P(AS-*co*-St) diblock copolymer showed micellization in the presence of BDA in this solvent. Figure 5 shows the variability in the distribution of the hydrodynamic radius of the copolymer in the NNLS analysis. The copolymer exists as the unimers in the absence of the diamine. The distribution of the unimers was observed around 3.5 nm of the hydrodynamic radius. When BDA was added to the copolymer solution (BDA/VPh = 0.5), another distribution appeared around ca. 40 nm. This distribution was attributed to the micelles. At BDA/VPh = 3, the distribution based on the unimers disappeared and only the distribution of the micelles was observed.

Figure 6 shows the variation in the hydrodynamic radius and the aggregation number of the PVPh-*b*-P(AS-*co*-St) copolymer through the micellization by BDA. The hydrodynamic radius of the copolymer was determined by the cumulant method of analysis. When the micelles and the unimers coexisted in the solution, the hydrodynamic radii were estimated as the averages of the hydrodynamic radii for the micelles and the unimers on the basis of ratios of their existence. The ratios of the micelles to the unimers were estimated from the integral intensity of the distributions of the hydrodynamic radii for the micelles and unimers. The aggregation numbers were represented as relative aggregation numbers estimated from the scattering intensities. This estimation is based on the fact that the copolymer concentration is constant during the micellization and that the interaction between the phenolic OH and the amino groups has no effect in the scattering intensity. The propriety of this estimation was supported by the result that the addition of *n*-butylamine to the copolymer solution made no

Fig. 1 Synthesis of the PVPh-*b*-P(AS-*co*-St) diblock copolymer



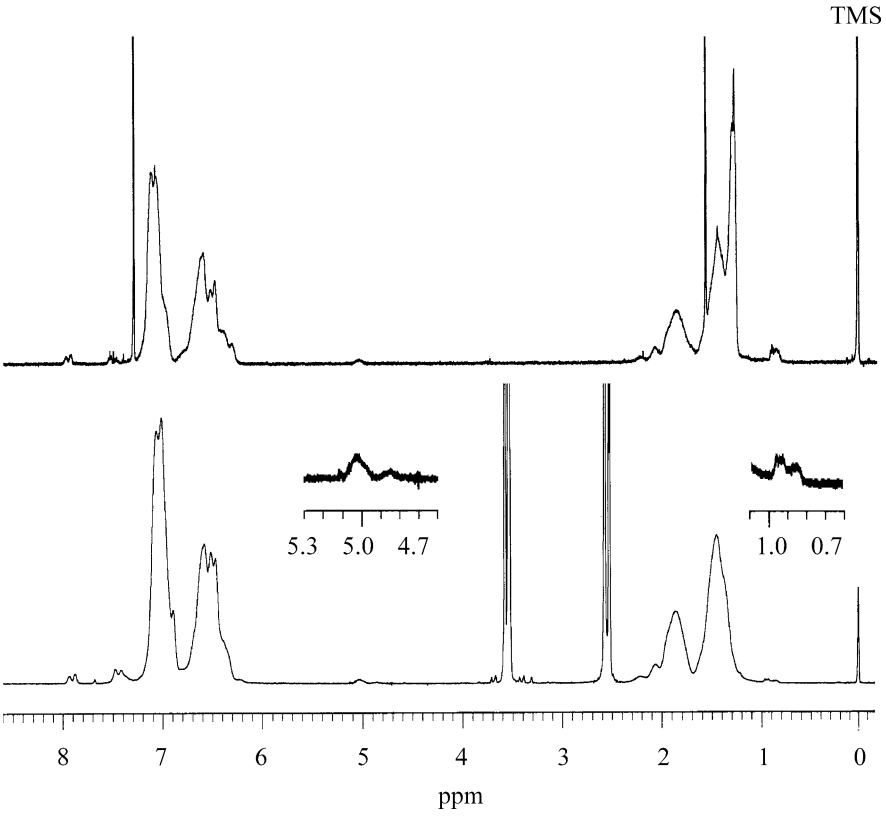


Fig. 2 ^{1}H NMR spectra of P^{t}BSt-*b*-P(AS-*co*-St) (*upper*, solvent: $CDCl_3$) and PVPh-*b*-P(AS-*co*-St) (*lower*, solvent: 1,4-dioxane-d_8)

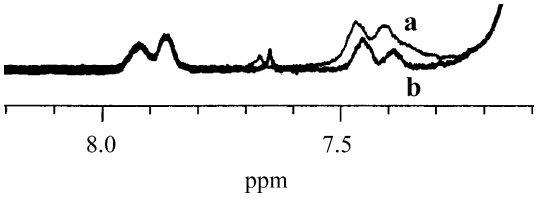


Fig. 3a,b ^{1}H NMR spectra of PVPh-*b*-P(AS-*co*-St): **a** before; **b** after the addition of CF_3COOH (solvent: 1,4-dioxane-d_8)

changes in the scattering intensity of the copolymer. The hydrodynamic radius and the aggregation number of the copolymer increased with an increase in the BDA/VPh ratio. The copolymer formed the micelles with 36.2 nm of the hydrodynamic radius and 26 of the aggregation number at BDA/VPh = 6.

