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Micellization of Random Block Copolymers in a Nonselective Solvent Using α,ω-Diamine

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ABSTRACT: Three different random block copolymers composed of vinyl phenol (VPh) and styrene (St) were prepared through living radical polymerization mediated by 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl: poly(vinyl phenol)-*block*-poly(VPh-*ran*-St) (PVPh-*b*-RC$_1$), poly(VPh-*ran*-St)-*block*-polystyrene (RC$_2$-*b*-PSt), and poly(VPh-*ran*-St)-*block*-poly(VPh-*ran*-St) with different unit ratios (RC$_2$-*b*-RC$_3$). All the copolymers formed micelles in the presence of 1,4-butanediamine (BDA) in 1,4-dioxane, a nonselective solvent. The effects of the unit ratios of the random copolymer blocks and the location in the diblock copolymers on the size of micelles, relative scattering intensity, and critical micelle concentration were investigated. Light scattering studies demonstrated that PVPh-*b*-RC$_1$ formed smaller micelles than PVPh-*b*-PSt, while there was a slight difference in the relative intensity. On the other hand, RC$_2$-*b*-PSt and PVPh-*b*-PSt produced the micelles with similar sizes, RC$_2$-*b*-PSt, however, needed more BDA to form micelles than PVPh-*b*-PSt. RC$_2$-*b*-RC$_3$ formed the largest micelles among the three random block copolymers, owing to the longest corona blocks. The relative intensity of the RC$_2$-*b*-RC$_3$ micelles was between those of PVPh-*b*-RC$_1$ and RC$_2$-*b*-PSt, suggesting that the RC$_2$-*b*-RC$_3$ formed the micelles through weaker aggregation force than PVPh-*b*-RC$_1$, but stronger than RC$_2$-*b*-PSt.

KEY WORDS Random Block Copolymers / Micellization / Unimers / Micelles / Hydrodynamic Radius / Relative Intensity /

Macromolecular micelles have a great variety of applications such as separation technologies, drug delivery, ink jet printing, paper manufacture, and water purification. The structures of micelles are dependent on those of unimers. Many diblock copolymers self-assemble into spherical micelles,[1—3] while polystyrene-*block*-poly(acrylic acid) changes the shapes of micelles into spheres, rods, lamellae, or vesicles, according to the block lengths and ratios.[4] AB multiblock copolymers yield flowerlike micelles,[5] as is amphiphilic random copolymers.[6] The structures of unimers dominate not only the shapes of micelles, but also critical micelle concentration (cmc). Particularly for random copolymers, the structures determine the aggregation form whether intermolecular or intramolecular.

Random block copolymers, consisting of a homopolymer and a random copolymer or of different random copolymers, have both properties originating from block and random copolymes. The random block copolymers have already been prepared by living radical polymerization catalyzed by 2,2,6,6-tetramethylpiepridine-1-oxyl (TEMPO).[7,8] Recently, we found that a poly(vinyl phenol)-*block*-polystyrene (PVPh-*b*-PSt) diblock copolymer formed micelles in a nonselective solvent in the presence of α,ω-diamine. This micellization proceeded through hydrogen bond cross-linking between the PVPh blocks *via* α,ω-diamine.[9,10] Here, three different random block copolymers containing random copolymers of poly(vinyl phenol-*ran*-styrene) (P(VPh-*r*-St)) were prepared through the TEMPO-mediated living radical polymerization: PVPh-*b*-P(VPh-*r*-St), P(VPh-*r*-St)-*b*-PSt, and P(VPh-*r*-St)-*b*-P(VPh-*r*-St)′. The random block copolymers attract considerable attention in the size of micelles, aggregation numbers, and cmc when the copolymers form micelles. This paper describes the micellization of the random block copolymers in a nonselective solvent using α,ω-diamine. The difference in the micellization between the random block copolymers and a PVPh-*b*-PSt homoblock copolymer is discussed.

