Colloid Polym Sci (2005) 283: 872–879
DOI 10.1007/s00396-004-1229-6

ORIGINAL CONTRIBUTIONS

Eri Yoshida
Masayo Ohta

Preparation of light-stable micelles with azo dyes from a nonamphiphilic random block copolymer

Received: 15 July 2004
Accepted: 30 October 2004

E. Yoshida (✉) · M. Ohta
Department of Polymer Science and Engineering, Kyoto Institute of Technology, Goshokaido-cho, Matsugasaki, Sakyo, Kyoto 606-8585, Japan
E-mail: eyoshida@tutms.tut.ac.jp
Tel.: +81-532-44-6814
Fax: +81-532-48-5833

Present address: E. Yoshida
Department of Materials Science, Toyohashi University of Technology, 1-1, Hibarigaoka, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan

Abstract Light-stable micelles with azo dyes were prepared by micelle formation of a nonamphiphilic diblock copolymer containing azobenzene and UV absorbent at ca. 1 mol% as the unit ratios. The nonamphiphilic block copolymer consists of two different kinds of random copolymer blocks: poly[4-(phenylazophenoxymethyl)styrene-*co*-vinylphenol] (P(AS-*co*-VPh)) and poly[4-(2-hydroxybenzophenoxymethyl)styrene-*co*-styrene] (P(HBS-*co*-St)). This random block copolymer, P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) formed the micelles in the presence of 1,4-butanediamine (BDA) through hydrogen bond cross-linking between the VPh units via BDA. The micelles had the azobenzene moieties at the cores and the UV absorbents at the coronas. The micelles showed a small color difference in color fading experiments, in comparison with the unimers and with micelles having no UV absorbent at the coronas. It is significant that the diblock copolymer forms the micelles and has the UV absorbents at the coronas to suppress the color fading. Furthermore, the chain length of α,ω-diamines had no effect on the hydrodynamic radius of the micelles, but affected the aggregation number and the cmc.

Keywords A nonamphiphilic diblock copolymer · 4-(Phenylazophenoxymethyl)styrene (AS) · 4-(2-Hydroxybenzophenoxymethyl) styrene (HBS) · Hydrodynamic radius · Aggregation number

Introduction

Azo dyes account for about half of the total number of dyes. The range of azo dyes extends from a wavelength of yellow at 350 nm [1] to over 650 nm for green [2]. This variety of azo dyes is based on the fact that the dyes are easily synthesized by diazonium coupling [3–6]. The wavelength of azo dyes is manipulated by selecting the kind, position, and number of substituents on the azobenzene [1]. Insertion of functional groups between the azo group and the phenyl groups in the azobenzene affects the wavelength. The functional groups can be, for instance, amido [7, 8] and amino groups [9]. Substitution of the phenyl groups of azobenzene by other aromatic rings also influences the wavelength. Examples include the use of biphenyl [8, 10, 11], naphthalene [8, 10–12], pyrazole [7, 10, 13], benzothiazole [14], triazine [13, 15], and pyradine [2] instead of the phenyl groups. And furthermore, extension of the conjugation of the azobenzene is another way to vary the wavelength. The extension of conjugation was attained by introducing C = C double bonds [14, 16] and over 2 moles of azo groups into azobenzene [8, 10, 13, 14]. The presence of functional groups and heterocyclic rings in azo dyes diminishes the stability of the dyes against oxidation and decomposition by UV, resulting in fading. Accordingly, many paints and inks containing azo dyes are often used with UV absorbents. Some azo dyes are supported on polymers to protect them from UV [17].

We prepared light-stable supermicrospheres with azo dyes through the micelle formation of a 'nonamphiphilic' block copolymer in a nonselective solvent. This method allows us to design a great variety of copolymers, and is useful to prepare micelles with functional groups. This is because the nonamphiphilic copolymers consist entirely of solvophilic polymer blocks, so that the balance of the solvophobic and the philic blocks is unnecessary when designing the copolymers. We have recently reported on the micelle formation of a nonamphiphilic poly(vinylphenol)-*block*-polystyrene diblock copolymer through hydrogen bond cross-linking using an α,ω-diamine [18–20]. By using this method, some micelles with unique structures including crew-cut micelles [19] and random block copolymer micelles [21] were prepared.