The ^{1}H NMR revealed that the AS moieties were located at the coronas of the micelles. The spectrum of the micelles is shown in Fig. 7. BDA in 1,4-dioxane-d_8 showed the two sharp signals at 2.61 and 1.41 ppm and the broad signals at 0.9–1.3 ppm. The former signals originate from the two different methylenes and the latter from the amino groups. By the micellization, the two sharp signals of the methylenes were broadened, while the signals of the amino groups disappeared. The signals of the phenolic OH at 7.3–7.5 ppm also disappeared by the micellization. The broadening of the

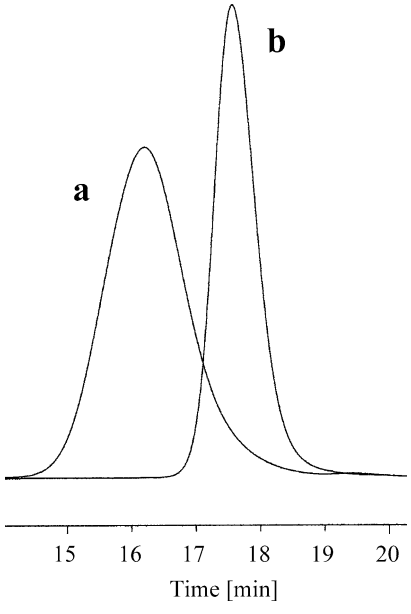


Fig. 4a,b GPC profiles of: **a** PVPh-*b*-P(AS-*co*-St); **b** the P^{t}BSt prepolymer

methylene signals of BDA and the disappearance of the signals of the amino and the hydroxyl protons indicate that BDA was covered with the micellar cores prepared

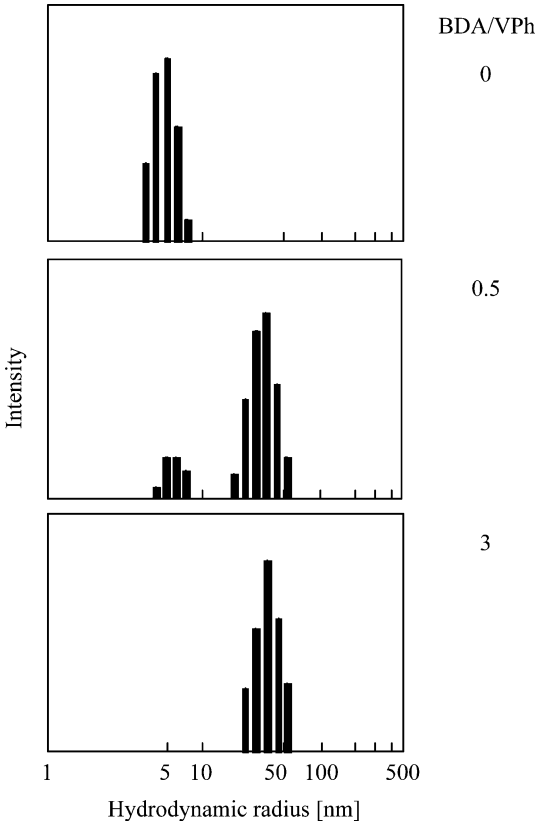


Fig. 5 Variability in the intensity distribution of the hydrodynamic radius of PVPh-*b*-P(AS-*co*-St) by the addition of BDA ([copolymer] = 3.33×10^{-3} g/mL)

