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ORIGINAL CONTRIBUTION

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Micelle formation of a nonamphiphilic poly(vinylphenol)-*block*-polystyrene diblock copolymer in ethyl acetate

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Abstract The micelle formation of a poly(vinylphenol)-*block*-polystyrene diblock copolymer was studied in ethyl acetate, a nonselective solvent using α,ω-diamine. The copolymer formed micelles in ethyl acetate in the presence of a small amount of the α,ω-diamine. Light scattering studies demonstrated that the micellization was dependent on the grade, the bulkiness, and the conformation of the diamines. The copolymer needed more diamine with the increasing grade of the diamine, due to a decrease in the basicity of the diamine. The bulkiness of the diamines also reduced the efficiency of the micellization by hindering the formation of the hydrogen bond cross-linking. Similarly, the conformation of the diamine affected the micellization, since the conformation determined the intramolecular spatial distance between the animo groups. Trans-1,2-cyclohexanediamine was more effective than the cis-isomer to produce the micelles. Furthermore, (1S,2S)-(+)-1,2-cyclohexanediamine, one of the mirror image isomers composing the trans-isomer, was more effective in producing the micelles than the trans-isomer. The interaction between the mirror image isomers also obstructed the micellization. The micellization, coupled with the thermoresponsivity of the micelles, were influenced by the solvent quality. The dissociation of the micelles into unimers was suppressed in ethyl acetate, while the reconstruction was promoted, in comparison with those in 1,4-dioxane and THF.

Keywords Poly(vinylphenol)-*block*-polystyrene (PVPh-*b*-PSt) · α, ω-Diamine · Micelles · Hydrodynamic radius · Aggregation number

Introduction

Macromolecular micelles have their applications in many fields such as separation technologies [1, 2], drug delivery [3, 4], detergent [5, 6], coating [7–9], dyeing [7, 10], food processing [11, 12] and cosmetics [13, 14]. Recently, the importance of micelles has been increasing in the field of information technology [15, 16] and in the area of fuel technology [17]. The macromolecular micelles are mostly amphiphilic copolymers consisting of solvophilic and solvophobic moieties. Accordingly, the balance of these moieties must always be taken into consideration for designing the amphiphilic copolymers. While the amphiphilic copolymers have such a limitation in the molecular design, nonamphiphilic copolymers have no dependence on this balance in solubility, since the nonamphiphilic copolymers consist entirely of solvophilic moieties. The nonamphiphilic copolymers

assemble into micelles through interaction with additives as the driving force [18–24]. The micelle formation using nonamphiphilic copolymers has certain advantages over that of the amphiphilic copolymers; it is able to choose the additives promoting the micellization, and provide a better selection of the driving force. The self-assembly of the amphiphilic copolymer is ordinarily through a Van der Waals interaction of the solvophobic moieties. The choice of additives and driving force leads to control of the copolymer assembly and the critical micelle concentration (cmc). Solvent quality also has the potential to control them.

We have already found that a poly(vinylphenol)-*block*-polystyrene diblock copolymer (PVPh-*b*-PSt) formed micelles in the presence of α,ω-diamine in 1,4-dioxane, the nonselective solvent [25, 26]. This micellization proceeded through hydrogen bond cross-linking between the PVPh blocks via the diamine. We explored the effects of the molecular weight of the diblock copolymers and the unit ratio of poly(vinylphenol-*co*-styrene) random copolymers on the micellar size and the cmc, with the results that the micellar size and the cmc were controlled by the molecular weight of the diblock copolymers [27] and by the unit ratio of the random copolymers [28]. Using this micelle formation of the nonamphiphilic copolymer, we prepared unique micelles including the crew-cut micelles [26], the random-block copolymer micelles [29], and the light-stable micelles with dyes [30]. We also succeeded in controlling the cmc and the thermoresponsivity of the micelles by the diamine content in the micelles. This paper describes the light scattering studies involving the micelle formation of PVPh-*b*-PSt by several diamines in ethyl acetate, another nonselective solvent for the copolymer. The effects of the copolymer concentration and solvent quality on the micellization are also described.

