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ORIGINAL CONTRIBUTION

Photolysis-induced micellization of a poly(4-*tert*-butoxystyrene)-*block*-polystyrene diblock copolymer

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Abstract A novel micellization induced by photolysis was attained using a poly(4-*tert*-butoxystyrene)-*block*-polystyrene diblock copolymer (PBSt-*b*-PSt). BSt-*b*-PSt showed no self-assembly in dichloromethane and existed as isolated copolymers. Dynamic light scattering demonstrated that the copolymer produced spherical micelles in dichloromethane by the irradiation with a high-pressure mercury lamp in the presence of photoacid generators, such as bis(alkylphenyl) iodonium hexafluorophosphate (BAI), diphenyliodonium hexafluorophosphate (DPI), and triphenylsulfonium triflate (TPS). The irradiation time to promote the micellization increased in the order of BAI < DPI < TPS, depending on the UV absorption intensity of the photoacid generators. The efficiency to promote the micellization was also dependent on the block length of the copolymer. Under an identical PBSt block length, the copolymer with the shorter PSt block length more easily formed micelles. The ^{1}H NMR analysis confirmed that the PBSt-*b*-PSt copolymer was converted into poly(4-vinyl phenol)-*block*-PSt, resulting in micelles by self-assembly.

Keywords Micelle formation · Self-assembly · Photolysis · Irradiation · Photoacid generators · Poly(4-*tert*-butoxystyrene)-*block*-polystyrene

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Introduction

Stimuli-responsive polymers have attracted considerable attention because these polymers have many industrial applications such as sensors [1–3], drug carriers [4–6], artificial muscles [7, 8], optical data storage [9], and electric devices with molecular switches [10, 11]. The polymers change their spatial structure by their response to stimuli, like aggregating [12], aligning [13], bending [14], and spiraling [15, 16]. Molecular self-assembly is an important responsive behavior for the stimuli-responsive polymers when constructing high-dimensional structures. The stimuli causing the self-assembly of the polymers involve pH [17, 18], temperature [19–22], pressure [23–26], electron transfer [27–30], and light. Especially, light is a handy, easily available, and environmentally clean stimulant to promote the structure changes. In vivo, the photoreceptor proteins in animal eye cells change their high-dimensional structure by receiving photons [31], while artificial polymers responsive to light contain photochromic compounds such as azobenzene [32–34], spiropyran [35, 36], stilbene [37–39], cinnamate [40], and triphenylmethane leuco residues [41]. The polymers reversibly change their structure through the *cis–trans* isomerization, dimerization, and conformational changes of the photochromic compounds. This reversible behavior is manipulated by UV wavelength of the compounds or sometimes temperature. Compared to these reversible reactions required as a function of the on–off switches, irreversible reactions are convenient to fix the spatial structure changed by photo-irradiation. The structure change effects by the photo-irreversible reaction have been investigated on the photolysis of diazosulfonates [42–44], 1-iminopyridinium ylides [45], [4(4′-alkoxybenzoyl) phenylmethyl]phosphonic acids [46], and didecyl-2-methoxy-5-nitrophenyl phosphate [47]. The former three kinds of surfactants lose their surface-active ability by photolysis, resulting in the destruction of the micelles and vesicles. On the other hand, didecyl-2-methoxy-5-nitrophenyl phosphate formed vesicles by the photolysis.

We determined the self-assembly induced by the photolysis of a poly(4-*tert*-butoxystyrene)-*block*-polystyrene diblock copolymer (PBSt-*b*-PSt) [48]. In this photolysis-induced self-assembly, a diblock copolymer produced by the photolysis formed micelles. This new way of molecular self-assembly induced by photo-irradiation has the potential to produce new applications for optical memory materials and optical devices using the photo-irreversible reaction. This paper describes the photolysis-induced micellization of PBSt-*b*-PSt in the presence of a photoacid generator.

