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ORIGINAL CONTRIBUTION

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Thermodynamics and kinetics on micelle formation of a nonamphiphilic poly(vinylphenol)-*block*-polystyrene by α,ω-diamine

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Abstract A poly(vinylphenol)-*block*-polystyrene diblock copolymer (PVPh-*b*-PSt) forms micelles in the presence of 1,4-butanediamine (BDA) in 1,4-dioxane, a nonselective solvent. The micellization proceeds through the formation of hydrogen bond cross-linking between the PVPh blocks via BDA, and the dissociation and reconstruction of the micelles is reversibly controlled by temperature. We explored the thermodynamics and kinetics on the micellization of the nonamphiphilic PVPh-*b*-PSt copolymer by BDA. Light scattering studies demonstrated that an equilibrium existed between the micelles and the unimers. The equilibrium constants were determined for the dissociation and the reconstruction of the micelles on the basis of variation in the aggregation number of the micelles. The equilibrium constant of the dissociation showed a good agreement with the reciprocal of the equilibrium constant of the reconstruction. Based on the equilibrium constants, the standard Gibbs energy, enthalpy, and entropy of the dissociation and reconstruction were estimated. The standard enthalpy was $\Delta H^\circ = 30$–$40\ \mathrm{kJ\ mol^{-1}}$ for the dissociation. The enthalpy of the reconstruction was obtained as a negative value, however, there was a negligible difference in the absolute values of ΔH° between the dissociation and the reconstruction. The rate constant of the micellization was ca. 10^2 times larger than the back reaction, and increased with a decrease in the temperature.

Keywords Poly(vinylphenol)-*block*-polystyrene (PVPh-*b*-PSt) · Micellization · Aggregation number · Dissociation · Reconstruction

Introduction

The thermodynamic and kinetic studies of micelle formation are important in fields where the control of the dissociation and reconstruction of the micelles is required. These fields include drug delivery [1] and separation technologies [2]. While a number of studies have been reported on the thermodynamic and kinetic studies of the micellization of low molecular weight surfactants [3], the studies of the micellization of macromolecules are still in the early stages. The thermodynamic studies for amphiphilic block copolymers were explored in some different solvents using membrane osmometry [4], calorimetry [5, 6], and light scattering [7, 8]. The thermodynamics revealed that the enthalpy and entropy of the micellization of the block copolymers are 10–10^2 times larger than those for small surfactants such as sodium *n*-dodecylsulfate [9]. The kinetic studies have also been investigated for some different amphiphilic diblock and triblock copolymers using calorimetry [6] and light scattering [10, 11]. The kinetics concerns not only the aggregation of the block copolymers into the micelles but also the sphere-to-rod [12, 13] and rod-to-vesicle transitions

[14] and the exchange between micelles and intermicellar solution [15, 16].

We have already reported the micelle formation of nonamphiphilic copolymers consisting entirely of solvophilic blocks. This micellization was found for poly(vinylphenol)-*block*-polystyrene (PVPh-*b*-PSt) [17]. The micellization proceeds in the presence of α,ω-diamines such as 1,4-butanediamine (BDA) through the formation of hydrogen bond cross-linking between the PVPh blocks via the diamine. The micellization of the nonamphiphilic copolymers has advantages over the conventional amphiphilic copolymers in enabling us to choose the driving force and to prepare a variety of amphiphilic copolymers in situ from a nonamphiphilic copolymer. While the micellization of the nonamphiphilic copolymers had some similarities to that of amphiphilic block copolymers regarding temperature-dependence [18, 19] and the relationship between the micellar size and the molecular weight of the copolymer [20], the micellization was distinct from that of the amphiphilic copolymers in cmc [21]. For the micellization of the nonamphiphilic copolymer, the cmc was determined by the diamine concentration, rather than by the copolymer concentration. The thermodynamic and kinetic studies of the micellization should involve similarities to and difference from that of amphiphilic block copolymers. This paper describes the thermodynamic and kinetic studies of the micellization of PVPh-*b*-PSt by BDA.