EXPERIMENTAL

Measurements

Gel permeation chromatography (GPC) was performed with a Tosoh HLC-802A instrument equipped with a RI detector and with a Tosoh CP-8000 chromatoprocessor. Two polystyrene gel columns, Tosoh TSK gel G4000 H$_8$ and G2000 H$_8$, were used with THF as the eluent at 42 °C. Gas chromatography (GC) was performed with a Shimadzu GC-14B gas chromatograph. Proton nuclear magnetic resonance (^{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 (MTEMPO) was prepared as reported previously.[11] P^{t}BSt prepolymer was also prepared as reported previously.[9] 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 (St) were washed with aqueous alkaline solution and water, and were distilled over calcium hydride. 1,4-Butanediamine (BDA) was distilled over calcium hydride. Tetrahydrofuran (THF) and 1,4-dioxane were purified by refluxing on sodium for several hours, and were distilled over sodium.

Synthesis of RC$_2$-b-PSt (M_n = 9K-b-110K)

^{t}BSt (5.00 g, 28.4 mmol), St (518 mg, 4.97 mmol), BPO (86 mg, 0.355 mmol), and MTEMPO (86 mg, 0.462 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 47 h and was terminated by cooling with liquid nitrogen. The reaction mixture was dissolved into dichloromethane and poured into methanol to precipitate the polymer. The precipitate was then dried *in vacuo* for several hours to obtain the P(^{t}BSt-*r*-St) random copolymer (3.51 g).

P(^{t}BSt-*r*-St) thus obtained (193 mg) and St (2.00 g, 19.2 mmol) were placed in an ampule. After the contents were degassed, the ampule was sealed *in vacuo*. Subsequent polymerization was carried out at 125°C for 4 d. The product was isolated and purified in the same manner as the procedure for the preparation of the P(^{t}BSt-*r*-St) prepolymer. The P(^{t}BSt-*r*-St)-*b*-PSt random block copolymer (1.91 g) was obtained.

P(^{t}BSt-*r*-St)-*b*-PSt (500 mg) 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 23 h. The resulting mixture was then poured into water (300 mL) to precipitate the polymer. After the polymer was dried, the product was suspended in 200 mL of methanol, and stirred for 3 h at room temperature to remove VPh homopolymers. The resulting precipitate was collected by filtration and then dried *in vacuo* for several hours. P(VPh-*r*-St)-*b*-PSt (= RC$_2$-*b*-PSt) (404 mg) was obtained.