Experimental

Instrumentation The ^{1}H NMR measurements were conducted using a Varian 300 FT NMR spectrometer. The size exclusion chromatography (SEC) was performed using a Tosoh GPC-8020 instrument equipped with a DP-8020 dual pump, a CO-8020 column oven, and a RI-8020 refractometer. Two polystyrene gel columns, Tosoh TSK G2000H$_{XL}$ and G4000H$_{XL}$, were used with THF as the eluent at 40 °C. Light scattering measurements were performed with a Photal Otsuka Electronics ELS-8000 electrophoretic light scattering spectrophotometer equipped with a system controller, an ELS controller, and a He–Ne laser operating at λ=632.8 nm. The irradiation reaction was carried out using a Wacom HX-500 illuminator with a 500-W high-pressure mercury lamp. The wavelength range of the lamp was 200–450 nm. Transmission electron microscopy (TEM) measurements were performed using a JEOL JEM-2010 electron microscope.

Materials The poly(4-*tert*-butoxystyrene) terminated with 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-methoxy-TEMPO) was prepared as reported previously [49]. The degree of polymerization was DP=87.3 and the molecular weight was M_n=15,000 by ^{1}H NMR. SEC estimated the molecular weight and the molecular weight distribution as M_n=10,000 and M_w/M_n=1.17, respectively, based on polystyrene standards. The PBSt-*b*-PSt diblock copolymer with Mn(PBSt-*b*-PSt)=15,000-*b*-97,000 estimated by ^{1}H NMR was also prepared as reported previously [48]. The molecular weight and molecular weight distribution by SEC were M_w=79,000, M_n=58,000, and M_w/M_n=1.36 based on polystyrene standards. Commercial grade styrene was washed with aqueous alkaline solution and water and distilled over calcium hydride. Dichloromethane was purified by refluxing on calcium hydride for several hours and distilled over calcium hydride. Bis(alkylphenyl)iodonium hexafluorophosphate (BAI) in 50 wt.% propylene carbonate solution was supplied from Wako Pure Chemical Industries. Diphenyliodonium hexaflurophosphate (DPI) and triphenylsulfonium triflate (TPS) were purchased from Sigma-Aldrich (Fig. 1). These photoacid generators were used without further purification.

Synthesis of PBSt-b-PSt with Mn(PBSt-b-PSt)=15,000-b-63,000 A mixture of the poly(4-*tert*-butoxystyrene) terminated with 4-methoxy-TEMPO (1.00 g) and styrene (2.5 mL) was placed in an ampoule. After degassing the contents, the ampoule was sealed in vacuo. The polymerization was carried out at 125 °C for 35 h and terminated by cooling with liquid nitrogen. The reaction mixture was dissolved in dichloromethane (8 mL) and poured into hexane (2 L). The suspension was subjected to a centrifugal separator to precipitate a polymer. The precipitate was collected then dried in vacuo for several hours to obtain PBSt-*b*-PSt (1.61 g). The molecular weight and molecular weight distribution of the copolymer were estimated by SEC as M_n=40,000 and M_w/M_n=1.31 based on polystyrene standards. The absolute molecular weight of the copolymer was determined by ^{1}H NMR as Mn(PBSt-*b*-PSt)=15,000-*b*-63,000. The molar ratio of the units was BSt/St=0.125:0.875.

Synthesis of PBSt-b-PSt with Mn(PBSt-b-PSt)=15,000-b-170,000 A mixture of the poly(4-*tert*-butoxystyrene) terminated with 4-methoxy-TEMPO (0.5 g) and styrene (5 mL) was placed in an ampoule. After degassing the contents, the ampoule was sealed in vacuo. The polymerization was carried out at 125 °C for 64 h and terminated by cooling with liquid nitrogen. The reaction mixture was dissolved in dichloromethane (30 mL) and poured into hexane (3 L) to precipitate a polymer. The precipitate was dried in vacuo for several hours to obtain PBSt-*b*-PSt (5.05 g). The molecular weight and molecular weight distribution of the copolymer were estimated by SEC as M_n=60,000 and M_w/M_n=1.97 based on polystyrene standards. The absolute molecular weight of the copolymer was determined by ^{1}H NMR as Mn(PBSt-*b*-PSt)=15,000-*b*-170,000. The molar ratio of the units was BSt/St=0.051:0.949.