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 λ = 488 nm.

Materials

The PVPh-*b*-PSt diblock copolymer was prepared as reported previously [17, 18]. The molecular weight of the copolymer was Mn(PVPh-*b*-PSt) = 10,000-*b*-120,000 by ^{1}H NMR. 1,4-Dioxane was purified by refluxing on sodium and distilled. BDA was distilled over calcium hydride.

Preparation of PVPh-*b*-PSt micelles with BDA in 1,4-dioxane

PVPh-*b*-PSt (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. A BDA solution was prepared from BDA (148 mg, 1.68 mmol) and 1,4-dioxane (1 mL). The BDA solution (12 μL) was added to the copolymer solution in the cell, and the mixture was vigorously shaken. The solution was allowed to stand at 10 °C just before subjected to light scattering measurements for the thermodynamic and kinetic studies.

Results and discussion

We have already found that the micellization of PVPh-*b*-PSt by BDA was reversibly controlled by temperature [18, 19]. In the present study, we prepared the micelles at BDA/VPh = 4 in 1,4-dioxane at 10 °C for the thermodynamic and kinetic studies. The micelles had the hydrodynamic radius of 35.4 nm and the aggregation number of 18.2 at 10 °C. Figure 1 shows the thermoresponsivity of the micelles throughout changes in the temperature. The copolymers existing as micelles at 10 °C were dissociated into the isolated unimers at 40 °C. The hydrodynamic radius and aggregation number of the micelles showed good hysteresis for changes in the temperature. This good hysteresis indicates that the dissociation and reconstruction of the micelles are well controlled by the temperature (Fig. 2). The aggregation number changed more sensitively with the temperature than with the hydrodynamic radius. We represented the aggregation numbers as apparent aggregation numbers estimated by the relative scattering intensity (I/I_0). The pertinence of this estimation is based on the fact that the copolymer concentration is immutable during the micellization and that the formation of hydrogen bonding

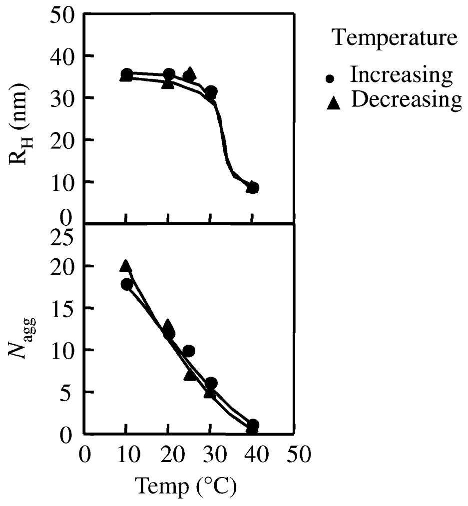

Fig. 1 Hysteresis curves of the PVPh-*b*-PSt micelles with BDA/VPh = 4 in 1,4-dioxane. [copolymer] = 3.33×10^{-3} g/mL

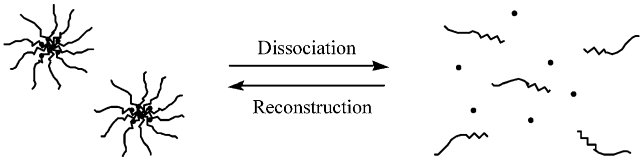

Fig. 2 The dissociation and reconstruction of the micelles

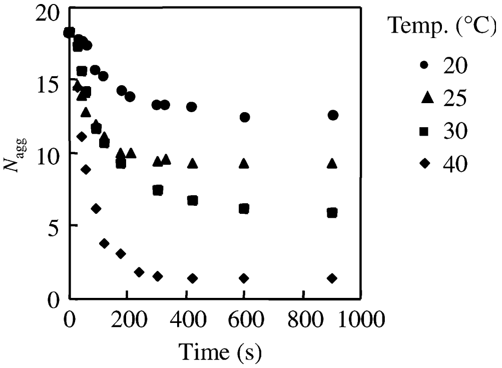

Fig. 3 Variation in the aggregation number of the micelles versus time. Initial temperature of the micellar solution = 10 °C. [copolymer] = 3.33×10^{-3} g/mL

has no effect on the scattering intensity. The hydrodynamic radius was estimated as an average of the hydrodynamic radii for the micelles and unimers in proportion to the existence at each temperature. Accordingly, the aggregation number more precisely reflects the changes in the micelles than the inhydrodynamic radius.