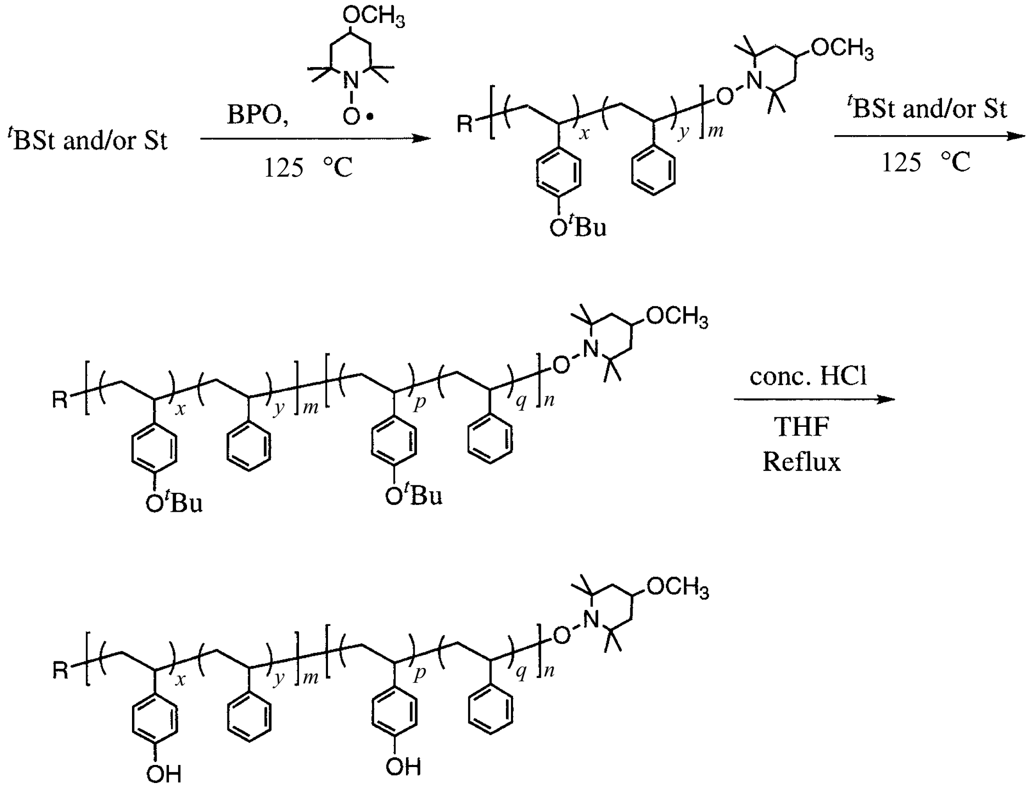
Light Scattering Measurements

RC$_2$-*b*-PSt (10 mg) was dissolved in 1,4-dioxane (3.1 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, 132 mg, 1.50 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 distribution due to the unimers was not observed as determined by non-negatively constrained least squares (NNLS) analysis.[12] Hydrodynamic radius of the copolymer was determined by cumulant analysis.

RESULTS AND DISCUSSION

Three different random block copolymers, PVPh-*b*-RC$_1$, RC$_2$-*b*-PSt, and RC$_2$-*b*-RC$_3$ were prepared through living radical polymerization of ^{t}BSt and St by MTEMPO as a mediator, and hydrolysis of the resulting copolymers (Scheme 1). The results are listed in Table I. PVPh-*b*-RC$_1$ is a diblock copolymer consisting of a VPh homopolymer and a P(VPh-*r*-St) random copolymer, while the RC$_2$-*b*-PSt diblock copolymer consists of P(VPh-*r*-St) and a St homopolymer. RC$_2$-*b*-RC$_3$ consists entirely of random copolymers with different unit ratios of VPh to St. Figure 1 shows ^{1}H NMR spectra of P^{t}BSt-*b*-P(^{t}BSt-*r*-St)$_1$, PVPh-*b*-RC$_1$, and also PVPh-*b*-RC$_1$ in the presence of CF_3COOH. The ^{t}BSt units were completely hydrolyzed into the VPh units. The unit ratio of VPh to St in the RC$_1$ blocks was estimated by GC to be VPh/St = 0.15/0.85 as the unit ratio of ^{t}BSt to St in the random copolymer blocks before hydrolysis. The molecular weight of PVPh-*b*-RC$_1$was determined on the basis of this VPh/St ratio, the degree of polymerization of the P^{t}BSt prepolymer (*DP* = 80),[9] and ^{1}H NMR data for PVPh-*b*-RC$_1$ using the relative intensity of the hydroxyl protons of the VPh units to the aromatic protons. The signals of the hydroxyl group were discerned at 7.2–7.5 ppm, and shifted to lower magnetic field over 10 ppm by the addition of CF_3COOH. The molecular weight was estimated as M_n(PVPh-*b*-RC$_1$) = 10K-*b*-150K. Thin layer chromatography (TLC) confirmed that no VPh homopolymer was included in the block copolymer. The TLC was performed with methanol as an eluent.

The random block copolymers have the potential to show micellization in a nonselective solvent in the presence of α,ω-diamine. This is based on the fact that a PVPh-*b*-PSt diblock copolymer formed micelles in the presence of BDA in 1,4-dioxane, the nonselective solvent through hydrogen bond cross-linking between the PVPh blocks *via* BDA.[10] The random block copolymers should produce different micellar structures. The



PVPh-*b*-RC$_1$: $x = 1, y = 0, p = 0.15, q = 0.85$
RC$_2$-*b*-PSt: $x = 0.89, y = 0.11, p = 0, q = 1$
RC$_2$-*b*-RC$_3$: $x = 0.89, y = 0.11, p = 0.15, q = 0.85$

Scheme 1.

Table I. Random block copolymers

Prepolymer	$M_n \times 10^{-3}$		M_w/M_n[a]	Block copolymer after hydrolysis	M_n[b] $\times 10^{-3}$	Unit ratio			
						Preblock[b]		Postblock[c]	
	NMR	GPC				VPh	St	VPh	St
P^{t}BSt	11	13	1.09	PVPh-*b*-PSt	10-*b*-125	1	0	0	1
P^{t}BSt	11	13	1.09	PVPh-*b*-P(VPb-*r*-St) (= PVPh-*b*-RC$_1$)	10-*b*-150	1	0	0.15	0.85
P(^{t}BSt-*r*-St)	11	15	1.14	P(VPh-*r*-St)-*b*-PSt (= RC$_2$-*b*-PSt)	9-*b*-110	0.89	0.11	0	1
P(^{t}BSt-*r*-St)′	11	10	1.20	P(VPh-*r*-St)-*b*-PSt (= RC$_2$′-*b*-PSt)	9-*b*-120	0.50	0.50	0	1
P(^{t}BSt-*r*-St)	11	15	1.14	P(VPh-*r*-St)-*b*-P(VPh-*r*-St) (= RC$_2$-*b*-RC$_3$)	9-*b*-180	0.89	0.11	0.15	0.85