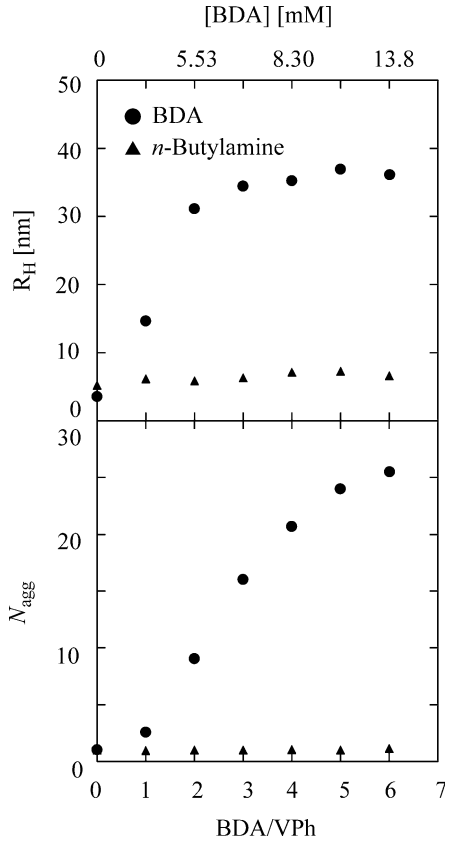


Fig. 6 Variation in the hydrodynamic radius and the aggregation number of the PVPh-*b*-P(AS-*co*-St) copolymer vs the BDA/VPh ratio through the micellization ([copolymer] = 3.33×10^{-3} g/mL)

through the interaction between the VPh blocks and BDA. On the other hand, the signals based on the azobenzene at 7.43 and 7.90 ppm were still discerned without any broadening and shifting even after the micellization (Fig. 8). The relative intensity of the signals at 7.90 ppm to those at 6.3–7.2 ppm was the same at any BDA/VPh. Accordingly, the azobenzene moieties were located at the micellar coronas (Fig. 9).

The UV analysis also demonstrated that the azobenzene moieties were located on the micelles. Figure 10 shows the UV spectra of the micelles prepared from PVPh-*b*-P(AS-*co*-St) and from the PVPh-*b*-PSt using BDA. The PVPh-*b*-PSt copolymer has the molecular weight of Mn = 9610-*b*-68800. The PVPh-*b*-P(AS-*co*-St) micelles showed the absorption at 348 and 436 nm originating from the azobenzene. The former is based on the $\pi \rightarrow \pi^*$ transition of the trans isomer, and the latter on the $n \rightarrow \pi^*$ of the cis. The ratio of the absorbance at 347 nm to that at 436 nm for the micelles was in good agreement with that for the unimers, indicating that the ratio of the isomers had no changes by the micellization. In addition, the unit ratio of AS to St in the P(AS-*co*-St) blocks was estimated by UV to AS/St = 0.013/0.987 for the micelles and 0.014/0.986 for the unimers based on the absorbance at 347 nm. These values are in good agreement with AS/St = 0.011/0.989 estimated by ^{1}H NMR.

Figure 11 shows the variation in the hydrodynamic radius and the aggregation number of PVPh-*b*-P(AS-*co*-St) for three different copolymer concentrations. The transition from the unimers to the micelles was shifted to a higher side of BDA/VPh as the copolymer concentration decreased, indicating that the copolymer at a lower concentration needed more BDA to form the micelles. However, there was a slight difference in the hydrodynamic radius at the complete micellization among the three copolymer concentrations, while the aggregation number at the micellization completed had somewhat dispersion for the copolymer concentration. These results are in good agreement with the results on the micellization of PVPh-*b*-PSt by BDA [43].

The transition from the unimers to the micelles was dependent not only on the copolymer concentration but also on the kind of the diamine. Figure 12 shows the variation in the hydrodynamic radius and the aggregation number of the copolymer through the micellization by EDA, BDA, and HMDA. As the chain length between the amino groups decreased, the transition from