Figure 3 shows variation in the aggregation number of the micelles versus time when the micellar solution at 10 °C was placed at the prescribed temperatures. Whereas the aggregation number rapidly reached to almost unity for 40 °C, the aggregation numbers for other temperatures decreased slowly and became steady at different values.

The light scattering study demonstrated that an equilibrium existed between the micelles and the unimers. Figure 4 shows two different variations in the aggregation number over time at each temperature. One is the variation when the micellar solution prepared at 10 °C was placed at the prescribed temperatures, and the other is when the isolated unimer solution at 40 °C was cooled to the selected temperatures. At 20, 25, and 30 °C, the aggregation numbers from the micelles and from the unimers converged into different values. The micelles and the unimers coexist in different proportions at equilibrium for each temperature.

The dissociation steps of the micelles into the unimers can be described by Eq. 1.

$$\begin{aligned}
&\mathrm{U_n} \underset{k_{n-1,n}}{\overset{k_{n,n-1}}{\rightleftharpoons}} \mathrm{U_{n-1}} + \mathrm{U}\\
&\mathrm{U_{n-1}} \underset{k_{n-2,n-1}}{\overset{k_{n-1,n-2}}{\rightleftharpoons}} \mathrm{U_{n-2}} + \mathrm{U}\\
&\vdots\\
&\mathrm{U_i} \underset{k_{i-1,i}}{\overset{k_{i,i-1}}{\rightleftharpoons}} \mathrm{U_{i-1}} + \mathrm{U}\\
&\vdots\\
&\mathrm{U_3} \underset{k_{23}}{\overset{k_{32}}{\rightleftharpoons}} \mathrm{U_2} + \mathrm{U}\\
&\mathrm{U_2} \underset{k_{12}}{\overset{k_{21}}{\rightleftharpoons}} \mathrm{U} + \mathrm{U}
\end{aligned} \tag{1}$$

U_x denotes the micelle, and U the unimer. The relationship between the concentrations of the micelles and the unimers are represented by Eq. 2 using k_{yx} and k_{xy}, as the rate constants for the dissociation and the reconstruction, respectively.

$$[U]^n = \left\{ \frac{(k_{n,n-1}k_{n-1,n-2}\cdots k_{I,I-1}\cdots k_{32}k_{21})}{k_{n-1,n}k_{n-2,n-1}\cdots k_{I-1,I}\cdots k_{23}k_{12}} \right\} [U_n] \tag{2}$$

Accordingly, the equilibrium constant is $K_x = k_{yx}/k_{xy}$. It is assumed that the equilibrium constants at each step are equal, and the equilibrium constant of the dissociation is obtained as an average value, K_d, of the respective equilibrium constants. Substituting K_d into Eq. 2 we obtained Eq. 3.

$$\frac{[U]^n}{[U_n]} = K_d^{n-1} \tag{3}$$

$$K_d^{n-1} = \frac{\left(k_{n,n-1}k_{n-1,n-2}\cdots k_{I,I-1}\cdots k_{32}k_{21}\right)}{\left(k_{n-1}k_{n-2,n-1}\cdots k_{I,I-1}\cdots k_{32}k_{21}\right)}.$$

The initial concentration of the unimers was 2.56×10^{-2} mmol/L on the basis of the total molecular weight of PVPh-*b*-PSt (Mn = 130,000). When all the unimers aggregated into the micelles by BDA, the concentration of the micelles was estimated to be 1.41×10^{-3} mmol/L based on the aggregation number, 18.2, for the micelles prepared at 10 °C. The concentration of the micelles is immutable even if any one of the unimers consisting of the micelles dissociates from the micelles, although the aggregation number of the micelles changes. Consequently, the concentration of the micelles is always 1.41×10^{-3} mmol/L unless all the unimers dissociate from the micelles. The unimer concen-