Experimental

Instrumentation

Light scattering experiments were performed 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

Poly(4-*tert*-butoxystyrene) having 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO-terminated P^{t}BSt) was prepared as previously reported [25]. The molecular weight was Mn = 12,700 estimated by GPC and Mn = 15,400 by ^{1}H NMR. The polydispersity was 1.15 by GPC. Commercial grade styrene was washed with aqueous alkaline solution and water, and distilled over calcium hydride. Ethyl acetate was purified by refluxing on calcium hydride and distilled. THF and 1,4-dioxane were purified by refluxing on sodium and distilled. Ethylenediamine (EDA), 1,4-butanediamine (BDA), *N,N′*-dimethylethylenediamine (DEDA), *N,N,N′N′*-tetramethylethylenediamine (TEDA), and *n*-butylamine were distilled over calcium hydride. Extra pure piperazine (PP), 1,4-diazabicyclo[2, 2, 2]octane (DABCO), cis-1,2-cyclohexanediamine (cis-CDA), trans-1,2-cyclohexanediamine (trans-CDA), (1S,2S)-(+)-1,2-cyclohexanediamine ((1S,2S)-(+)-CDA), and 2-butanone were used without further purification.

Synthesis of PVPh-*b*-PSt

The PVPh-*b*-PSt diblock copolymer was prepared as previously reported [31]. Styrene (8.90 g, 85.5 mmol) and TEMPO-terminated P^{t}BSt (2 g) were placed in an ampule. After degassing the contents, the ampule was sealed in vacuo. The polymerization was carried out at 125 °C for 24 h and terminated by cooling with liquid nitrogen. The reaction mixture was dissolved into dichloromethane and poured into methanol to precipitate the polymer. The polymer was purified by repeated reprecipitation from dichloromethane into methanol. The precipitate was then dried in vacuo for several hours to obtain poly(4-*tert*-butoxystyrene)-*block*-polystyrene (10.3 g).

The obtained poly(4-*tert*-butoxystyrene)-*block*-polystyrene (6.00 g) was dissolved in THF (200 mL); then, conc. HCl (20 mL) was added to the solution at room temperature. The mixture was kept at 85 °C for 4.5 h. The resulting mixture was evaporated to half the volume to remove the THF and then poured into water (2 L) to precipitate the polymer. After drying the polymer, the product was suspended in 800 mL of methanol, and stirred for 8 h at room temperature to remove the vinylphenol homopolymer. The resulting precipitate was collected by filtration and then dried in vacuo for several hours. A total of 3.01 g of the PVPh-*b*-PSt diblock copolymer was obtained. The molecular weight was determined by ^{1}H NMR as Mn(PVPh-*b*-PSt) = 10490-*b*-119000 (= 10 K-*b*-120 K).

Light scattering measurements: general procedure

The PVPh-*b*-PSt (10 mg) was dissolved in ethyl acetate (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, 2 μL of a solution of BDA (34 μL, 29.8 mg, 0.338 mmol) in ethyl acetate

(2 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 10 min, then subjected to light scattering again. This procedure was repeated until distribution based on the unimers disappeared completely in non-negatively constrained least-squares (NNLS) analysis [32].

Results and discussion

The PVPh-*b*-PSt diblock copolymer showed no self-assembly in ethyl acetate, because this solvent is non-selective for the copolymer. Light scattering studies demonstrated that the copolymer formed the micelles in the presence of BDA in the solvent. Figure 1 shows the intensity distribution obtained by the NNLS analysis for the hydrodynamic radius (R_H) of the copolymer during the micellization. The copolymer formed no micelles in the absence of BDA, so that the distribution was attributed to the unimers. As BDA was added to the copolymer solution, two distributions based on the unimers and the micelles were observed at the BDA/VPh molar ratio of 0.15. At BDA/VPh = 0.25, the distribution of the unimers disappeared, and only the distribution of the micelles was observed. The micellization in ethyl acetate was completed at only BDA/VPh = 0.25, while that in 1,4-dioxane required over one equivalent of BDA to the VPh unit to produce the micelles [26]. It is more efficient for the copolymer to form the micelles in ethyl acetate than in 1,4-dioxane. The cumulant analysis revealed that the micelles with a 33.0-nm hydrodynamic radius were formed from the unimers with a 7.4-nm hydrodynamic radius in the presence of BDA in ethyl acetate. The hydrodynamic radius of the micelles had almost no angle-dependence, as shown in Fig. 2.