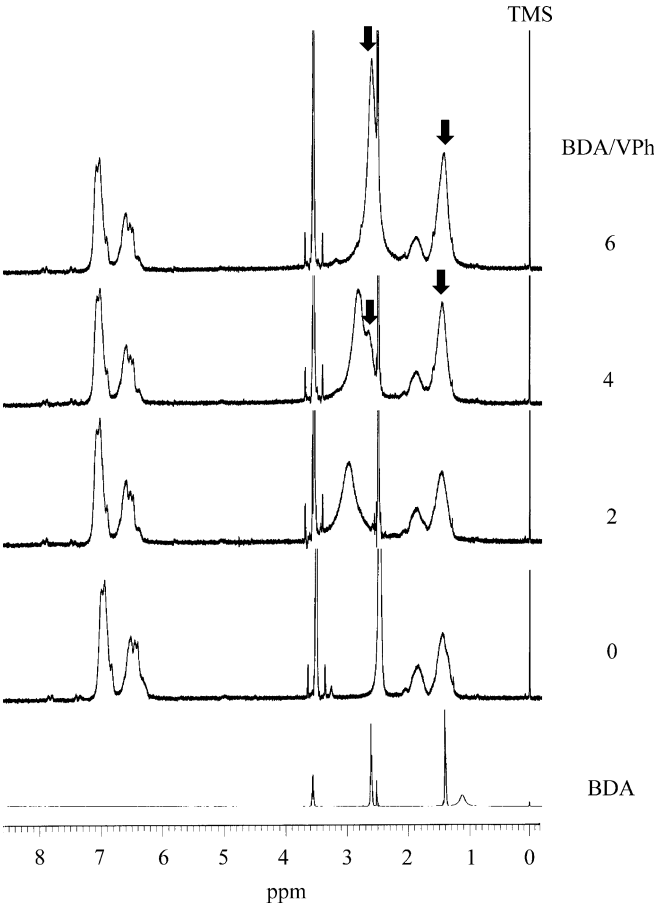


Fig. 7 ^{1}H NMR spectra of PVPh-*b*-P(AS-*co*-St) in the micellization by BDA ([copolymer] = 6.67×10^{-3} g/mL, solvent: 1,4-dioxane-d_8)

the unimers to the micelles was shifted to a higher side of the diamine/VPh ratio. In particular, EDA gave a great shift in the unimers-to-micelles transition. The copolymer needed much more EDA to form the micelles because of the low ability to form the hydrogen bond cross-linking. This low ability of EDA was caused by the formation of intramolecular hydrogen bonding. The size of the micelles prepared by EDA was almost the same as that by BDA at the complete micellization, although the micelles by EDA had the markedly low aggregation number.

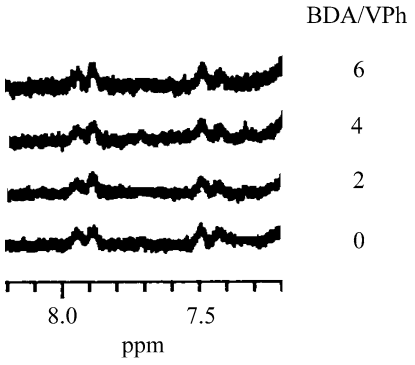


Fig. 8 ^{1}H NMR spectra of the azobenzene in the micellization of PVPh-*b*-P(AS-*co*-St) by BDA ([copolymer] = 6.67×10^{-3} g/mL, solvent: 1,4-dioxane-d_8)

Preparation of micelles with azobenzene at the cores

P(AS-*co*-VPh)-*b*-PSt was prepared by the nitroxide-mediated living radical polymerization, followed by the hydrolysis (Fig. 13). The living radical copolymerization of AS and ^{t}BSt was carried out by BPO as an initiator and 4-methoxy-TEMPO at 125 °C for 24 h. The block copolymerization with St was performed at 125 °C for 45 h using the resulting P(AS-*co*-^{t}BSt) random copolymer as an initiator, producing a P(AS-*co*-^{t}BSt)-*b*-PSt diblock copolymer. The P(AS-*co*-VPh)-*b*-PSt was obtained by the hydrolysis of the P(AS-*co*-^{t}BSt)-*b*-PSt copolymer.

Figure 14 shows ^{1}H NMR spectra of the P(AS-*co*-^{t}BSt) random copolymer and the P(AS-*co*-VPh)-*b*-PSt diblock copolymer. The AS/^{t}BSt unit ratio was 0.015/0.985 on the basis of the signal intensities at 7.90 ppm and at 6.0–6.9 ppm. The DP of the random copolymer was estimated as 86.2, using the integral intensities at 3.22 ppm attributed to 4-methoxy-TEMPO and at 6.0–6.9 ppm. Accordingly, the molecular weight of the P(AS-*co*-^{t}BSt) copolymer was Mn = 15400. P(AS-*co*-^{t}BSt)-*b*-PSt was converted to P(AS-*co*-VPh)-*b*-PSt by

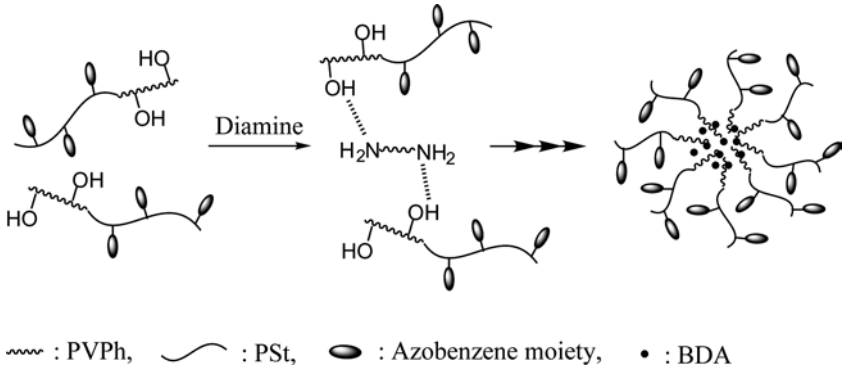


Fig. 9 The micelle formation of PVPh-*b*-P(AS-*co*-St) by BDA through hydrogen bond cross-linking