This paper describes the synthesis of the micelles having azo dyes at the cores and UV absorbents at the coronas using a nonamphiphilic diblock copolymer.

Experimental

Instrumentation

Gel-permeation chromatography (GPC) was performed with a Tosoh DP-8020 dual plunger pump with an 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 a 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 an LS-71 control unit, an LS-72 pump controller, and an argon ion laser operating at $\lambda = 488$ nm. Dye fading experiments were carried out at 63 °C for 24 h with a Suga Test Instruments SX75 super xenon weathermeter equipped with a xenon lamp (7.5 kW). Color difference experiments were measured with a Macbeth Color-Eye 3100 colorimeter.

Materials

4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-methoxy-TEMPO) was prepared as reported previously [22]. 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 stirring 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 [18]. The degree of polymerization (DP) of the prepolymer and the molecular weight were DP = 87.3 and Mn = 15,400, respectively, on the basis of ^{1}H NMR. A poly(vinylphenol)-*block*-poly[4-(phenylazophenoxymethyl)styrene-*co*-St] random block copolymer (PVPh-*b*-P(AS-*co*-St)) was also prepared as reported previously [23]. The molecular weight and the AS/St unit ratio were estimated by ^{1}H NMR as Mn = 10,490-*b*-95,000 and AS/St = 0.011/0.989, respectively.

Synthesis of 4-(2-hydroxybenzophenoxymethyl)styrene (HBS)

A solution of 2,4-dihydrobenzophenone (3.51 g, 0.0164 mmol) in DMF (20 mL) was added to K_2CO_3 (2.72 g, 0.0197 mmol) in DMF (20 mL) at 0 °C. The mixture was stirred at 0 °C for 5 min and at room temperature for 30 min. To the mixture, a solution of 4-chloromethylstyrene (3.00 g, 0.0197 mmol) in DMF (10 mL) was added at 0 °C. After the mixture was stirred at room temperature for 20 h, ether (100 mL) was added to it. The ether layer was washed with water, concentrated by evaporation, and dried in vacuo for several hours. A crude product (3.13 g) was obtained. HBS was separated by a silica gel column with benzene as the eluent, and purified by recrystallization from benzene. HBS (0.88 g) was obtained. ^{1}H NMR ($CDCl_3$): δ 5.11 (2H, s, methylene, C H_2), 5.28 (1H, d, $J = 10$ Hz, vinyl C H), 5.77 (1H, d, $J = 17$ Hz, vinyl C H), 6.48 (1H, dd, $J = 2$, 8 Hz, aromatic O–C = C H–CH), 6.59 (1H, d, $J = 2$ Hz, aromatic O–C = C H–C(OH)–), 6.73 (1H, dd, $J = 10$, 17 Hz, vinyl C H), 7.38 (2H, d, $J = 8$ Hz, aromatic $CH_2=CH–C=CH–C$ *H*), 7.45 (2H, d, $J=8$ Hz, aromatic $CH_2=CH–C=C$ *H*–CH), 7.50 (3H, dd, $J=8$, 17 Hz aromatic $O=C–C=CH–C$ *H*$=C$ *H*), 7.55 (1H, d, $J=7$ Hz, aromatic, $O–C=CH–C$ *H*$=C$), 7.64 (2H, d, $J=7$ Hz, aromatic $O=C–C=C$ *H*), and 12.67 (1H, s, hydroxy O *H*). Mass (M + 1): 331.13.

Synthesis of a P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) diblock copolymer

4-*tert*-Butoxystyrene (6.93 g, 39.3 mmol), AS (125 mg, 0.398 mmol), BPO (109 mg, 0.450 mmol), and 4-methoxy-TEMPO (109 mg, 0.586 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 34 h. The reaction mixture was dissolved in 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) random copolymer (4.68 g).