[a] Estimated by GPC based on PSt standards. [b] Estimated by ^{1}H NMR. [c] Estimated by GC.

structures expected are shown in Scheme 2. PVPh-*b*-RC$_1$ is expected to give micelles with random copolymer blocks at the coronas, while RC$_2$-*b*-PSt can produce micelles with the random blocks at the cores. Furthermore, RC$_2$-*b*-RC$_3$ forms micelles consisting entirely of random copolymers. Dynamic light scattering demonstrated that PVPh-*b*-RC$_1$ showed micellization in the presence of BDA in 1,4-dioxane. This copolymer formed no micelles in the absence of BDA, because 1,4-dioxane was nonselective for the PVPh and RC$_1$ blocks. Figure 2 shows the distributions of hydrodynamic radii during the micellization of PVPh-*b*-RC$_1$. The distributions were obtained by the NNLS method of analysis for the four different BDA/VPh ratios: 0, 0.5, 1.0, and 2.0. At BDA/VPh = 0, one distribution was observed around a hydrodynamic radius of 8.5 nm, originating from the isolated copolymer chains. The transition from the unimers to the micelles occurred at BDA/VPh = 0.5, and two distributions, one each for the unimers and the micelles were observed. The inten-

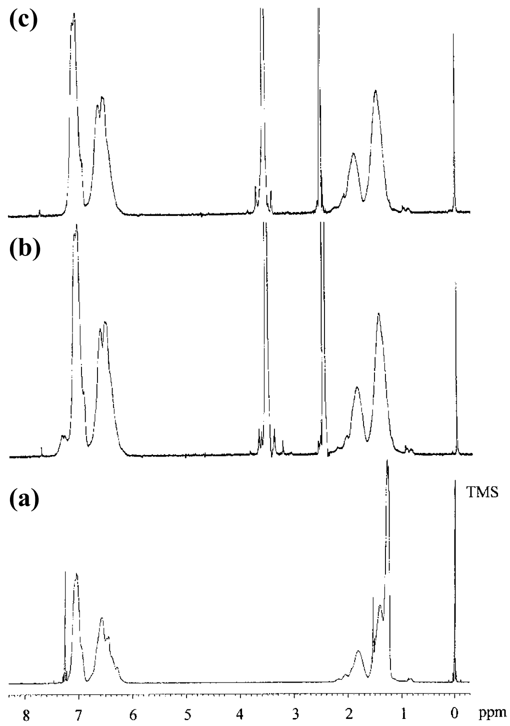
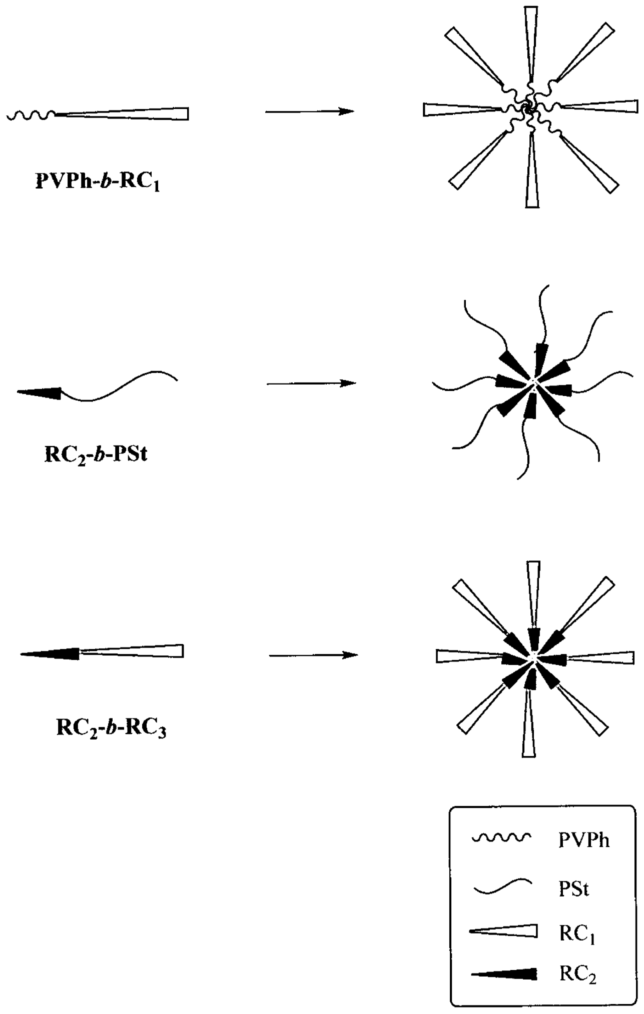