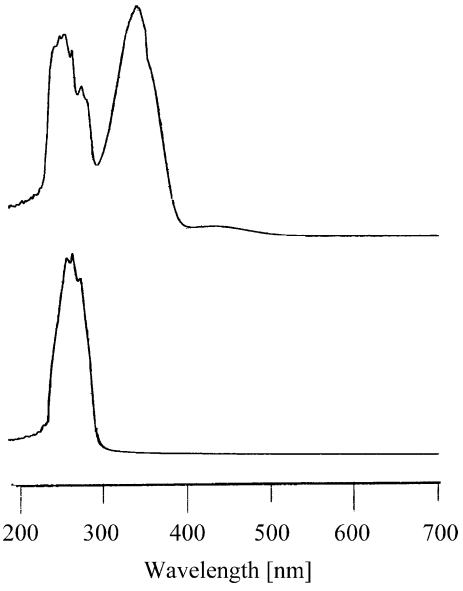


Fig. 10 UV spectra of the PVPh-*b*-P(AS-*co*-St) micelles (*upper*, BDA/VPh = 10) and the PVPh-*b*-PSt micelles (*lower*, BDA/VPh = 12) (solvent: 1,4-dioxane, [copolymer] = 0.833×10^{-3} g/mL)

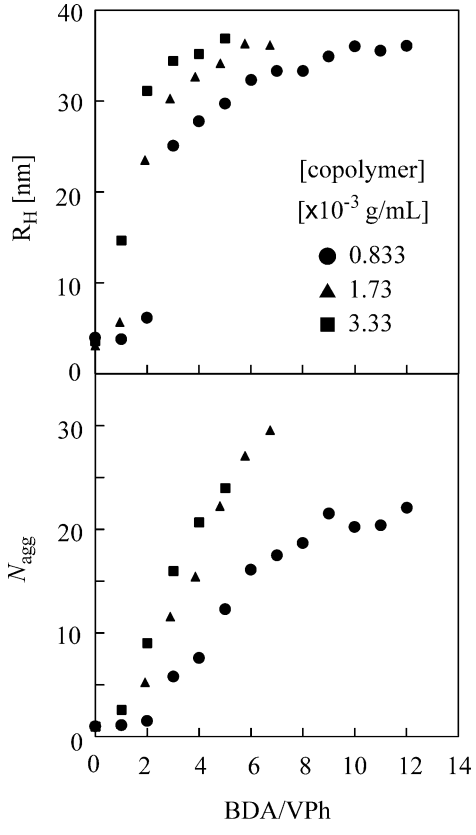


Fig. 11 Variation in the hydrodynamic radius and the aggregation number of PVPh-*b*-P(AS-*co*-St) in the micellization by BDA for different copolymer concentrations

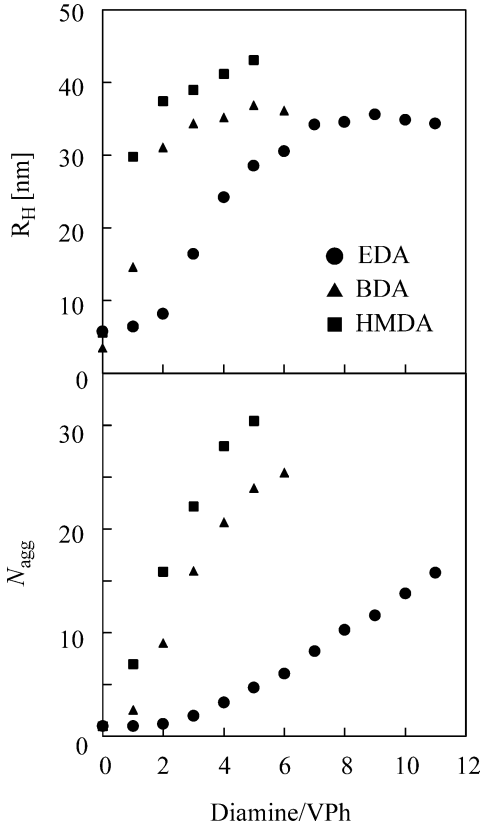


Fig. 12 Variability in the hydrodynamic radius and the aggregation number of PVPh-*b*-P(AS-*co*-St) through the micellization by the different kinds of the diamines ([copolymer] = 3.33×10^{-3} g/mL)