Irradiation reaction of PBSt-b-PSt: general procedure PBSt-*b*-PSt with M_n=15,000-*b*-97,000 (330 mg, the BSt

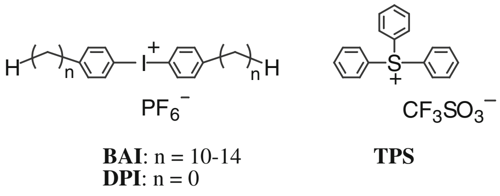


Fig. 1 Photoacid generators

unit=0.257 mmol) was dissolved in dichloromethane (70 mL) in a 100-mL round flask. After the solution was stood at room temperature for 1 h, the solution was let through a microporous filter using a syringe. DPI (42 mg, 0.0986 mmol) was dissolved in dichloromethane (30 mL). After the DPI solution was stood at room temperature for 1 h in dark, the solution was let through a microporous filter using a syringe. The DPI solution was poured into the copolymer solution, then the mixture was irradiated with a high-pressure mercury lamp at room temperature. The resulting solution (3.5 mL) was taken at a definite time and subjected to light scattering measurement. The solution was evaporated to remove the dichloromethane and was freeze-dried with benzene. The product was subjected to ^{1}H NMR to determine conversion.

Light scattering measurements The light scattering measurements were performed at 20 °C at the angle θ=90°. The hydrodynamic diameter of the copolymer was estimated by the cumulant analysis, while the scattering intensity distribution of hydrodynamic diameter was obtained by the Marquadt analysis [50].

TEM measurements A drop of the micellar solution obtained by the irradiation was allowed to fall on a Cu grid with a carbon substrate, and the solvent was immediately evacuated using a filter paper. The grid was dried in air for a few hours and then subjected to TEM observations.

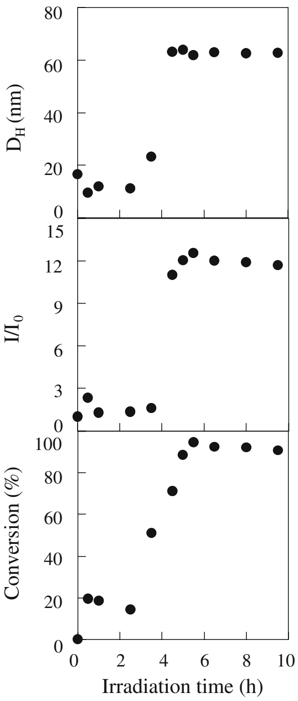


Fig. 2 The variation in the hydrodynamic diameter (D_H), relative scattering intensity (I/I_0), and conversion of the copolymer during the irradiation using BAI. Mn(PBSt-*b*-PSt)=15,000-*b*-97,000, [copolymer]$_0$=3.30 g/L