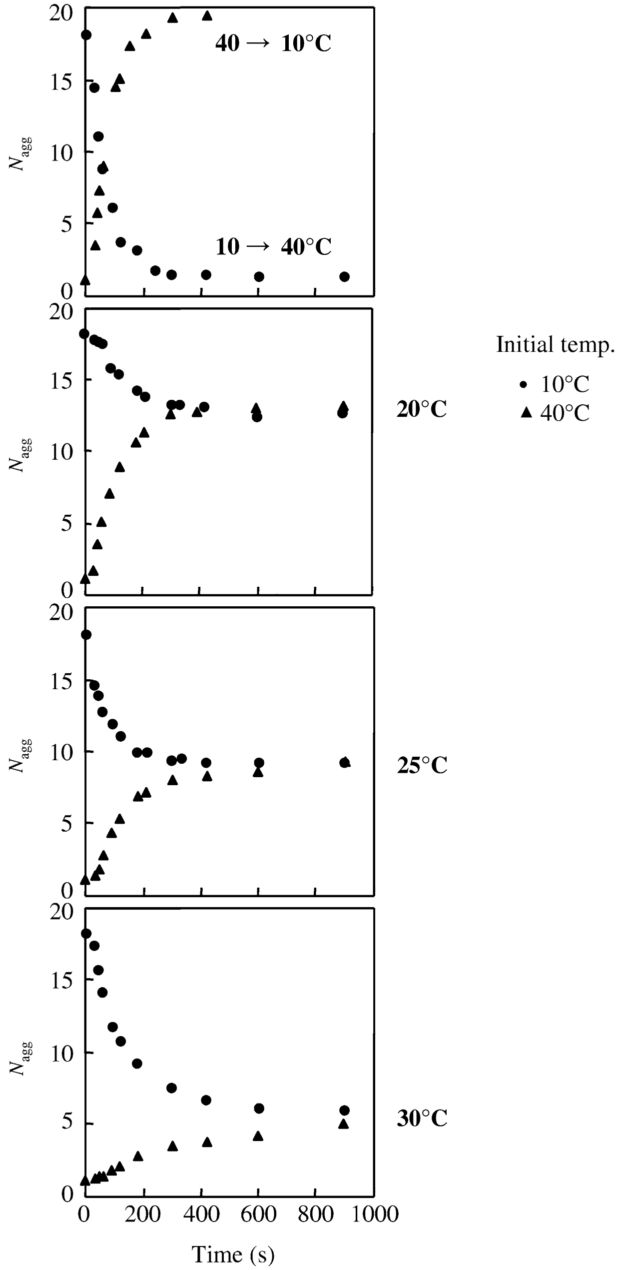

Fig. 4 Variations in the aggregation number over time when the temperature of the copolymer solution decreased from 40 °C or increased from 10 °C to the prescribed temperatures. [copolymer] = 3.33×10^{-3} g/mL

trations at equilibrium, $[U]_e$, for each temperature were determined using the initial concentration of the unimers and the unimer conversions. The conversions were estimated from the change in the aggregation number. The values at each temperature, the aggregation number of the micelles, N_{agg}, the number of unimers, $N(U)$, the unimer conversion, and the equilibrium constant are summarized in Table 1. From the equilibrium constants, the standard Gibbs energy of the dissociation was obtained on the basis of Eq. 4.

$$\Delta G^\circ = -RT\ln K \tag{4}$$

Plotted $-\ln K_d$ versus $1/T$, the slope gives $\Delta H^\circ/R$. This estimation is based on the Gibbs energy (Eq. 5).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