the hydrolysis, because the signal of the *tert*-butyl groups at 1.22 ppm was absent in the spectrum of P(AS-*co*-VPh)-*b*-PSt. The signals based on the azobenzene were not discerned in the spectrum of the block copolymer, because of too low content of the AS units in the block copolymer. The molecular weight of P(AS-*co*-VPh)-*b*-PSt was estimated to be Mn = 10600-*b*-80900, using the DP of P(AS-*co*-^{t}BSt) and the signal intensities at 6.0–6.9 ppm and at 7.3–7.6 ppm. The broad signal at 7.3–7.6 ppm was based on the hydroxyl protons of the VPh units. GPC profiles of the block copolymer and the prepolymer are shown in Fig. 15. The molecular weights and the polydispersities of P(AS-*co*-VPh)-*b*-PSt and P(AS-*co*-^{t}BSt) were Mn = 44700 (Mw/Mn = 1.81) and Mn = 9900 (Mw/Mn = 1.24), respectively.

As can be seen in Fig. 16, the P(AS-*co*-VPh)-*b*-PSt copolymer formed the smaller micelles than PVPh-*b*-P(AS-*co*-St), caused by the lower molecular weight of P(AS-*co*-VPh)-*b*-PSt. However, there were no significant differences in the unimers-to-micelles transition and in the aggregation number between these block copolymers. The dependence of the copolymer concentration on the hydrodynamic radius and the aggregation

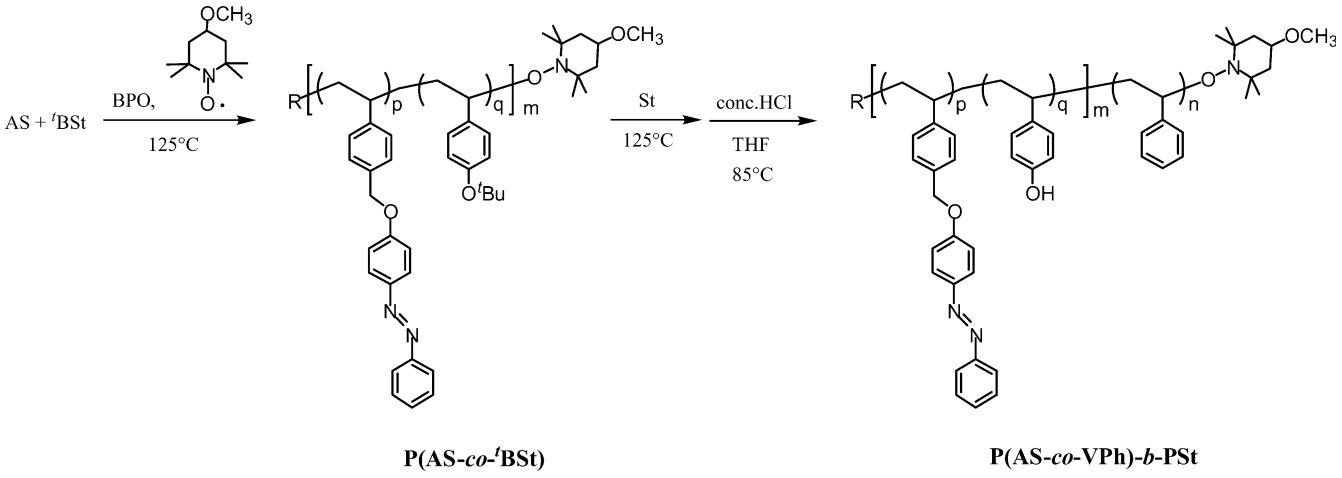


Fig. 13 Synthesis of the P(AS-*co*-VPh)-*b*-PSt diblock copolymer

number of the micelles is shown in Fig. 17. The unimers-to-micelles transition was shifted to a higher side of BDA/VPh as the copolymer concentration decreased. The copolymer at a lower copolymer concentration had smaller aggregation number at the complete micellization, although the size of the micelles was independent of the copolymer concentrations. These results are in agreement with those on the PVPh-*b*-P(AS-*co*-St) micelles.