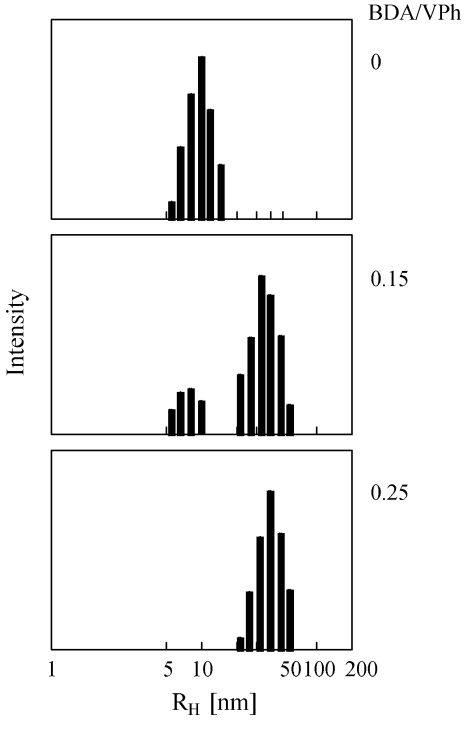

Fig. 1 Intensity distributions of the hydrodynamic radius of the PVPh-*b*-PSt copolymer through the micellization at BDA/VPh = 0, 0.15, and 0.25. [copolymer] = 3.33×10^{-3} g/mL

The copolymer also produced the micelles in the presence of EDA. The hydrodynamic radius and the aggregation number of the micelles formed from EDA were similar to those of the micelles from BDA. However, the copolymer needed more EDA to form the micelles in comparison with BDA. This tendency has also been found for the micellization in 1,4-dioxane [25]. The presence of *n*-butylamine promoted no micellization, indicating that the formation of the hydrogen bonding cross-linking was indispensable for the formation of the micelles.

We explored the micellization using a different class of diamines in ethyl acetate. Figure 3 shows the variation in the hydrodynamic radius and the aggregation number (N_{agg}) of the copolymer through the micellization by EDA, DEDA, and TEDA. EDA and DEDA produced micelles in ethyl acetate, although DEDA promoted no micellization in 1,4-dioxane [25]. The copolymer needed more DEDA to form the micelles as compared with EDA, because the unimers-to-micelles transition for DEDA was observed at a higher diamine/VPh ratio than that for EDA. The bulkiness in DEDA prevents the amino groups from forming the hydrogen bond cross-linking with the VPh units. TEDA with more bulkiness produced no micelles.

We also investigated the micellization using another class of diamines having less steric hindrance. Figure 4 shows the variation in the hydrodynamic radius and the aggregation number of the copolymer during the

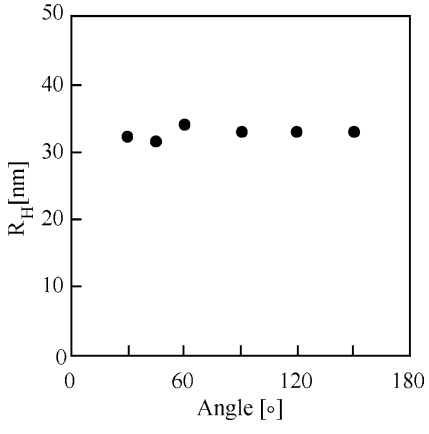

Fig. 2 Angle-dependence on the hydrodynamic radius of the PVPh-*b*-PSt micelles with BDA/VPh = 0.25. [copolymer] = 3.33×10^{-3} g/mL

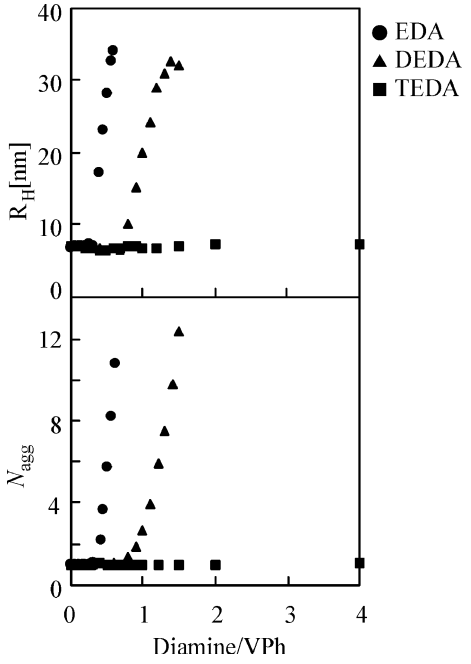

Fig. 3 Variation in the hydrodynamic radius and the aggregation number of the copolymer through the micellization by EDA, DEDA, and TEDA. [copolymer] = 3.33×10^{-3} g/mL