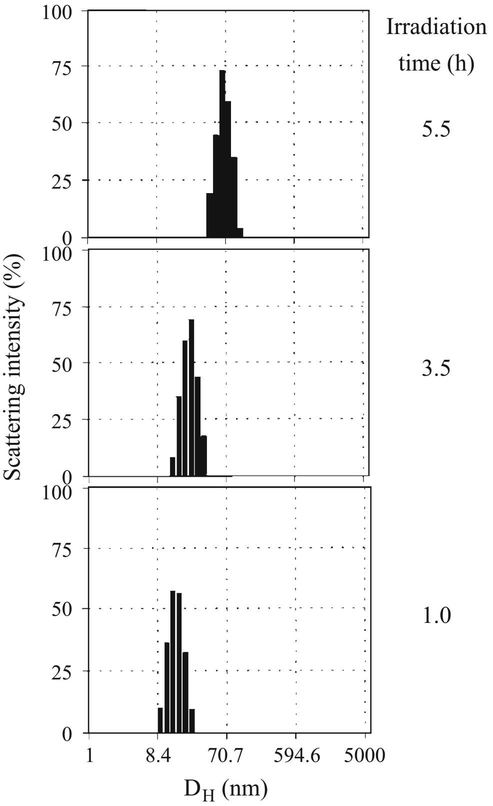


Fig. 3 Scattering intensity distributions of the hydrodynamic diameter of the copolymer. [copolymer]$_0$=3.30 g/L

Results and discussion

The PBSt-*b*-PSt diblock copolymer shows no self-assembly in dichloromethane since the PBSt and PSt blocks are solvophilic to it. Light scattering studies have demonstrated that the copolymer is self-assembled into micelles in dichloromethane by irradiation in the presence of a photoacid generator. Figure 2 shows the variation in the hydrodynamic diameter and the relative scattering intensity (I/I_0) of the copolymer with the molecular weight of

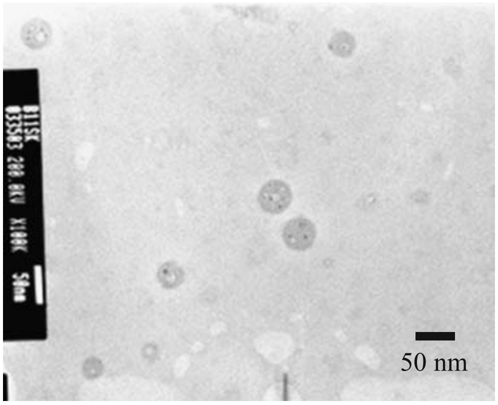


Fig. 4 A TEM image of the micelles. Mn(PBSt-*b*-PSt)=15,000-*b*-97,000,

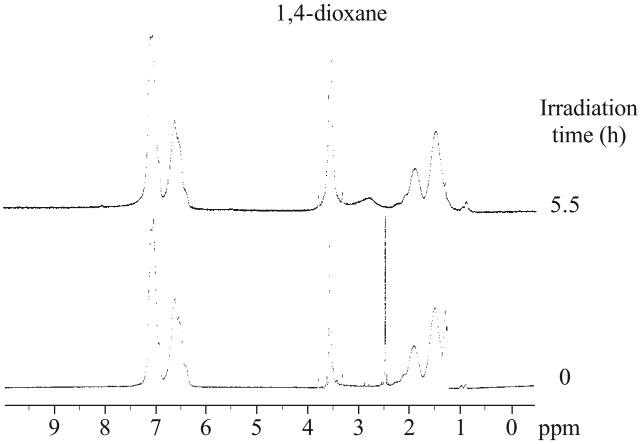


Fig. 5 ^{1}H NMR spectra of the copolymer before (bottom) and after the irradiation (upper, the irradiation time=5.5 h). Solvent: 1,4-dioxane-d_8

Mn(PBSt-*b*-PSt)=15,000-*b*-97,000 during the irradiation using BAI as a photoacid generator. The molar ratio of BAI to the BSt unit was 0.38. The hydrodynamic diameter and scattering intensity showed a good correlation. They increased at 4.5 h and became constant over 5 h, indicating that the micellization was completed over 5 h. The hydrodynamic diameter of the micelles averaged 63.0 nm, while that of the isolated copolymer, which is a unimer, was 16.6 nm based on the cumulant analysis. The observation of the jump and the constant state within the short time period suggests the rapid micellization due to the strong aggregation force.