Figure 1. ^{1}H NMR spectra of P^{t}BSt-*b*-P(^{t}BSt-*r*-St) (a) with $CDCl_3$ as the solvent and PVPh-*b*-RC_1 in the absence (b) and presence (c) of CF_3COOH with 1,4-dioxane-d_8 as the solvent.



Scheme 2.

sity of the distribution for the unimers decreased as the BDA/VPh ratio increased (BDA/VPh = 1.0). Finally, one distribution for the micelles was observed at complete micellization (BDA/VPh = 2.0).

Figure 3a presents the variation of hydrodynamic radii for PVPh-*b*-RC_1 and PVPh-*b*-PSt. The hydrodynamic radii of the unimers and micelles could be estimated by cumulant analysis, although they were the binary system of the diblock copolymers and BDA. This is because the scattering intensity of BDA was extremely low compared with that of the copolymer. The hydrodynamic radii of PVPh-*b*-RC_1 and PVPh-*b*-PSt increased as the amount of BDA increased, PVPh-*b*-RC_1, however, formed smaller micelles than PVPh-*b*-PSt. The hydrodynamic radius of PVPh-*b*-RC_1 was 33.5 nm at the complete micellization, while the radius of the PVPh-*b*-PSt micelles was 41.5 nm. This difference in the micellar size does not originate from the molecular weight of the block copolymers, because the diblock copolymers have a slight difference in the molecular weight: M_n(PVPh-*b*-RC_1) = 10K-*b*-150K and M_n(PVPh-*b*-PSt) = 10K-*b*-125K. The VPh units located at the RC_1 blocks should interact with BDA in the cores of the micelles, resulting in the coronas of the RC_1 blocks extending not entirely in the solvent (Scheme 3).

The cmc in the micellization of PVPh-*b*-RC_1 by BDA is determined by the BDA concentration, rather than by the copolymer concentration as is PVPh-*b*-PSt.[9] This is because the copolymer concentration is immutable during the micellization. Therefore, it is difficult to determine the aggregation number of the micelles by using usual methods such as zim plots. However, the relative scattering intensity of the micelles to the unimers can be regarded as an aggregation number roughly estimated. This is based on the fact that the addition of *n*-butylamine to the copolymer solution brought no changes in both hydrodynamic radius and scattering intensity of the copolymers. This indicates that the formation of hydrogen bonding between the hydroxyl and amino groups makes no changes in the scattering intensity. Figure 3b shows the plots of relative aggregation number versus the BDA/VPh ratio. PVPh-*b*-RC_1 formed the micelles at a slightly higher BDA/VPh than PVPh-*b*-PSt, suggesting that PVPh-*b*-RC_1 needed more BDA to form micelles. Some BDA molecules should be consumed by interacting with the VPh units in the RC_1 blocks. However, the copolymers showed a slight difference in the relative intensity at the compete micellization. The relative intensity of the