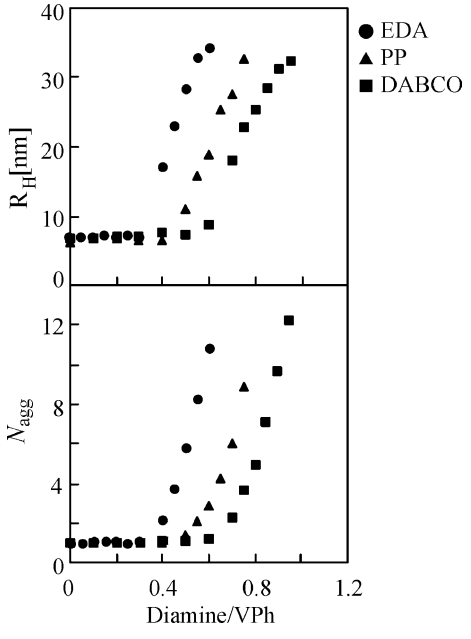

Fig. 4 Variation in the hydrodynamic radius and the aggregation number of the copolymer through the micellization by EDA, PP, and DABCO. [copolymer] = 3.33×10^{-3} g/mL

micellization by EDA, PP, and DABCO. The copolymer formed the micelles even in the presence of the tertiary diamine, DABCO. The hydrodynamic radius and the aggregation number for the complete micellization were

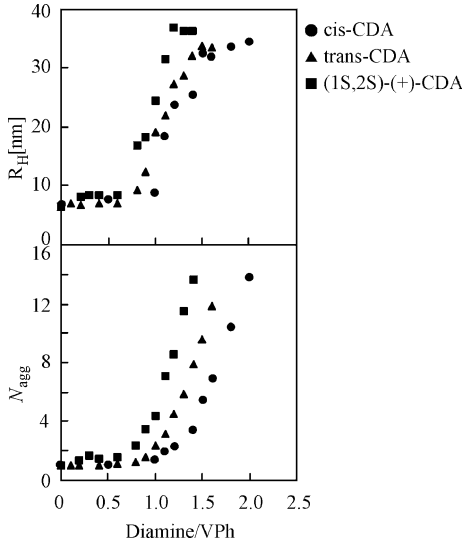

Fig. 5 Variability in the hydrodynamic radius and the aggregation number of the copolymer through the micellization by cis-CDA, trans-CDA, and (1S,2S)-(+)-CDA. [copolymer] = 3.33×10^{-3} g/mL

almost independent of the diamine grade. As the grade of the diamine increased, the micellization was more difficult to complete. The basicity of the diamines decreases in the order of EDA > PP > DABCO [33, 34], so that the hydrogen bonding with the PVPh blocks becomes weaker in this order. The copolymer needed more diamine to increase the cross-linking points to assemble into the micelles because of the weak hydrogen bonding. Additionally, 4,4′-bipyridil and the primary diamines of 1,2-diphenylethylenediamine and phenylenediamine promoted no micellization due to their low basicity.

The light scattering studies revealed that the conformation of the diamine had a significant effect on the micellization. Figure 5 shows the variability in the hydrodynamic radius and the aggregation number of the copolymer through the micellization by three different isomers of 1,2-cyclohexanediamine, the cis, the trans, and the (1S,2S)-(+) isomers. The transition from the unimers to the micelles was significantly shifted to the higher value of the diamine/VPh ratio in the order of (1S,2S)-(+)-CDA < trans-CDA < cis-CDA. These results are based on the intramolecular spatial distance between the amino groups, rather than on the basicity, because there is a slight difference in the basicity between these isomers. The basicity is $pK_1 = 9.93$ and $pK_2 = 6.13$ for the cis isomer, and $pK_1 = 9.94$ and $pK_2 = 6.47$ for the trans [35]. The spatial distance is longer in the trans isomer than in the cis, resulting in the fact that trans-CDA formed the hydrogen bond cross-linking between the PVPh blocks more efficiently. Trans-CDA consists of two different mirror image isomers, (1S,2S)-(+)-CDA and (1R,2R)-(−)-CDA. The intermolecular attraction between the amino groups more easily occurs between the different isomers than between the identical isomers

because the isomers are related to the mirror image. The interaction between the amino groups hinders the diamine from forming the hydrogen bond cross-linking between the PVPh blocks. Consequently, (1S,2S)-(+)-CDA is more effective for promoting the micellization than trans-CDA.