The UV analysis demonstrated the presence of the azobenzene in the micelles. Figure 18 shows the UV spectrum of the P(AS-*co*-VPh)-*b*-PSt micelles. The absorbance of azobenzene was observed at 348 and 436 nm, and had no changes in the ratio by the micellization. The unit ratio of AS/VPh in the P(AS-*co*-VPh) blocks also had no changes between the unimers and the micelles. The AS/VPh ratio was estimated by UV as 0.013/0.987 on the basis of the absorbance at 348 nm. This ratio showed a good agreement with that by ^{1}H NMR. In spite of the azobenzene located at the cores of the micelles, no changes in the absorbance and the unit

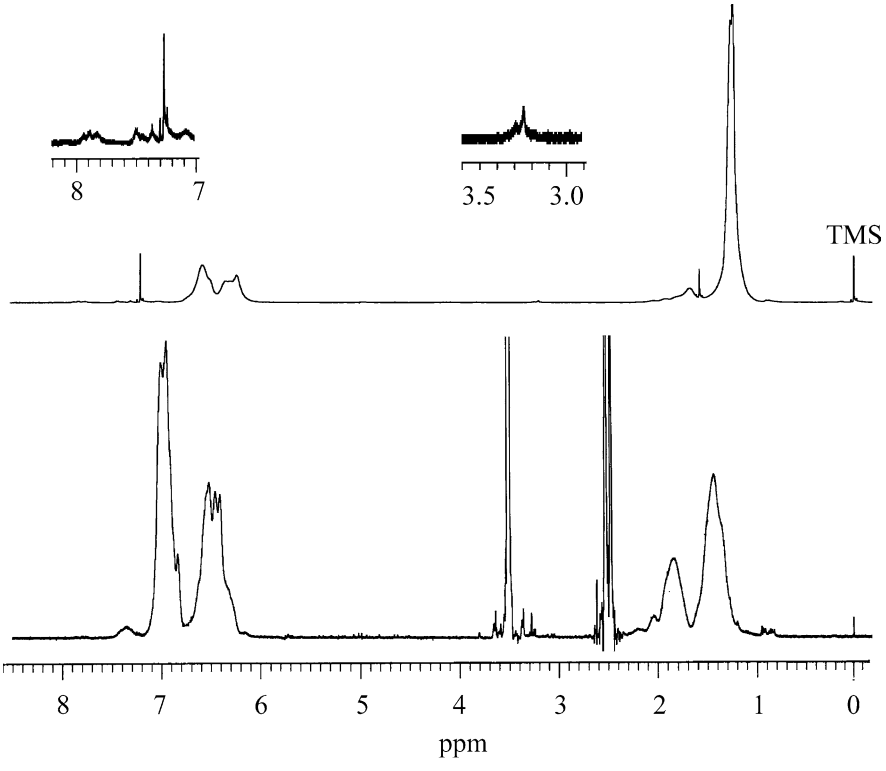


Fig. 14 ^{1}H NMR spectra of P(AS-*co*-^{t}BSt) (*upper*, solvent: $CDCl_3$) and P(AS-*co*-VPh)-*b*-PSt (*lower*, solvent: 1,4-dioxane-d_8)

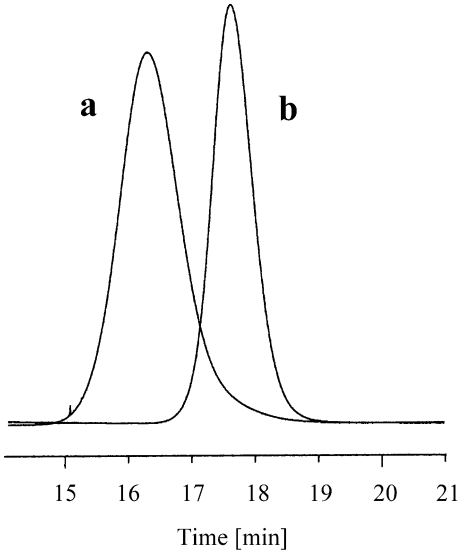


Fig. 15a,b GPC profiles of: **a** P(AS-*co*-VPh)-*b*-PSt; **b** the P(AS-*co*-^{t}BSt) prepolymer

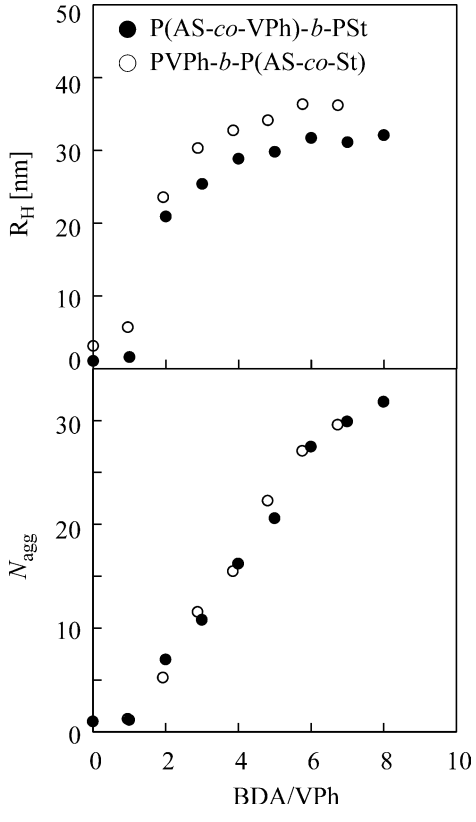


Fig. 16 Variation in the hydrodynamic radius and the aggregation number of P(AS-*co*-VPh)-*b*-PSt and PVPh-*b*-P(AS-*co*-St) vs BDA/VPh ([copolymer] = 1.67×10^{-3} g/mL)