Styrene (2 g, 19.2 mmol), HBS (63 mg, 0.191 mmol), and the P(AS-*co*–^{t}BSt) copolymer (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 5 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

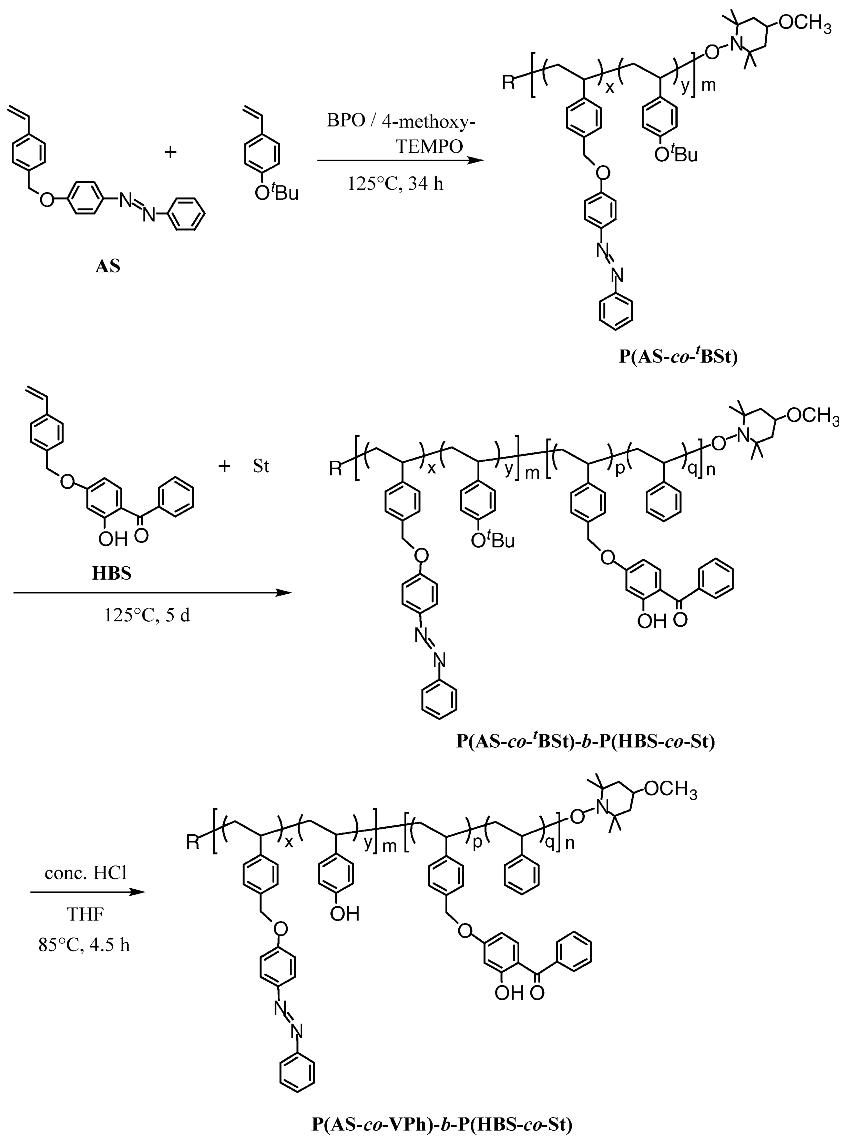

Fig. 1 Synthesis of the P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) diblock copolymer

vacuo for several hours to obtain a P(AS-*co*–^{t}BSt)-*b*-P(HBS-*co*-St) block copolymer (2.12 g).

The P(AS-*co*–^{t}BSt)-*b*-P(HBS-*co*-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 24 h at room temperature to remove a P(AS-*co*-VPh) prepolymer. The precipitate was collected by filtration, and dried in vacuo for several hours. The P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) random block copolymer (390 mg) was obtained.

Light-scattering measurements: general procedure

P(AS-*co*-VPh)-*b*-P(HBS-*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, 8 μL of BDA solution (BDA, 93 μL, 81.6 mg, 0.925 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 a non-negatively constrained least squares (NNLS) analysis [24]. Aggregation numbers were estimated by using the scattering intensity of the micelles and the unimers.

