

# Micelle formation induced by photolysis of a poly(*tert*-butoxystyrene)-*block*-polystyrene diblock copolymer

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**Abstract** We found the novel photolysis-induced micellization of the poly(*tert*-butoxystyrene)-*block*-polystyrene diblock copolymer (PBSt-*b*-PSt). PBSt-*b*-PSt with a molecular weight of  $M_n(\text{PBSt-}b\text{-PSt})=15,000\text{--}97,000$  showed no self-assembly in dichloromethane and existed as isolated copolymers with a hydrodynamic diameter of 16.6 nm. Dynamic light scattering demonstrated that the copolymer produced micelles with a 63.0 nm hydrodynamic diameter when the copolymer solution was irradiated with a high-pressure mercury lamp at room temperature in the presence of bis(alkylphenyl) iodonium hexafluorophosphate, a photoacid generator. The  $^1\text{H}$  NMR analysis revealed that the micellization resulted from the photolysis of the PBSt blocks into insoluble poly(vinyl phenol) blocks based on the fact that the signal intensity of the *tert*-butyl protons decreased over time during the irradiation. It was found that the micellization rapidly proceeded as the degree of the photolysis reached over 50% and was completed at 90%.

**Keywords** Poly(*tert*-butoxystyrene)-*block*-polystyrene · A photoacid generator · Photolysis · Self-assembly · Micelles · Micellization

## Introduction

Intelligent polymers, which respond to external and internal stimuli to change their shapes and aggregation forms, have attracted considerable attention in recent years. Such polymers

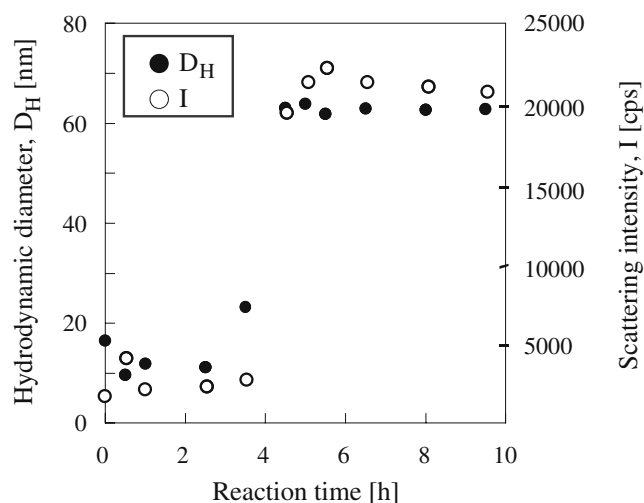
have a variety of applications in many fields, such as drug delivery [1], reduction of the cholesterol level in blood [2], wound healing [3], and attenuators for ultrasonic waves [4], intelligent switches, and control valves [5]. The stimuli to trigger the structure changes of the intelligent polymers include temperature [6–9], pH [10, 11], pressure [12–14], electrochemical potential [15, 16], and the addition of electrolytes [17, 18]. Light is a swift, handy, and inexpensive trigger to cause the polymer forms to change. Light-sensitive polymers play significant roles in electronics as optical sensors, optical memory materials, and electronic devices with molecular switches. To cause such changes in polymer forms by light, several photochemical reactions have been employed. Examples include the *cis-trans* isomerization of azobenzene [19–21], dimerization of stilbene [22, 23] and cinnamate [24], photoisomerization of spiropyran [25], and photocleavage of azosulfonates [26], didecyl-2-methoxy-5-nitrophenyl phosphate [27], and 1-iminopyridinium ylides [28]. When a light-sensitive polymer is irradiated, the structure and solubility of part of the polymer change, resulting in polymer bending or self-assembling into high-dimensional structures.

We found a novel micelle formation induced by the photolysis of a poly(*tert*-butoxystyrene)-*block*-polystyrene diblock copolymer (PBSt-*b*-PSt). Poly(*tert*-butoxystyrene) has an important application in photoresists [29]. This short communication describes the photolysis-induced micellization of PBSt-*b*-PSt.