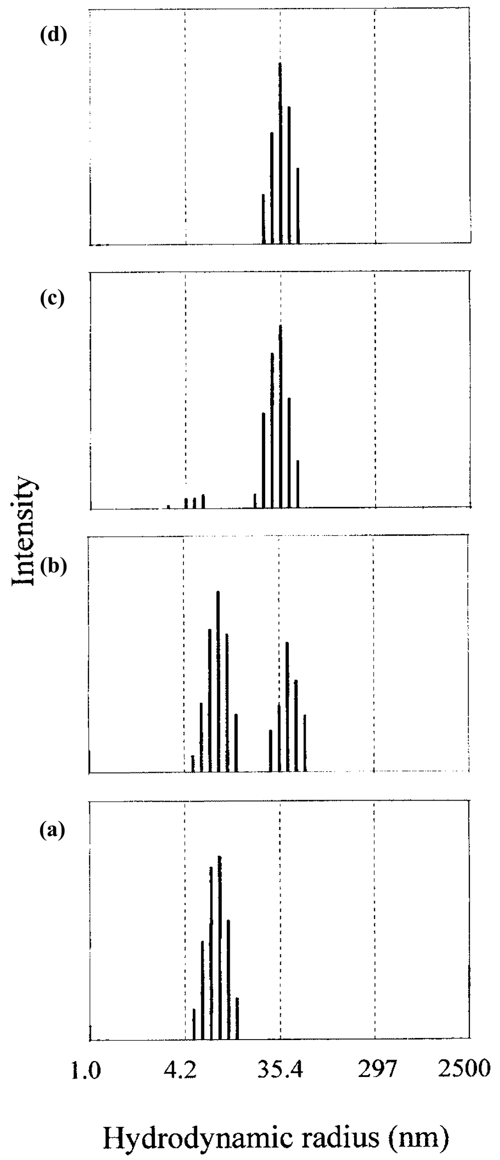


Figure 2. Intensity distribution obtained by NNLS analysis for PVPh-*b*-RC$_1$ at the BDA/VPh ratios: (a) 0, (b) 0.5, (c) 1.0, and (d) 2.0. Copolymer concentration $c = 3.23 \times 10^{-3}$ g mL^{-1}.

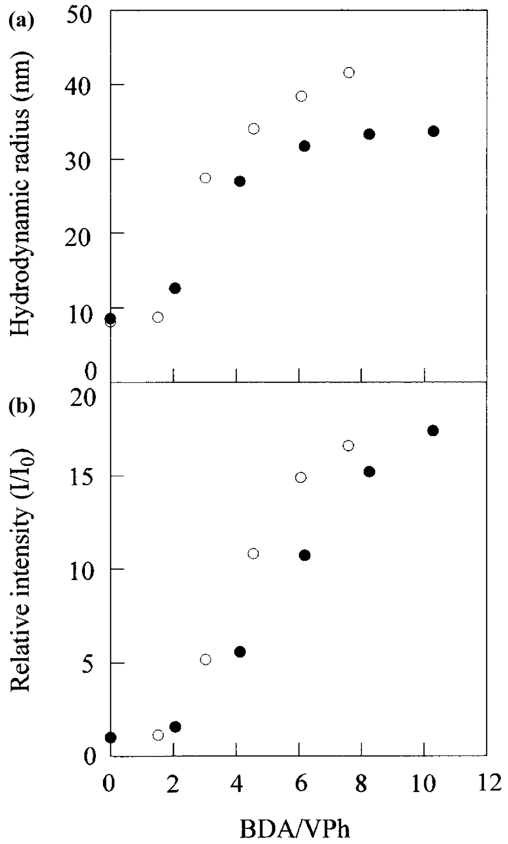
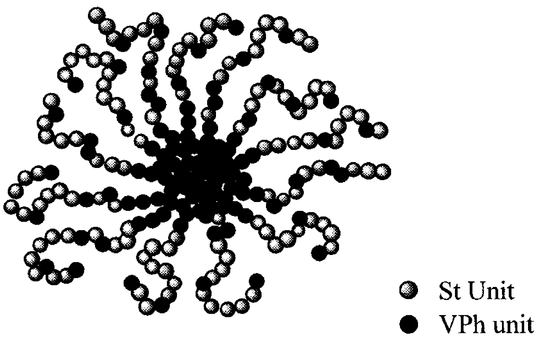


Figure 3. Variations of hydrodynamic radius (a) and relative intensity (b) versus BDA/VPh for (●) PVPh-*b*-RC$_1$ and (○) PVPh-*b*-PSt. Copolymer concentration: 3.23×10^{-3} g mL^{-1}.



The PVPh-*b*-RC$_1$ micelles

Scheme 3.

micelles was 17.4 for PVPh-*b*-RC$_1$ and 16.6 for PVPh-*b*-PSt, respectively. Consequently, the VPh units at the coronas make the micelles smaller, but had negligible effect on the aggregation number.