Results and discussion

We used 4-(phenylazophenoxymethyl)styrene (AS) and 4-(2-hydroxybenzophenoxymethyl)styrene (HBS) as monomers with an azo dye and a UV absorbent, respectively. The P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) diblock copolymer was prepared by living radical polymerization mediated by 4-methoxy-TEMPO (Fig. 1). The radical copolymerization of ^{t}BSt and AS was carried out at 125 °C by BPO as an initiator and 4-methoxy-TEMPO as a mediator. The resulting P(AS-*co*–^{t}BSt) copolymer having 4-methoxy-TEMPO at the chain end initiated the radical copolymerization of HBS and St, giving a P(AS-*co*–^{t}BSt)-*b*-P(HBS-*co*-St) diblock copolymer. This block copolymer was hydrolyzed by concentrated HCl to a P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) diblock copolymer. Figure 2 shows GPC profiles of the P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) copolymer and the P(AS-*co*–^{t}BSt) prepolymer. The curve for P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) was observed at a higher molecular weight side than that for the P(AS-*co*–^{t}BSt) prepolymer. The molecular weights and the polydispersities of P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) and P(AS-*co*–^{t}BSt) were estimated as Mn = 45,200 (Mw/Mn = 1.81) and Mn = 9,820 (Mw/Mn = 1.25), respectively, based on polystyrene standards. The block copolymer included no prepolymer, because the copolymer showed no peak of the prepolymer in the GPC.

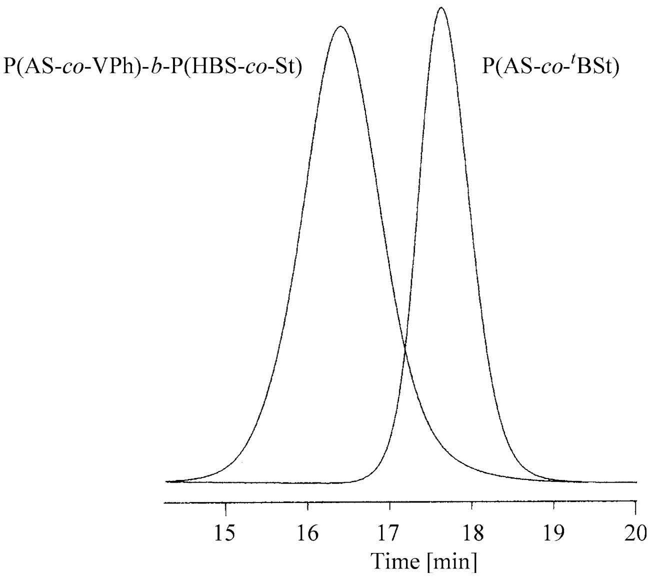

Fig. 2 Gel-permeation chromatography profiles of the P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) diblock copolymer and the P(AS-*co*–^{t}BSt) prepolymer

^{1}H NMR spectra of the P(AS-*co*–^{t}BSt) and P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) copolymers are shown in Fig. 3a, b. P(AS-*co*–^{t}BSt) had a sharp signal at 1.20 ppm based on the *tert*-butyl group. The random copolymer also showed small signals at 7–8 ppm originating from the azobenzene. The signals at 7.8–8.0 ppm were attributed to the aromatic protons located at the *ortho* positions of the azo group. The signals at 7.3–7.6 ppm were based on the aromatic protons at the *meta* and *para* positions on the phenyl group having no substituents except for the azo group. The signals at 7.0–7.3 ppm were assigned to the protons at the *meta* position on the other aromatic ring of the azobenzene. The molar ratio of the AS to ^{t}BSt was estimated as AS/^{t}BSt = 0.015/0.985 on the basis of the signal intensities at 7.8–8.0 ppm and at 6.1–7.0 ppm. The signals at 6.1–7.0 ppm originated from the aromatic protons of the ^{t}BSt units and from the phenyl groups attached to the main chain in the AS units. The DP of P(AS-*co*–^{t}BSt) was estimated as 86.2, using the signal intensities at 6.1–7.0 ppm for these aromatic protons and at 3.1–3.2 ppm for the methoxy protons of 4-methoxy-