Figure 5 shows the plots of $-\ln K_d$ versus $1/T$ for the dissociation of the micelles with BDA/VPh = 4. The standard mole enthalpy of the dissociation was estimated to be ΔH_d° = 39.3 kJ mol^{-1}. By obtaining a positive ΔH_d° value indicates that the dissociation is endothermic and proceeds by an increase in the temperature. $T\Delta S_d^\circ$ also showed positive, suggesting that the randomness increased by the dissociation of the micells. Similarly, the thermodynamics for the reconstruction from the unimers into the micelles was explored. The copolymers existing as the isolated unimers at 40°C formed the micelles again by decreasing the temperature. The micelles reconstructed had the

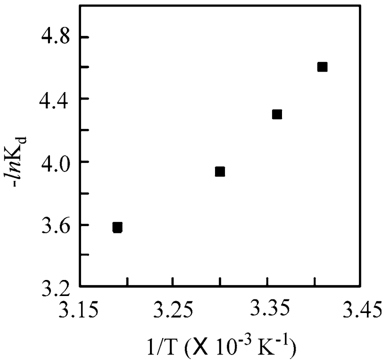

Fig. 5 Plots of $-\ln K_d$ versus $1/T$ for the dissociation of the micelles with BDA/VPh = 4

Table 1 K_d, ΔG_d°, and $T\Delta S_d^\circ$ of the dissociation of the micelles with BDA/VPh = 4

Temp/°C	N_{agg}	$N(U)$	Conv/%	$[U]_e\times10^2$/mmol·L^{-1}	$K_d\times10^2$	$-\ln K_d$	ΔG_d °/ kJ mol $^{-1}$	$T\Delta S_d$ °/kJ mol $^{-1}$
20	11.8	6.4	35.2	0.902	1.00	4.60	11.2	28.1
25	9.7	8.5	46.8	1.20	1.36	4.30	10.7	28.6
30	6.3	11.9	65.5	1.68	1.94	3.94	9.93	29.3
40	1.4	16.8	92.5	2.37	2.80	3.58	9.31	30.0

Table 2 K_{m}, $\Delta G_{\mathrm{m}}°$, $T\Delta S_{\mathrm{m}}$ Δ of the reconstruction at BDA/VPh = 4

Temp/°C	N_{agg}	$N(U)$	Conv/%	$[U]_{\mathrm{e}} \times 10^2$/mmol L^{-1}	K_{m}	$(1/K_{\mathrm{m}})\times10^2$	$-\ln K_{\mathrm{m}}$	$\Delta G_{\mathrm{m}}°$/kJ mol^{-1}	$T\Delta S_{\mathrm{m}}°$ kJ mol^{-1}
20	13.1	6.4	32.8	0.842	107.5	0.930	−4.68	−11.4	−27.6
25	7.3	12.2	62.5	1.60	54.5	1.83	−4.00	−9.91	−29.1
30	4.7	14.8	75.9	1.95	44.4	2.25	−3.79	−9.56	−29.5
40	1.1	18.4	94.3	2.42	35.3	2.83	−3.56	−9.28	−29.8

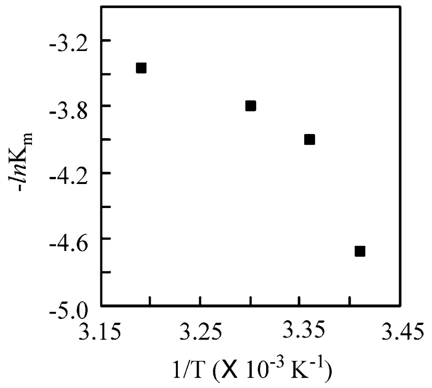

Fig. 6 Plots of $-\ln K_{\mathrm{m}}$ versus $1/T$ for the reconstruction of the micelles. BDA/VPh = 4