## Experimental

**Instrumentation** The  $^1\text{H}$  NMR measurements were conducted using a Varian 300 FT NMR spectrometer. The size exclusion chromatography (SEC) was performed using a

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**Fig. 1** The variation in hydrodynamic diameter and scattering intensity of the copolymer during the irradiation.  $[\text{PBSt-}b\text{-PSt}]_0 = 3.30 \text{ g/L}$ ,  $20^\circ\text{C}$ ,  $\theta = 90^\circ$

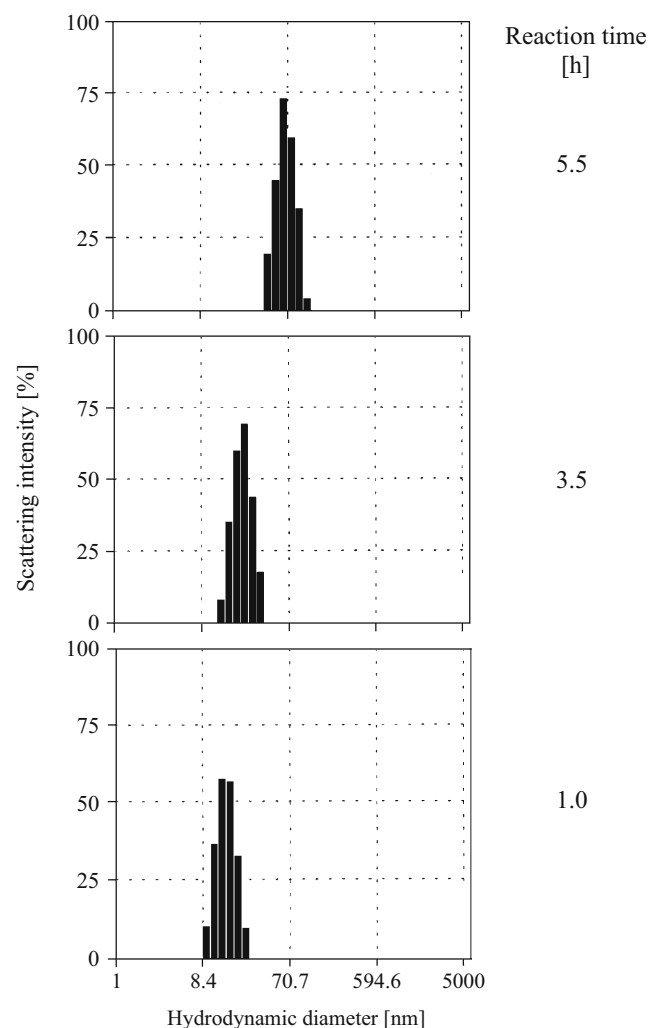
Tosoh GPC-8020 instrument equipped with a DP-8020 dual pump, a CO-8020 column oven, and a RI-8020 refractometer. Two polystyrene gel columns, Tosoh TSK G2000H<sub>XL</sub> and G4000H<sub>XL</sub>, were used with tetrahydrofuran as the eluent at  $40^\circ\text{C}$ . Light scattering measurements were performed with a Photol Otsuka Electronics ELS-8000 electrophoretic light scattering spectrophotometer equipped with a system controller, an ELS controller, and a He–Ne laser operating at  $\lambda = 632.8 \text{ nm}$ . The irradiation reaction was carried out using a Wacom HX-500 illuminator with a 500-W high-pressure mercury lamp.

**Materials** The poly(*tert*-butoxystyrene) terminated with 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-methoxy-TEMPO) was prepared as reported previously [30]. The degree of polymerization was  $\text{DP} = 87.3$  and the molecular weight was  $M_n = 15,000$  by  $^1\text{H}$  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. 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 in 50 wt.% propylene carbonate solution was supplied by Wako Pure Chemical Industries.