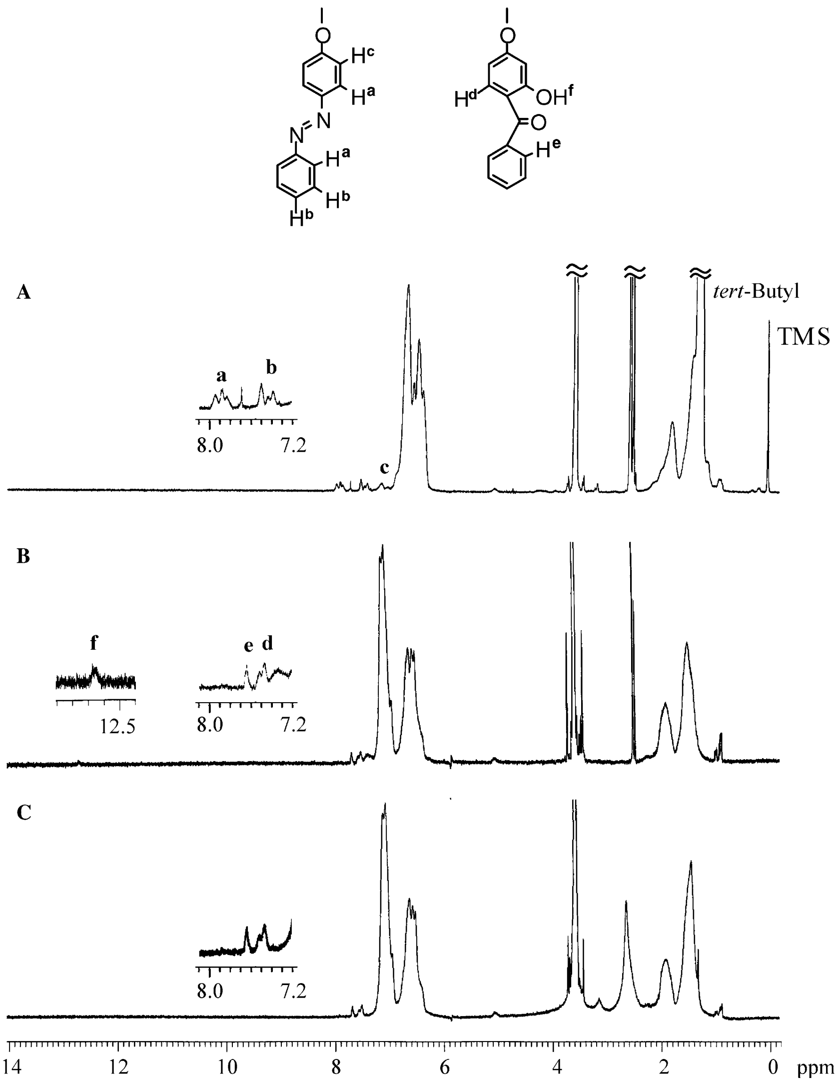

Fig. 3 ^{1}H NMR spectra of P(AS-*co*–^{t}BSt) (**a**), P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) (**b**), and the micelles prepared from P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) at BDA/VPh = 4 (**c**). Solvent: 1,4-dioxane-d_8. [copolymer] = 3.33×10^{-3} g/mL

TEMPO attached to the polymer chain end. Consequently, the molecular weight of P(AS-*co*–^{t}BSt) was estimated by ^{1}H NMR as *M*n = 15400. In addition, the tetramethyl protons of 4-methoxy-TEMPO were discerned at 0.18, 0.30, 0.90, and 1.11 ppm.

In Fig. 3b, P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) had no signal based on the *tert*-butyl groups, indicating that all the ^{t}BSt units were converted to the VPh units by the hydrolysis. The signal of the hydroxyl protons of the VPh units was observed at 7.2–7.4 ppm. This signal partly overlapped with the signals at 7.4–7.7 ppm; those signals originated from the HBS units. The signals at 7.4–7.6 ppm were attributed to the aromatic proton at the *ortho* position to the carbonyl group bounded to the aromatic ring with the hydroxyl group. The signals at 7.6–7.7 ppm were also attributed to the aromatic protons at the other *ortho* positions of the carbonyl group attached to the aromatic ring without the hydroxyl group. The signal of the hydroxyl group in the HBS units was discerned at 12.65 ppm. The molar ratio of the HBS to St units was estimated as HBS/St = 0.011/0.989, while the molecular weights of the blocks were *M*n[P(AS-*co*-VPh)-*b*-P(HBS-*co*-St)] = 10600-*b*-105000 based on the signal intensities at 7.6–7.7 ppm and at 7.2–7.4 ppm and on the DP of the P(AS-*co*–^{t}BSt) prepolymer. In addition, the signals of the azobenzene units in P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) were too small in intensity to observe by ^{1}H NMR.