hydrodynamic radius of 36.0 nm and the aggregation number of 19.5 at 10°C. The conversions of the unimers, the concentrations of the unimers and the micelles, and the equilibrium constants of the reconstruction were estimated on the basis of this aggregation number. The equilibrium constant of the reconstruction, K_{m}, its reciprocal, $\Delta G_{\mathrm{m}}°$, and $T\Delta S_{\mathrm{m}}°$ are listed in Table 2. At each temperature, the reciprocals of the equilibrium constants were in good agreement with the equilibrium constants of the dissociation. The plots of $\ln K_{\mathrm{m}}$ versus $1/T$ for the reconstruction was shown in Fig. 6. The plots were not perfectly linear. This is accounted for by the fact that this estimation is a noncalorimetric method of determining the standard enthalpy and that the enthalpy is actually temperature-dependent. However, the temperature-dependence is small in many cases [22]. The standard enthalpy of the reconstruction were estimated to be $\Delta H_{\mathrm{m}}° = -39.0$ kJ mol^{-1}. A negative $\Delta H_{\mathrm{m}}°$ value suggests that the reconstruction exothermically proceeds. The absolute value of the enthalpy for the reconstruction showed a good agreement with that for the dissociation. The negative entropy is also indicative of a decrease in the randomness by the reconstruction.We also investigated the thermodynamics of the dissociation and reconstruction of the micelles containing BDA/VPh = 6. The micelles prepared at BDA/VPh = 6 had the hydrodynamic radius of 37.8 nm and the aggregation number of 25.8 at 10 °C. After the hysteresis, the micelles showed a 39.8 nm hydrodynamic radius and a 31.2 aggregation number. The results for the dissociation are listed in Table 3. The plots of $-\ln K_{\mathrm{d}}$ versus $1/T$ are shown in Fig. 7. The standard enthalpy of the dissociation was $\Delta H_{\mathrm{d}}° = 33.2$ kJ mol^{-1} for the micelles with BDA/VPh = 6. Compared to the micelles with BDA/VPh = 4, there was a slight difference in the enthalpy of the dissociation.

The micelles with BDA/VPh = 6 were not completely dissociated into the unimers at 40 °C, although the aggregation number was close to unity at this temperature. Accordingly, we decreased the temperature from 50 °C to the prescribed temperatures for the thermodynamics of the reconstruction. The results and

Table 3 K_{d}, $\Delta G_{\mathrm{d}}°$, and $T\Delta S_{\mathrm{d}}$ ° of the dissociation of the micelles with BDA/VPh = 6

Temp/°C	N_{agg}	$N(U)$	Conv/%	$[U]_{\mathrm{e}} \times 10^2$/mmol L^{-1}	$K_{\mathrm{d}} \times10^2$	$-\ln K_{\mathrm{d}}$	$\Delta G_{\mathrm{d}}°$/ kJ mol^{-1}	$T\Delta S_{\mathrm{d}}°$/kJ mol^{-1}
20	15.6	10.2	39.5	1.01	1.11	4.50	11.0	22.2
30	8.7	17.1	66.4	1.71	1.91	3.96	9.97	23.2
40	2.3	23.5	91.1	2.33	2.65	3.63	9.45	23.7

Table 4 K_{m}, $\Delta G_{\mathrm{m}}°$ and $T\Delta S_{\mathrm{m}}°$ of the reconstruction at BDA/VPh = 6

Temp/°C	N_{agg}	$N(U)$	Conv/%	$[U]_{\mathrm{e}} \times10^2$/mmol L^{-1}	K_{m}	$(1/K_{\mathrm{m}})\times10^2$	$-\ln K_{\mathrm{m}}$	$\Delta G_{\mathrm{m}}°$/kJ mol^{-1}	$\Delta S_{\mathrm{m}}°$/kJ mol^{-1}
20	18.9	12.3	39.5	1.01	90.8	1.10	−4.51	−11.0	−22.7
30	8.1	23.1	74.0	1.90	47.5	2.11	−3.86	−9.73	−24.0
40	2.3	28.9	92.6	2.37	37.7	2.65	−3.63	−9.45	−24.3