**Synthesis of PBSt-*b*-PSt** A mixture of the poly(*tert*-butoxystyrene) terminated with 4-methoxy-TEMPO (2.00 g) and styrene (10 mL) was placed in an ampule. After degassing the contents, the ampule was sealed in vacuo. The polymerization was carried out at  $125^\circ\text{C}$  for 14 h and terminated by cooling with liquid nitrogen. The reaction mixture was dissolved in dichloromethane and poured into hexane to

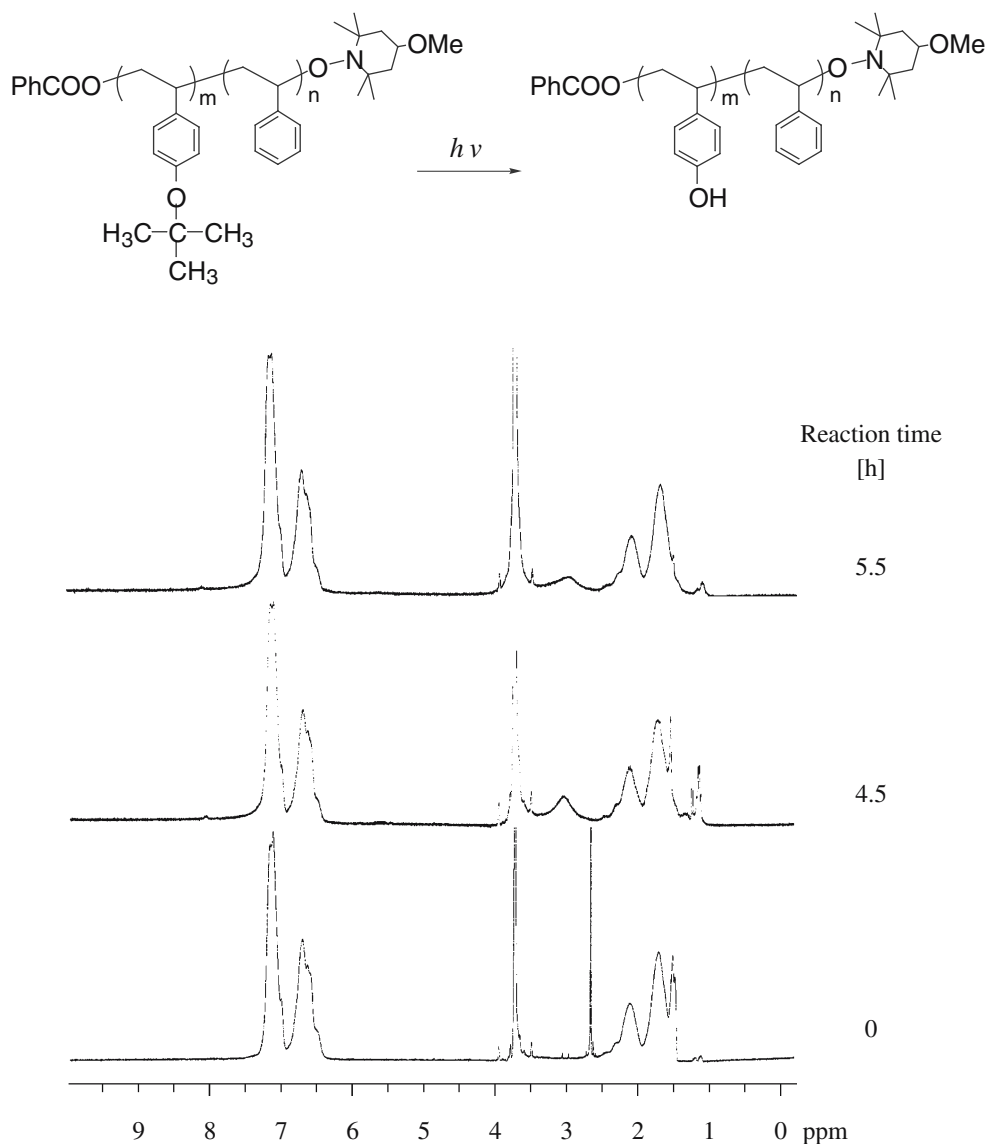
precipitate the polymer. The polymer was purified by repeated reprecipitation from dichloromethane into hexane. The precipitate was then dried in vacuo for several hours to obtain PBSt-*b*-PSt (9.78 g).