RC$_2$-*b*-PSt also formed micelles in the presence of BDA in 1,4-dioxane. The unit ratio of VPh to St in the RC$_2$ blocks was VPh/St = 0.89/0.11, and the molecular weight was M_n(RC$_2$-*b*-PSt) = 9K-*b*-110K, on the basis of ^{1}H NMR analysis. Figure 4a shows the plots of hydrodynamic radius versus BDA/VPh ratio for RC$_2$-*b*-PSt and PVPh-*b*-PSt. The hydrodynamic radius of RC$_2$-*b*-PSt was 42.8 nm at the complete micellization. Compared with 41.5 nm for the PVPh-*b*-PSt micelles, there is no significant difference in the micellar size between the block copolymers. On the other hand, the transition from the unimers to the micelles for RC$_2$-*b*-PSt shifted to the higher BDA/VPh side, indicating that RC$_2$-*b*-PSt needed more BDA to form micelles. Figure 4b shows the variation of the relative intensity of the block copolymers. The intensity of RC$_2$-*b*-PSt increased slowly with increasing BDA/VPh compared with PVPh-*b*-PSt, and finally reached to 7.2. When it is taken into account that the intensity of the PVPh-*b*-PSt micelles was 16.6, it can be deduced that RC$_2$-*b*-PSt aggregated more weakly than PVPh-*b*-PSt.

RC$_2'$-*b*-PSt contained more VPh units in the random copolymer blocks than RC$_2$-*b*-PSt, and the VPh/St ratio in the RC$_2'$ blocks was estimated as 0.5/0.5 on the basis

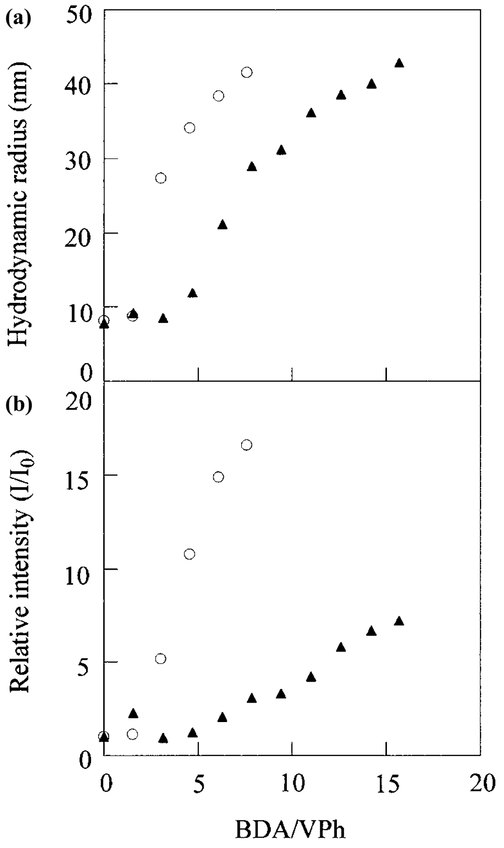


Figure 4. Plots of hydrodynamic radius (a) and relative intensity (b) versus BDA/VPh for (▲) RC$_2$-*b*-PSt and (○) PVPh-*b*-PSt. Copolymer concentration: 3.23×10^{-3} g mL^{-1}.