Light-scattering studies demonstrated that the P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) diblock copolymer showed the micellization in 1,4-dioxane, the nonselective solvent in the presence of BDA. The micellization was completed at four of the molar ratio of BDA to the VPh unit, producing the micelles with 26.4 nm of the hydrodynamic radius and 8.6 of the aggregation number. 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 on 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 changes in the scattering intensity of the copolymer. Figure 4 shows the variation in intensity distribution of the hydrodynamic radius of the copolymer during the micellization. In the absence of BDA, the copolymer showed one distribution based on the unimers around ca. 7 nm hydrodynamic radius. In addition to the distribution of the unimers, another distribution attributed to the micelles was observed at BDA/VPh = 2 on a higher side of the hydrodynamic radius. At BDA/VPh = 4, no observation was made of the unimer distribution, indicating that the micellization was completed.

The ^{1}H NMR confirmed that the micellization proceeded through hydrogen bond cross-linking between the VPh units via BDA. Figure 3c showed the ^{1}H NMR spectrum of the micelles prepared at BDA/VPh = 4. In the spectrum of the micelles, no signals were observed based on the hydroxyl groups of the VPh units, indicating that the hydroxyl groups had the interacted with the amino groups of BDA in the cores of the micelles. The hydroxyl proton of the HBS units also interacted with BDA, because the signal at 12.65 ppm observed in Fig. 3b was not discerned in Fig. 3c. Accordingly, the micelles should have the azobenzene at the micellar cores and the UV absorbents at the coronas (Fig. 5).

UV analysis confirmed the presence of the azobenzene at the cores of the micelles (Fig. 6). The micelles had absorption at 436 nm originating from the n → π^* transition of the *cis* isomer of the azobenzene. Absorption of the $\pi \rightarrow \pi^*$ transition for the *trans* isomer was not confirmed, because absorptions of the HBS moieties covered the absorption of the *trans* isomer.

The dye fading studies demonstrated that the light-stable supermicrospheres were obtained through the micelle formation. The dye fading experiment was performed by irradiation with a Xe lamp at 63 °C for 1 day. The degree of fading was determined by color difference. A greater color difference means a higher degree of fading. The color difference of the P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) micelles was 3, while that of the unimers was 10. Micelles prepared from a P(AS-*co*-VPh)-*b*-PSt

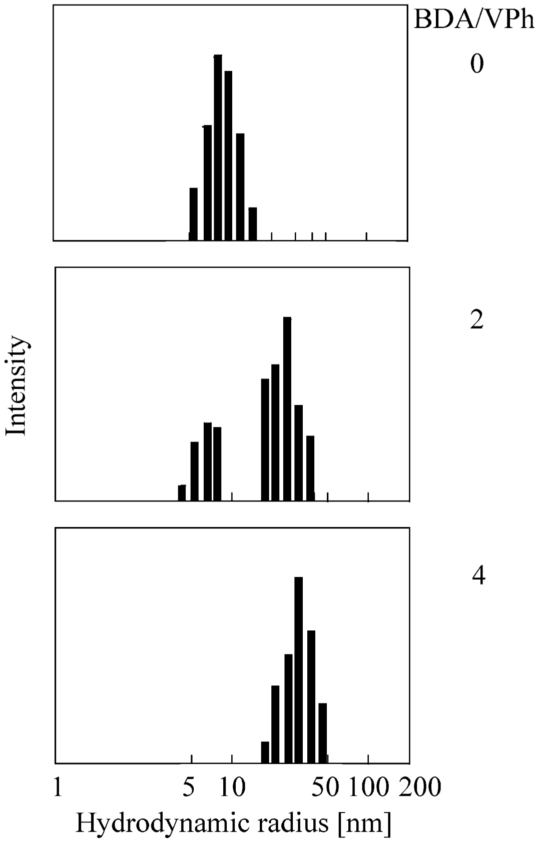

Fig. 4 Variation in intensity distribution of the hydrodynamic radius of the P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) copolymer. [copolymer] = 3.33×10^{-3} g/mL

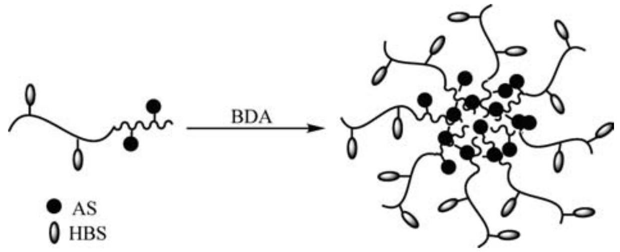

Fig. 5 The micelles prepared from P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) and BDA