The ease of the micellization should be dependent on the copolymer concentration, because the copolymer concentration affects the formation of the hydrogen bonding. Figure 6 shows the variation in the hydrodynamic radius and aggregation number of the copolymer through the micellization by BDA for three different copolymer concentrations. The copolymer at the higher concentration formed the micelles at the lower BDA/VPh ratio. However, the difference was small among the copolymer concentrations, when it is taken into account that the micellization in 1,4-dioxane made a significant difference in the unimers-to-micelles transition for the copolymer concentration [26]. The hydrodynamic radii and the aggregation numbers were almost the same for the complete micellization in ethyl acetate.

The strength of the hydrogen bonding decreases with the increasing temperature. Figure 7 illustrates the temperature-dependence on the micellization by BDA in ethyl acetate. The micellization was carried out at 10, 20, 30, and 40 °C. The unimers-to-micelles transition was shifted to the higher value of the BDA/VPh ratio, indicating that the copolymer has a more difficult time forming the micelles at higher temperatures. The strength of the hydrogen bonding decreases as the temperature increased, resulting in the copolymer needing more BDA to make the cross-linking points for the hydrogen bonding. The size of the micelles and the aggregation number slightly decreased with an increase in the temperature.

The hydrogen bond formation is also dependent on solvent quality. Figure 8 shows the solvent effect on the micellization. The copolymer in ethyl acetate produced micelles in the presence of a small amount of BDA (BDA/VPh = 0.25), while the copolymer in 1,4-dioxane and THF needed over one equivalent of BDA to form the micelles. On the other hand, no micelles were obtained in 2-butanone. These results are not accounted for by the solvent polarity, because the polarity increases in the order of 1,4-dioxane < THF < ethyl acetate < 2-butanone [34]. The results are also not based on the hydrophilicity of the solvents. The order of their solubility in water was ethyl acetate < 2-butanone < 1,4-dioxane, THF [36]. The ease of the hydrogen bonding in these solvents should be determined by some factors in addition to the solvent polarity and hydrophilicity.

We already found for the micellization in 1,4-dioxane that the micelles with BDA were dissociated into unimers by increasing the temperature and that those were reconstructed by decreasing the temperature [31]. This dissociation–reconstruction of the micelles also occurred in ethyl acetate. Figure 9 shows the variation in the distribution of the hydrodynamic radius of the copolymer for changes in temperature. The micellar solution prepared at 10 °C in ethyl acetate at BDA/VPh = 0.15 was heated to 20 °C, with the result that the distribution based on the unimers appeared in addition to that of the micelles. The distribution intensity of the unimers in-

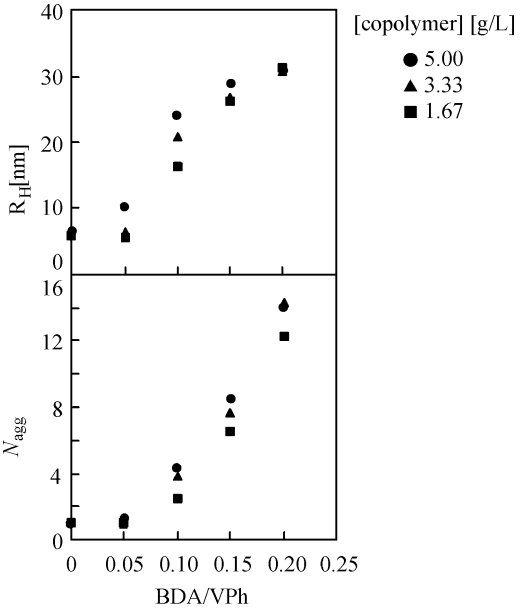

Fig. 6 Variation in the hydrodynamic radius and aggregation number of the copolymer through the micellization by BDA for three different copolymer concentrations. [copolymer] = 1.67, 3.33, and 5.00 ($\times 10^{-3}$ g/mL)