The variation in the scattering intensity distribution of the hydrodynamic diameter also supported the formation of the micelles by the rapid association. Figure 3 shows the scattering intensity distribution obtained by the Marquadt analysis. The Marquadt method is much better than the cumulant one in analyzing the intensity distribution of the hydrodynamic diameter for polymers with a comparatively narrow molecular weight distribution [50]. The distribution was shifted to the higher side of the hydrodynamic diameter over time by the irradiation. The slight shift in the distribution at 3.5 h implies that aggregates with a lower aggregation number were formed during the first stage and those associated into micelles rather than that the unimers inserted step by step into the micelles.

TEM observation confirmed the formation of spherical micelles through the irradiation. The TEM image of the micelles is shown in Fig. 4. The diameter of the micelles was estimated to average 40.6 nm based on the TEM. Compared to the micellar size determined by the cumulant analysis, the TEM exhibited a smaller diameter of the micelles than the dynamic light scattering. The estimation of the micelles as the smaller size can be accounted for by the fact that the micelles in the solution contracted when isolated in air.

The irradiation of the copolymer in the absence of BAI and the dark reaction in its presence produced no changes in the hydrodynamic diameter and scattering intensity. These two control experiments suggest that the structure of PBSt-*b*-PSt was changed by the irradiation on BAI. The ^{1}H NMR confirmed that the micellization was caused by the elimination of the *tert*-butyl groups in the copolymer. Figure 5 shows the ^{1}H NMR spectra of the copolymer before and after the irradiation. The ^{1}H NMR measurements were performed in 1,4-dioxane-d_8. Signals at 1.29 ppm based on the *tert*-butyl groups were hardly observed after the irradiation. The disappearance of the signals implies that the *tert*-butyl groups were eliminated from the copolymer. PBSt-*b*-PSt should have been converted into poly(4-vinyl phenol)-*block*-PSt (PVPh-*b*-PSt) by the hydrolysis of the *tert*-butoxy groups with the photoacid generator as a catalyst (Fig. 6) based on the mechanism of the hydrolysis of poly(4-*tert*-butoxystyrene) [51]. A signal based on the hydroxyl groups of the PVPh blocks could not be discerned due to the fact that it

Fig. 6 The micellization induced by photolysis of PBSt-*b*-PSt

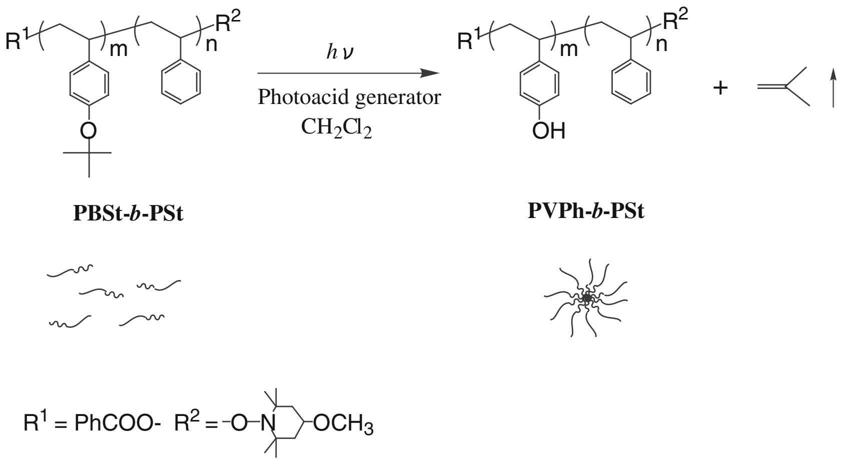
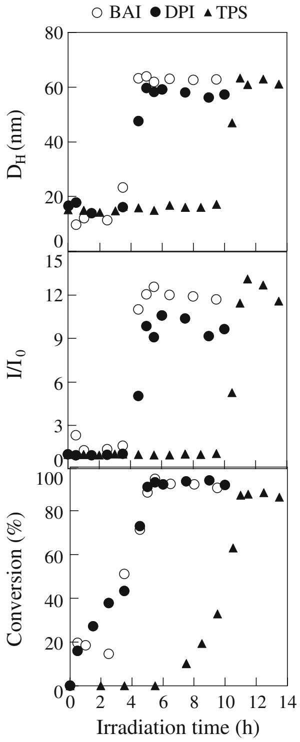