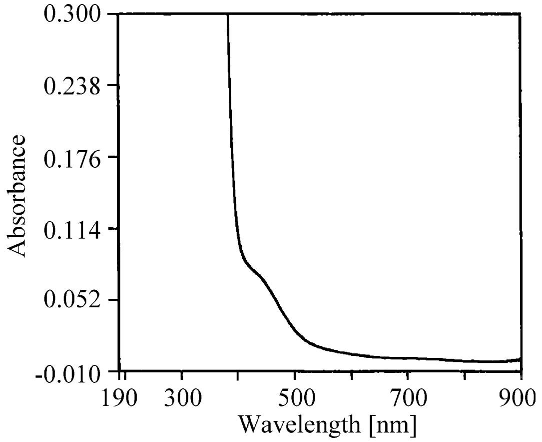

Fig. 6 A UV spectrum of the P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) micelles. Solvent: 1,4-dioxane, [copolymer] = 3.33×10^{-3} g/mL, BDA/VPh = 4

diblock copolymer had a color difference of 12. The P(AS-*co*-VPh)-*b*-PSt copolymer produced the micelles with the azo dyes at the cores but without UV absorbents at the coronas. The HBS moieties served as efficient UV absorbents at the coronas of the P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) micelles, in spite of the fact that the hydroxyl groups of the HBS units interacted with BDA. It is significant that the copolymer forms the micelles and has the UV absorbents at the coronas of the micelles to suppress the fading of the dyes.

We explored the dependence of the copolymer concentration on the micellar size and the aggregation number. Figure 7 shows the variation in the hydrodynamic radius and the aggregation number of the P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) copolymer versus the BDA/VPh ratio for three different copolymer concentrations. As a result of decreasing the copolymer concentration, the transition from the unimers to the micelles was shifted to a higher side of the BDA/VPh ratio, and the region of the transition was expanded. The copolymer at a lower concentration is more difficult to aggregate and needs more BDA to form the micelles. However, the hydrodynamic radius and the aggregation number of the micelles were independent of the copolymer concentration. Figure 8 represents the variation in the hydrodynamic radius and the aggregation number of the copolymer by different kinds of α,ω-diamines. The micellar size was independent of the diamines, while the copolymer required more EDA to form the micelles, in comparison with BDA and HMDA. These results were in good agreement with our previous results on the micellization of a poly(vinylphenol)-*block*-polystyrene diblock copolymer by α,ω-diamines [18].

Conclusion

We prepared the light-stable micelles with azo dyes through the micellization of the nonamphiphilic P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) diblock copolymer by the α,ω-diamine. The micelles had the azobenzene moieties at the cores and the UV absorbents at the coronas. The micelles were formed through hydrogen bond cross-linking between the VPh units via BDA. BDA interacted not only with the hydroxyl groups of the VPh units but also with those of the HBS units. However, the HBS moieties

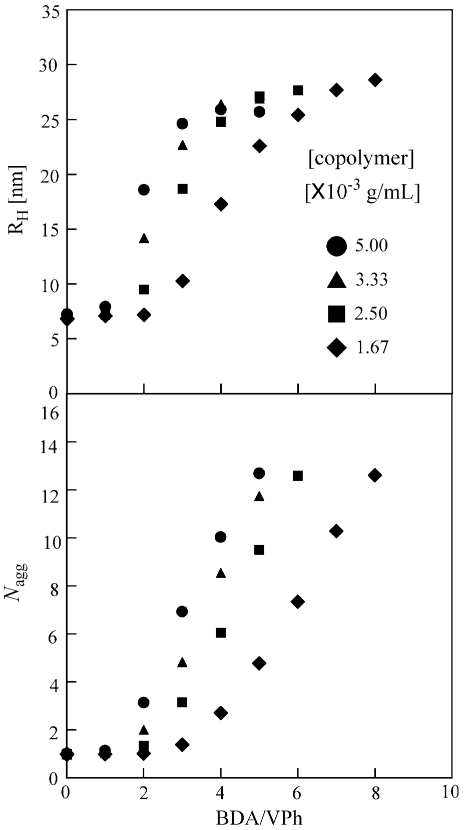

Fig. 7 Variation in the hydrodynamic radius and the aggregation number of P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) through the micellization by BDA for different copolymer concentrations