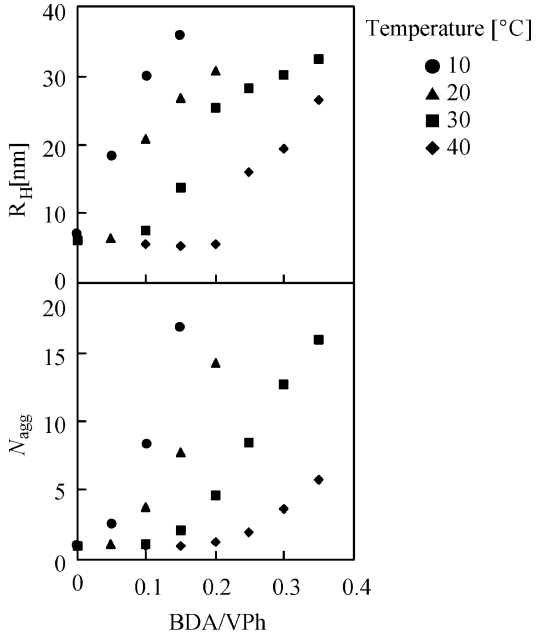

Fig. 7 Variation in the hydrodynamic radius and aggregation number of the copolymer through the micellization by BDA at 10, 20, 30, and 40 °C. [copolymer] = 3.33×10^{-3} g/mL

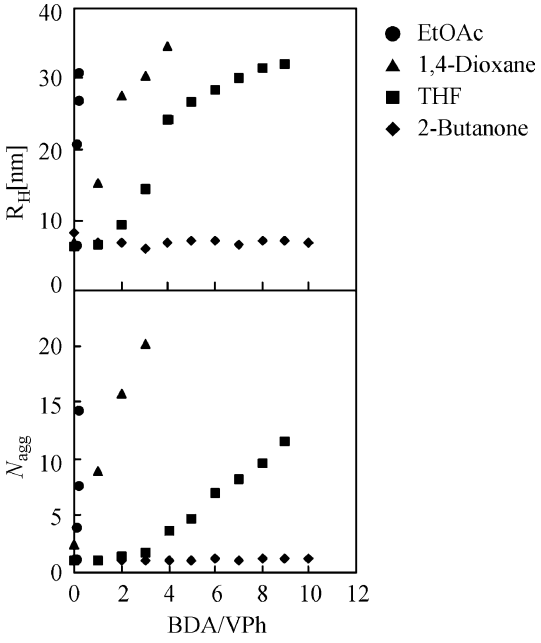

Fig. 8 Variation in the hydrodynamic radius and aggregation number of the copolymer through the micellization by BDA in ethyl acetate, 1,4-dioxane, and THF. [copolymer] = 3.33×10^{-3} g/mL

creased with an increase in the temperature, and the distribution of the unimers completely took the place of that of the micelles at 40 °C; and vice versa when the temperature decreased.

We investigated the solvent effect on the thermoresponsivity of the micelles. Figure 10 shows the hysteresis curves for the hydrodynamic radii and aggregation numbers of the micelles vs. the temperature in the solvents. In all solvents, the hydrodynamic radius of the micelles decreased as a result of increasing the temperature, and was equal to the unimer size at 40 °C. The aggregation number also decreased with the increase in the temperature, and finally reached unity at 40 °C. The micelles were then dissociated into unimers. As the temperature decreased, the hydrodynamic radius and the aggregation number reverted to the initial values at 10 °C, following the same course as for the increase in the temperature. The micelles were reconstructed by the decrease in the temperature. The good hysteresis of the micelles for the changes in the temperature indicates that the dissociation–reconstruction of the micelles was reversibly controlled by the temperature in these solvents. The hysteresis curves were shifted to the upper side in the order of THF < 1,4-dioxane < ethyl acetate. This shift indicates that the micelles are more difficult to dissociate into unimers and are more easily reconstructed in this order, although the content of BDA in the micelles was lower in this order. It has been reported that an increase in the BDA content prevents the