Fig. 7 The variation in the hydrodynamic diameter, scattering intensity, and conversion of the copolymer during the irradiation in the presence of BAI (*open circle*), DPI (*filled circle*), and TPS (*triangle*). [copolymer]$_0$=3.30 g/L. Photoacid generator/BSt unit=0.38



overlapped with the signals of the aromatic protons and had too low an intensity. In addition, it is clear that the disappearance of the butyl proton signals and no observation of the hydroxyl signal were not based on the self-assembly of the copolymer into micelles. This is because PVPh-*b*-PSt showed no self-assembly in 1,4-dioxane-d_8 and existed as unimers. The conversion of the BSt units into the VPh units was estimated based on the signal intensity of the *tert*-butyl protons to that of the aromatic protons at 6.3–7.7 ppm. The time conversion plots are shown in Fig. 2. The conversion started increasing at an earlier stage than the scattering intensity. The scattering intensity jumped when the conversion reached 50%, indicating that the micellization was dependent on the degree of the VPh unit formation.

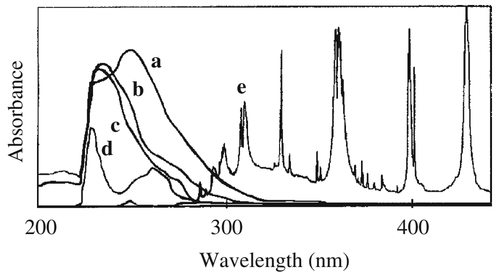
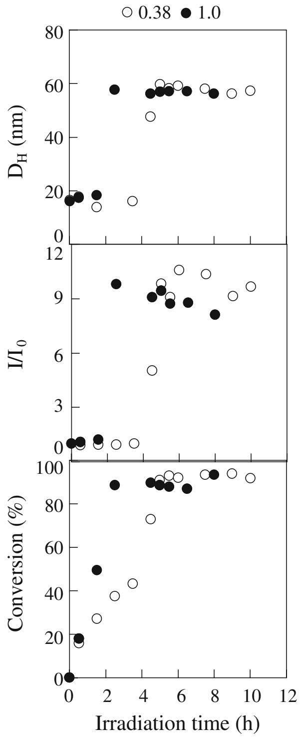


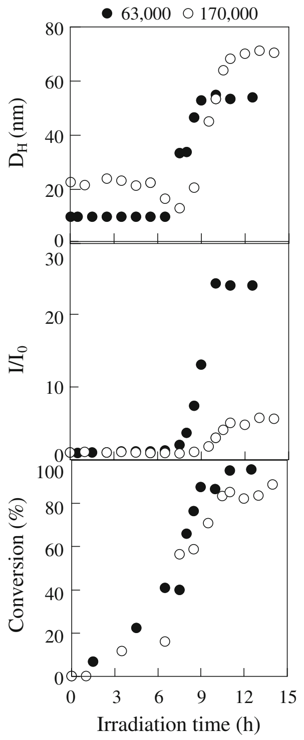
Fig. 8 UV spectra of BAI (**a**), DPI (**b**), TPS (**c**), and PBSt-*b*-PSt (**d**) with the illumination intensity of the irradiation of the high-pressure mercury lamp (**e**). Solvent: dichloromethane. Mn(PBSt-*b*-PSt)=15,000-*b*-97,000

Fig. 9 The variation in the hydrodynamic diameter, scattering intensity, and conversion during the irradiation at 0.38 (*open circle*) and 1.00 (*filled circle*) of DPI/BSt. [copolymer]$_0$=3.30 g/L, Mn(PBSt-*b*-PSt)=15,000-*b*-97,000



The study of the micellization using different kinds of photoacid generators demonstrated that the micellization, coupled with the conversion, were dependent on the ability of the photoacid generator. The micellization by the irradiation was evaluated using DPI and TPS. Figure 7