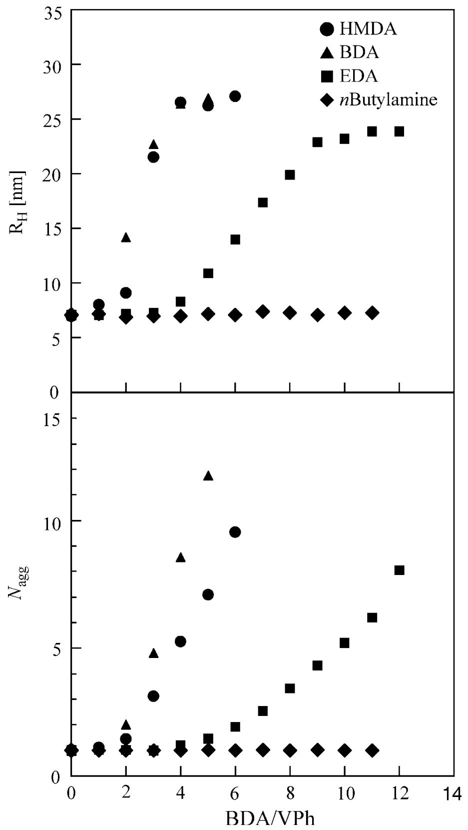

Fig. 8 Variability in the hydrodynamic radius and the aggregation number of P(AS-*co*-VPh)-*b*-P(HBS-*co*-St) through the micellization by EDA, BDA, and HMDA. [copolymer] = 3.33×10^{-3} g/mL

served as efficient UV absorbents at the coronas of the micelles. It was important that the copolymer formed the micelles and had the UV absorbents at the coronas to suppress the dye fading. In addition, the copolymer concentration had no effect on the size of the micelles and the aggregation number. The chain length of the α,ω-diamines also had no effect on the micellar size, but affected the aggregation number and the cmc.

Acknowledgements We acknowledge the support of Mr. Seiji Sugimori at Ipposha Oil Industries Co., Ltd. for the dye fading and color difference experiments.

References

1. Radu S, Bratulescu G (1996) Rev Roum Chim 41:119
2. Karadag E, Saraydin D, Guven O (1996) J Appl Polym Sci 61:2367
3. Saunders K (1949) The aromatic diazo compounds. Longmans Green
4. Hauser CR, Breslow DS (1941) J Am Chem Soc 63:418
5. Zollinger H (1955) Helv Chim Acta 38:1597
6. Bunnett JF, Hoey GB (1958) J Am Chem Soc 80:3142
7. Vytras K, Lalous J, Jiraskova IS (1993) Dyes Pigm 23:43
8. Straub RF, Voyksner RD, Keever JT (1993) Anal Chem 65:2131
9. Windsor SA, Harrison NJ, Tinker MH, (1996) Clay Miner 31:81
10. Abd El Wahed MG (1991) J Mater Sci Lett 10:1349
11. Gilmore DA, Gurka D, Denton MB (1995) Appl Spectrosc 49:508
12. Vinodgopal K, Bedja I, Hotchandani S, Kamat PV (1994) Langmuir 10:1767
13. Okada Y, Satoh E, Motomura H, Morita Z (1992) Dyes Pigm 19:1
14. Richardson SD, McGuire JM, Thruston AD Jr, Baughman GL (1992) Org Mass Spectrom 27:289
15. Ferguson J, Khan A (1994) J Non-Newtonian Fluid Mech 54:33
16. Maekawa M, Murakami K, Yoshida H (1995) Colloid Polym Sci 273:793
17. Limaye RV, Samant SD, Shenoy MA (1991) J Polym Mater 8:167
18. Yoshida E, Kunugi S (2002) J Polym Sci Part A Polym Chem 40:3063
19. Yoshida E, Kunugi S (2002) Macromolecules 35:6665
20. Yoshida E (2003) Polym J 35:965
21. Yoshida E (2003) Polym J 35:484
22. Miyazawa T, Endo T, Shiihashi S, Okawara M (1985) J Org Chem 50:1332
23. Yoshida E, Ohta M (2004) Colloid Polym Sci (in press)
24. Morrison D, Grabowski EF, Herb CA (1985) Langmuir 1:496