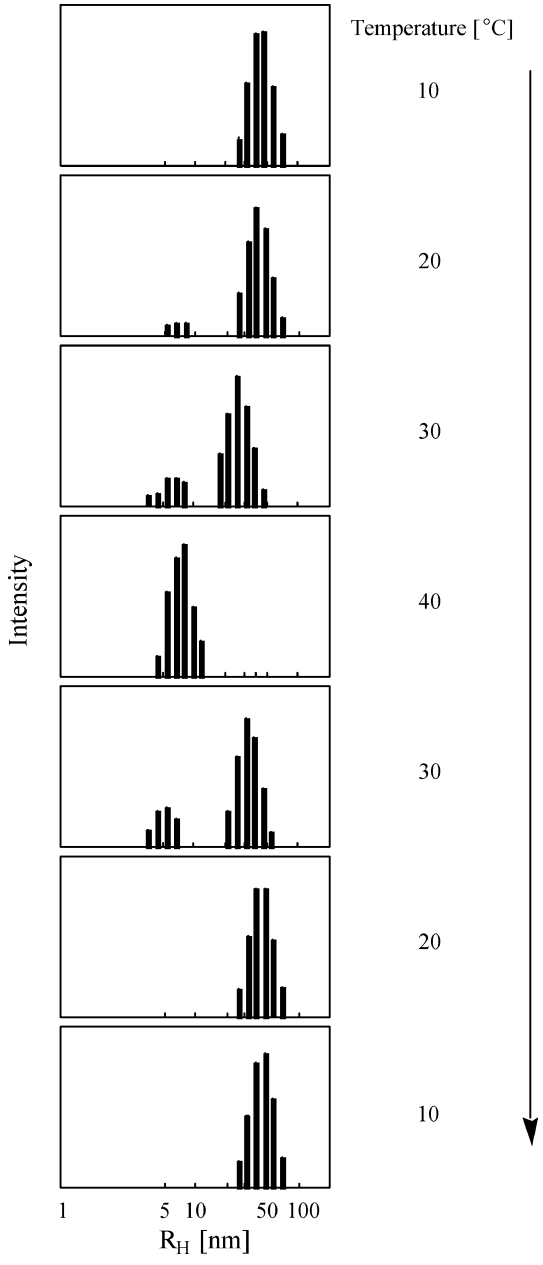

Fig. 9 Variation in the intensity distribution of the hydrodynamic radius of the PVPh-*b*-PSt copolymer for changes in the temperature. BDA/VPh = 0.15, [copolymer] = 3.33×10^{-3} g/mL

dissociation of the micelles and promotes their reconstruction. The solvent quality had a large effect on the thermoresponsivity of the micelles.

Conclusion

The PVPh-*b*-PSt copolymer effectively formed micelles in ethyl acetate in the presence of α,ω-diamine. The micellization was dependent on the grade, the bulkiness,

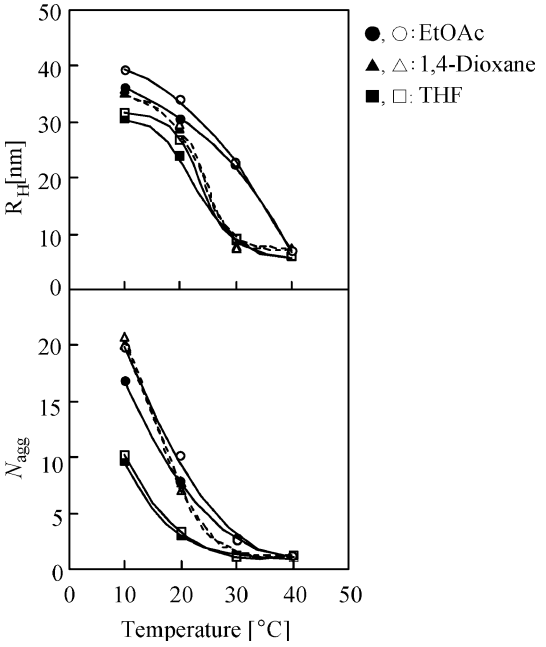

Fig. 10 Hysteresis curves of the PVPh-*b*-PSt micelles with BDA in ethyl acetate (*circle*, *solid lines*, BDA/VPh = 0.15), 1,4-dioxane (*triangle*, *broken lines*, BDA/VPh = 3.0), and THF (*square*, *solid lines*, BDA/VPh = 9.0) as the temperature increased (closed) and decreased (open). [copolymer] = 3.33×10^{-3} g/mL