Fig. 10 The variation in the hydrodynamic diameter, scattering intensity, and conversion during the irradiation using copolymers with Mn(PSt block)=63,000 (*filled circle*) and 170,000 (*open circle*). Mn(PBSt block)=15,000, [copolymer]$_0$=3.30 g/L, DPI/BSt=0.38



shows the variation in the hydrodynamic diameter, scattering intensity, and conversion during the irradiation by BAI, DPI, and TPS. The conversion for DPI started increasing slightly earlier than that for BAI, although there is a negligible difference in the transition of the scattering intensity and hydrodynamic diameter. On the other hand, TPS needed a longer irradiation time to promote the micellization as compared to BAI and DPI. This difference in promoting the micellization was clarified on the basis of the UV analysis of the photoacid generators. Figure 8 shows the UV spectra of the photoacid generators and the PBSt-*b*-PSt copolymer coupled with the illumination intensity of the irradiation versus the wavelength for the high-pressure mercury lamp. It is considered that the irradiation reaction of the photoacid generators occurred around 290 nm because at this wavelength, the absorption of the photoacid generator overlapped at a highest proportion with the illumination intensity of the lamp without any obstruction by the copolymer. The absorbance of the photoacid generators decreased in the order of BAI > DPI > TPS. In particular, TPS had a slight absorption at 290 nm. It can be deduced that the difference in the absorption intensity among the photoacid generators was reflected in the irradiation time needed to initiate the micellization.

The efficiency of the micellization was also dependent on the concentration of the photoacid generator. Figure 9 shows the variation in the hydrodynamic diameter, scattering intensity, and conversion during the irradiation in the presence of DPI at the DPI/BSt molar ratios of 0.38 and 1.00. More sharp and earlier jumping was observed at 1.00, indicating that the micellization was promoted more effectively at 1.00. Consequently, the irradiation time needed for the micellization was manipulated by the concentration of the photoacid generator.

The block length of the copolymer had an effect not only on the micellar size and scattering intensity but also on the conversion. For the identical PBSt block length (M_n= 15,000), the effect of the PSt block length on the micellization was explored. Figure 10 shows the variation in the hydrodynamic diameter, scattering intensity, and conversion during the irradiation using copolymers with the different PSt block lengths: M_n=63,000 and 170,000. Regarding the hydrodynamic diameter and the scattering intensity, it was observed that the copolymer with the shorter PSt block showed a transition at an earlier stage than that with the longer PSt. The copolymer with the shorter PSt more easily aggregated into micelles. The shorter PSt sample produced smaller micelles with a higher aggregation number due to the shorter length of the PSt blocks. The conversion of the shorter PSt sample also started increasing slightly earlier than that for the longer sample. This earlier increase in the conversion of the shorter sample may be accounted for by the difference in the concentration of BSt units. At the identical copolymer concentration (3.30 g/L), the BSt unit concentrations were 0.644 g/L for the 63,000 sample and 0.275 g/L for the 170,000 sample. The photolysis of the BSt units was accelerated at the higher concentration. The earlier initiation of the micellization for the shorter PSt sample should also be based on the faster conversion.

Conclusion

We attained a novel micellization induced by photolysis using the PBSt-*b*-PSt diblock copolymer. The PBSt-*b*-PSt copolymer was converted into PVPh-*b*-PSt in dichloromethane by irradiation in the presence of the photoacid generators, resulting in the self-assembly into micelles. TEM confirmed that the copolymer produced spherical micelles. The irradiation time required for the micellization was dependent on the UV absorption intensity of the photoacid generators, coupled to their concentration, and the block length of the copolymer. For an identical PBSt block length, the copolymer with the shorter PSt block length more easily formed micelles. This photolysis-induced micellization is a new method of molecular self-assembly having the potential to produce new applications for optical sensors, optical memory materials, and electronic devices with molecular switches.

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