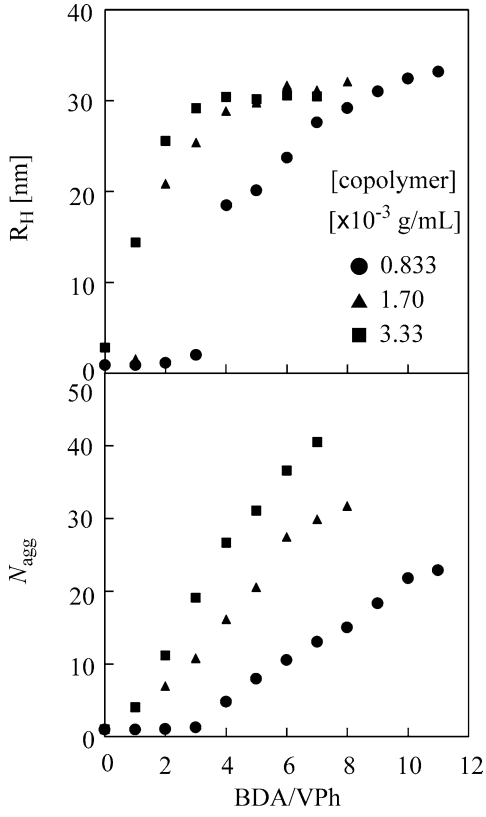


Fig. 17 Variation in the hydrodynamic radius and the aggregation number of P(AS-*co*-VPh)-*b*-PSt in the micellization by BDA for different copolymer concentrations

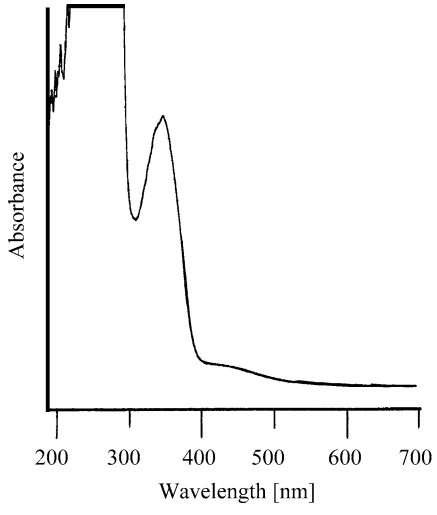


Fig. 18 UV spectrum of the P(AS-*co*-VPh)-*b*-PSt micelles (solvent: 1,4-dioxane, [copolymer] = 0.833×10^{-3} g/mL, BDA/VPh = 10)

ratio between the unimers and micelles can be accounted for by the fact that the micellar cores consist of the solvophilic P(AS-*co*-VPh) blocks. Consequently, the P(AS-*co*-VPh)-*b*-PSt micelles are expected to function as photorefractive switching, as are the PVPh-*b*-P(AS-*co*-St) micelles.

Conclusion

We prepared the PVPh-*b*-PSt diblock copolymers with the azobenzene in the PSt blocks or in the PVPh blocks by the convenient living radical polymerization. The PVPh-*b*-P(AS-*co*-St) formed the micelles in the nonselective solvent in the presence of the α,ω-diamines. The ^{1}H NMR analysis demonstrated that the azobenzene moieties were located at the coronas of the micelles, because the signals of the aromatic protons originating from the azobenzene had no changes in the shape and the intensity by the micellization. The hydrodynamic radius of the micelles was independent of the copolymer concentration, while the aggregation number was dependent on it. The aggregation number of the micelles was also dependent on the kind of the diamine.

The P(AS-*co*-VPh)-*b*-PSt diblock copolymer formed the micelles with azobenzene at the cores of the micelles by BDA. The UV analysis demonstrated that the azobenzene still had the potential to function as photorefractive switching, in spite of the fact that the azobenzene was located at the micellar cores. This was attributed to the formation of the micellar cores by the solvophilic polymer blocks.

This is an example of the preparation of the micelles with the functional material at the cores or the coronas. This method of preparing the micelles can be applied to the synthesis of supermicrospheres having a great variety of functional materials by taking the place of the azobenzene by other functional materials.

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