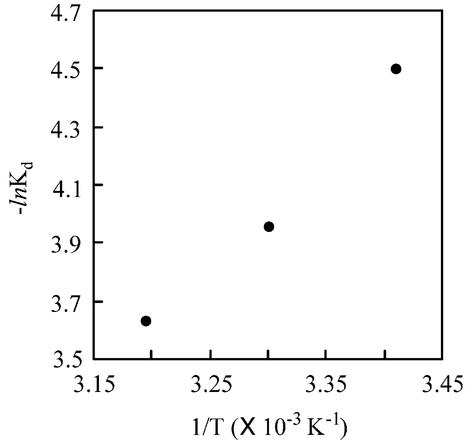

Fig. 7 Plots of $-\ln K_\mathrm{d}$ versus $1/T$ for the dissociation of the micelles with BDA/VPh = 6

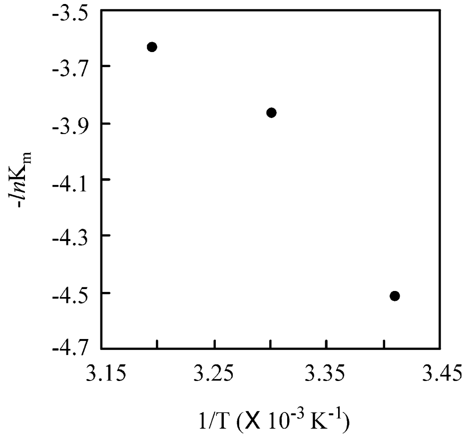

Fig. 8 Plots of $-\ln K_\mathrm{m}$ versus $1/T$ for the reconstruction of the micelles. BDA/VPh = 6

the plots of $-\ln K_\mathrm{m}$ versus $1/T$ are shown in Table 4 and Fig. 8, respectively. The thermodynamics for the reconstruction of the micelles with BDA/VPh = 6 provided $\Delta H_\mathrm{m}{}^\circ = -33.7\ \mathrm{kJ\ mol^{-1}}$. For the micelles with BDA/VPh = 6, there was a negligible difference in the enthalpy between the dissociation and the reconstruction as was for the micelles with BDA/VPh = 4. The standard enthalpy obtained in these studies was close to those for the micellization of amphiphilic block copolymers [5, 8]. This similarity implies that there is a slight difference in the thermodynamics between the micellizations of the nonamphiphilic block copolymer through the hydrogen bonding cross-linking and the conventional amphiphilic block copolymers through van der Waals interaction.

Equation 1 can be rewritten into Eq. 6 for the aggregation of the unimers.

$$\mathrm{nU} \underset{k_{-f}}{\overset{k_f}{\rightleftharpoons}} \mathrm{U_n} \tag{6}$$

The rate constants, k_f and k_{-f} are for the aggregation and the dissociation. The concentration of the unimers is reduced by the aggregation, but increased by the dissociation. Therefore, the net rate of change is

$$\frac{\mathrm{d}[U]}{\mathrm{d}t} = -k_f[U] + k_{-f}[U_n]. \tag{7}$$

If the initial concentration of U is $[U]_0$, and no U_n is initially present, then at all times $[U] + [U_\mathrm{n}] = [U]_0$. Therefore,

$$\frac{\mathrm{d}[U]}{\mathrm{d}t} = -k_f[U] + k_{-f}([U]_0 - [U]) \tag{8}$$

$$\frac{\mathrm{d}[U]}{\mathrm{d}t} = -(k_f + k_{-f})[U] + k_f[U]_0 \tag{9}$$

The solution of this first-order differential equation is

$$[U]_t = [U]_0\left[\frac{\left(k_{-f} + k_f \exp\{-(k_f + k_{-f})t\}\right)}{(k_f + k_{-f})}\right] \tag{10}$$

The equilibrium constant, $K_\mathrm{m} = k_f/k_{-f}$. Substituting $k_{-f} = k_f/K_\mathrm{m}$ into Eq. 10, we obtain Eq. 11.

$$-k_f t = \left\{\frac{\mathrm{K_m}}{\mathrm{K_{m+1}}}\right\} \ln\left[\frac{(1 + 1/\mathrm{K_m})[U]_t}{[U]_0} - \frac{1}{\mathrm{K_m}}\right] \tag{11}$$