and the conformation of the diamines. The ease of the micellization decreased with an increase in the grade of the diamine, because of a decrease in the basicity. A diamine with a low basicity was significantly required in order to increase the cross-linking points of the hydrogen bonding with the PVPh blocks. The bulkiness of the diamines also reduced the efficiency of the micellization by hindering the formation of the hydrogen bond cross-linking. Similarly, the diamine conformation determining the intramolecular spatial distance between the amino groups affected the micellization. Trans-CDA was more effective than cis-CDA for producing the micelles. Furthermore, the interaction between the mirror image isomers composing the trans isomer also obstructed the micellization. The micellization, coupled with the thermoresponsivity of the micelles, were greatly influenced by the solvent quality. The dissociation of the micelles into unimers was suppressed in ethyl acetate, while the reconstruction was promoted, in comparison with that in 1,4-dioxane and THF. This is the first light scattering studies demonstrating that the micellization induced by the formation of the hydrogen bond cross-linking is controlled by the grade of the diamines, the bulkiness, the conformation, and the solvent quality in addition to the copolymer concentration and the temperature.

References

1. Ismael M, Tondre C (1992) Langmuir 8:1039
2. Chang QL, Chen JY (1995) Chem Eng J 59:303
3. Yoon KA, Burgess DJ (1997) J Pharm Pharmacol 49:478
4. Lawrence MJ, Lawrence SM, Barlow DJ (1997) J Pharm Pharmacol 49:594
5. Piero ARL, Petrone G (1994) Biocehm Mol Biol Int 32:181
6. Normand BV, Eisele JL (1993) Anal Biochem 208:241
7. Knoef AJM, Slingerland H (1992) Surf Coat Int 75:335
8. Saji T, Ebata K, Sugawara K, Liu S, Kobayashi K (1994) J Am Chem Soc 116:6053
9. Pitt R, Morley SD, Burbidge NJ, Qiuckenden EL (1996) Colloids Surf A 114:321
10. Rajaraman H (2002) US Pat US 6500896 B1 31 Dec
11. Lin JJ, Knifton JF (1991) J Organomet Chem 417:99
12. Dralle-Voss G, Oetter G, Wekel H, Oppenlaender K (1996) In: Ger Offen DE (ed) 19505100 A1, 22 August 1996
13. Schlossman DS (1994) US 5314683 A 24 May 1994:12
14. Bara I, Mellul M (1996) Can Pat Appl CA 2153545 AA 12 Jan 1996:18
15. Kommareddi NS, Tata M, John VT, McPherson GL, Herman MF, Lee YS, O'Connor CJ, Akkara JA, Kaplan DL (1996) Chem Mater 8:801
16. Eastoe J, Warne B (1996) Curr Opin Colloid Interface Sci 1:800
17. Ogura T, Tanoura M, Hiraki A (1993) Bull Chem Soc Jpn 66:1343
18. Brontein LM, Sidorov SN, Valetsky PM (1999) Langmuir 15:6256
19. Zhao H, Douglas EP (2002) Mater Res Soc Symp Proc 43
20. Liu S, Zhang G, Jiang M (1999) Polymer 40:5449
21. Gohy JF, Varshney SK, Jerome R (2001) Macromolecules 34:3361
22. Chernyshov DM, Bronstein LM, Boerner H, Berton B, Antonietti M (2000) Chem Mater 12:114
23. Liu S, Zhu H, Zha H, Jiang M, Wu C (2000) Langmuir 16:3712
24. Harada A, Kataoka K (1995) Macromolecules 28:5294
25. Yoshida E, Kunugi S (2002) J Polym Sci Part A Polym Chem 40:3063
26. Yoshida E, Kunugi S (2002) Macromolecules 35:6665
27. Yoshida E (2003) Polym J 35:965
28. Yoshida E, Hironaka A (2004) Polym J 36:248
29. Yoshida E (2003) Polym J 35:484
30. Yoshida E, Ohta M, Coll Polym Sci (in press)
31. Yoshida E, Ohta M, Terada Y, Polym Adv Technol (in press)
32. Morrison D, Grabowski EF, Herb CA (1985) Langmuir 1:496
33. Aggarwal VK, Emme I, Fulford SY (2003) J Org Chem 68:692
34. Reichardt C (1979) Angew Chem Int Ed Engl 18:98
35. Lide DR, Frederikse HPR (1995) Handbook of chemistry and physics, 76th edn. CRC, Boca Raton, pp 8-45–8-55
36. Riddick JA, Bunger WB (1970) Organic solvents, 3rd edn. Wiley, New York