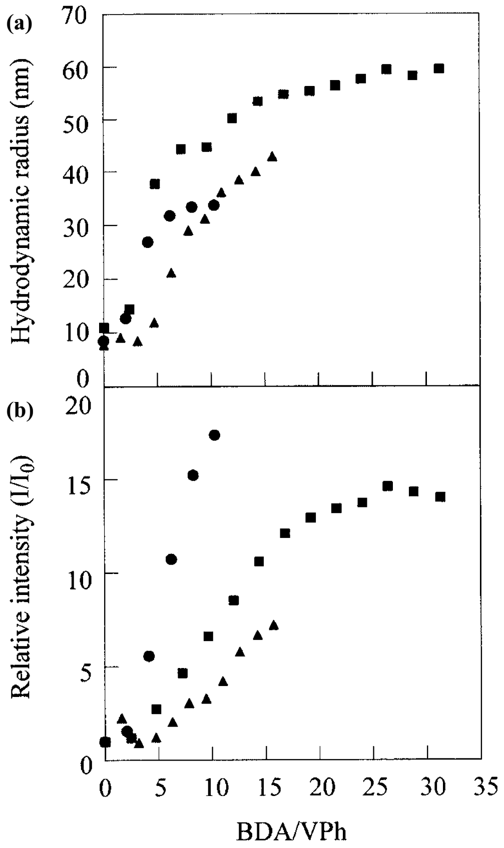


Figure 5. Plots of hydrodynamic radius (a) and relative intensity (b) versus BDA/VPh for (■) RC$_2$-*b*-RC$_3$, (●) PVPh-*b*-RC$_1$, (▲) RC$_2$-*b*-PSt. Copolymer concentration: 3.23×10^{-3} g mL^{-1}.

of ^{1}H NMR analysis. The molecular weight was also estimated by ^{1}H NMR to be 9K-*b*-120 K. The diblock copolymer formed no micelles in 1,4-dioxane even in the presence of a large amount of BDA, the copolymer, however, showed micellization in the presence of PVPh-*b*-PSt and BDA. When RC$_2'$-*b*-PSt was mixed with PVPh-*b*-PSt in the ratio of 5/5 (wt/wt), the mixture formed micelles with 40.0 nm as hydrodynamic radius. No distribution due to both the unimers for RC$_2'$-*b*-PSt and PVPh-*b*-PSt was observed at the complete micellization, suggesting that PVPh-*b*-PSt assisted RC$_2'$-*b*-PSt in aggregating into micelles. Furthermore, the relative intensity of the mixed micelles was 11.4. This indicates that the mixture produced the micelles with smaller aggregation number than PVPh-*b*-PSt alone.

RC$_2$-*b*-RC$_3$ consists entirely of the P(VPh-*r*-St) random copolymers with different VPh/St ratios. The VPh/St ratios of RC$_2$ and RC$_3$ were estimated as 0.89/0.11 and 0.15/0.85 by ^{1}H NMR and GC, respectively. The molecular weight of RC$_2$-*b*-RC$_3$ was determined to be 9K-*b*-180K by ^{1}H NMR. Figure 5a shows the plots of hydrodynamic radii versus BDA/VPh for RC$_2$-*b*-RC$_3$, PVPh-*b*-RC$_1$, and RC$_2$-*b*-PSt. RC$_2$-*b*-RC$_3$ formed the largest micelles, owing to the longest corona blocks. The RC$_2$-*b*-RC$_3$ copolymer needed the most BDA to complete the micellization. BDA should be consumed not only by forming the cores of the micelles with the RC$_2$ blocks, but also by interacting with the VPh units in the RC$_3$ blocks. RC$_2$-*b*-RC$_3$ showed smaller intensity than PVPh-*b*-RC$_1$, but larger than RC$_2$-*b*-PSt (Figure 5b). The larger intensity of RC$_2$-*b*-RC$_3$ than that of RC$_2$-*b*-PSt suggests that RC$_2$-*b*-RC$_3$ aggregated more tightly than RC$_2$-*b*-PSt, and that the VPh units in the RC$_3$ blocks assist the RC$_2$ blocks in aggregating.

CONCLUSIONS

The random copolymer blocks in the diblock copolymers affected the micellar size, the relative intensity, and the cmc. The random copolymer blocks at the coronas made the micelles smaller in comparison with the homoblock copolymer micelles. The chains of the random copolymer blocks should not fully extend in the solvent, because of interaction of the VPh units at the coronas with BDA in the cores of the micelles. However, the VPh units at the coronas had a negligible effect on the cmc and the relative intensity of the micelles. The random copolymer blocks at the cores of the micelles dominated the strength of the aggregation force.

RC_2-*b*-PSt needed more BDA to form micelles. The St units in the core blocks weakened the aggregation force of the copolymer, while the units had no effect on the size of micelles. The diblock copolymer consisting entirely of the random copolymers also produced micelles through weak aggregation force. However, the VPh units at the coronas of RC_2-*b*-RC_3 assisted the block copolymer in aggregating tightly.

This is the first light-scattering studies demonstrating the effect of the random copolymer blocks in the diblock copolymers on the size of micelles, the critical micelle concentration, and the relative intensity. These findings suggest that the unit ratios of the random copolymer blocks can become an effective factor to manipulate the strength of the aggregation force, micellar size, and aggregation numbes.

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