The rate constants of the aggregation were determined by cooling the unimer solution containing BDA/VPh = 4 from 40 °C to the prescribed temperatures. The equilibrium is considered to exist even at 10 °C between the micelles and the unimers, although most of the unimers compose the micelles. This is because the micellization from 40 °C to 10 °C is also comprised of the forward and backward reactions. Accordingly, we estimated the equilibrium constant at 10 °C on the basis of the plots in Fig. 6. The equilibrium constant, $\Delta G^\circ_\mathrm{m}$, and $T\Delta S^\circ_\mathrm{m}$ of the reconstruction for 10 °C was $K_\mathrm{m} = 152.9$, $\Delta G^\circ_\mathrm{m} = -11.8\ \mathrm{kJ\ mol^{-1}}$, and $T\Delta S^\circ_\mathrm{m} = -27.2\ \mathrm{kJ\ mol^{-1}}$, respectively. Using this equilibrium constant, we estimated the right side in Eq. 11 for 10 °C. Figure 9 shows plots of the right side in Eq. 11 versus time at each temperature. The plots were for the initial stage of the aggregation before approaching the equilibrium. The plots linearly decreased over time at the respective temperatures. The k_f was obtained from the slope, and k_{-f} from $k_f/\mathrm{K_m}$. The k_f and k_{-f} at each temperature are listed in Table 5. The k_f increased with a decrease in the temperature, indicating that the micellization proceeds more rapidly at lower temperature. The back reaction also tended to

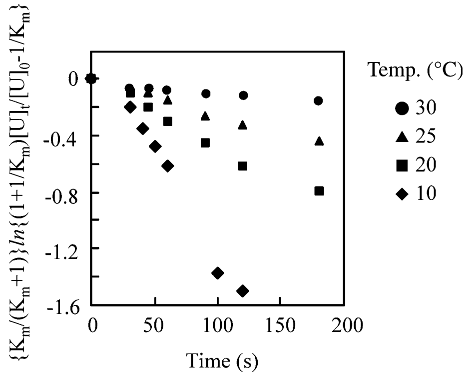

Fig. 9 Plots of $\{K_m/(K_m + 1)\}$ ln $\{(1 + 1/K_m)[U]_f/[U]_0 - 1/K_m\}$ versus time at each temperature. BDA/VPh = 4

Table 5 The rate constants of the micellization

Temp/°C	$k_f \times 10^3/s^{-1}$	$k_{-f} \times 10^5/s^{-1}$
10	13.8	9.04
20	4.66	4.34
25	2.55	4.68
30	0.727	1.64

increase with the temperature decreasing, however, the rate constant was ca. 10^2 times smaller than that of the micellization. The rate constants obtained for the micellization of the nonamphiphilic block copolymer were close to those for the micellization of the gangliosides [23], the exchange of amphiphilic copolymer molecules between the micelles [16], and the rod-to-vesicle transition of a block copolymer [14].

Conclusion

We determined the equilibrium constant, the standard enthalpy and entropy, and the rate constant for the micellization of the nonamphiphilic PVPh-*b*-PSt copolymer by BDA using the variation in the aggregation number. The equilibrium constants of the dissociation were in good agreement with the reciprocals of the reconstruction. There was also a negligible difference in the absolute value of the standard enthalpy and entropy between the dissociation and the reconstruction. By obtaining the negative enthalpy and entropy values for the micellization indicates that the micellization exothermically proceeded with a decrease in the randomness. The increase in the BDA content in the micelles had a slight effect on the thermodynamics of the micellization. The rate constant of the micellization of the nonamphiphilic copolymer increased with a decrease in the temperature. The micelle formation of the nonamphiphilic block copolymer by the α,ω-diamine showed some similarities to that of amphiphilic block copolymers in the thermodynamics and kinetics. These similarities suggest that the nonamphiphilic block copolymer along with the additive can be a new type of surfactant behaving like amphiphilic copolymers.

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