**Irradiation reaction of PBSt-*b*-PSt: general procedure** PBSt-*b*-PSt (363 mg) was dissolved dichloromethane (110 mL). After the solution was stood at room temperature for 1 h, the solution was let through a microporous filter using a syringe. Bis(alkylphenyl) iodonium hexafluorophosphate in 50 wt.% propylene carbonate solution (146 mg) was put in a 100-mL round flask covered with aluminum foil. The PBSt-*b*-PSt solution (97.3 mL) was poured into the flask containing the photoacid generator. The mixture was irradiated with a high-pressure mercury lamp under a nitrogen atmosphere at room temperature for the definite time. The resulting solution was subjected to light scattering measurement at  $\theta = 90^\circ$  at  $20^\circ\text{C}$ . The solution was concentrated by an evaporator and was



**Fig. 2** Scattering intensity distributions of the hydrodynamic diameter of the copolymer during the irradiation.  $[\text{PBSt-}b\text{-PSt}]_0 = 3.30 \text{ g/L}$ ,  $20^\circ\text{C}$ ,  $\theta = 90^\circ$

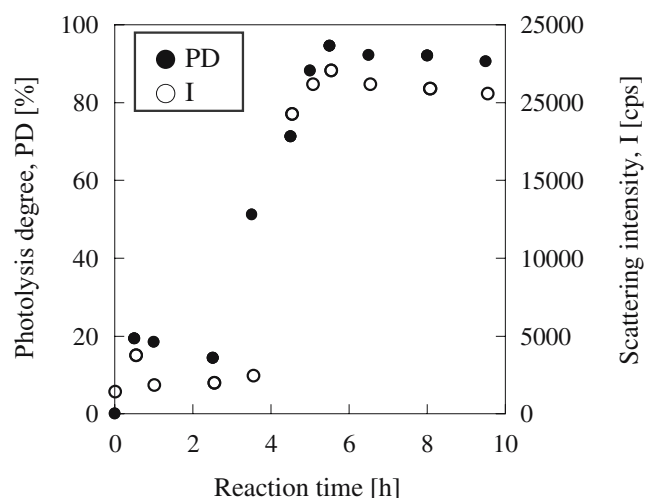
**Fig. 3**  $^1\text{H}$  NMR spectra of the copolymer during the irradiation. Solvent: 1,4-dioxane- $d_8$



poured into hexane to remove the photoacid generator. The precipitated polymer was purified by repeated reprecipitation from dichloromethane into hexane. The precipitate was then dried in vacuo for several hours to quantitatively obtain the resulting polymer.

## Results and discussion

The PBSt-*b*-PSt diblock copolymer was prepared with the living radical polymerization mediated by 4-methoxy-TEMPO. The molecular weight of the copolymer was determined by  $^1\text{H}$  NMR as  $M_n(\text{PBSt-}b\text{-PSt})=15,000$ – $97,000$  based on the signal intensity of the aromatic protons to the aliphatic protons of the main chains. SEC estimated the molecular weight and molecular weight distribution as  $M_n=79,000$  and  $M_w/M_n=1.36$  based on polystyrene standards.



**Fig. 4** The plots of photolysis degree and scattering intensity of the copolymer vs the reaction time

Light scattering studies demonstrated that the copolymer self-assembled into micelles due to irradiation in the presence of a photoacid generator. The irradiation was performed in dichloromethane at room temperature using bis(alkylphenyl) iodonium hexafluorophosphate as a photoacid generator. Figure 1 shows the variation in the hydrodynamic diameter of the copolymer and the scattering intensity during the irradiation. The hydrodynamic diameters were estimated by the cumulant analysis. The hydrodynamic diameter rapidly increased at 4.5 h and became constant over 5 h. The hydrodynamic diameter of the micelles averaged 63.0 nm, while that of the isolated PBSt-*b*-PSt copolymer was 16.6 nm. The scattering intensity also increased at 4.5 h and was steady after 5 h. No more changes in the scattering intensity indicated that the micellization was completed because the scattering intensity is proportional to the aggregation number density [31].

We also explored the micellization of PBSt-*b*-PSt by the Marquadt analysis. The Marquadt method is much better than the cumulant in analyzing the intensity distribution of the hydrodynamic diameter for polymers with a comparatively narrow molecular weight distribution [32]. Figure 2 shows the scattering intensity distributions of the hydrodynamic diameter for PBSt-*b*-PSt during the irradiation. The sample before the irradiation had too low a scattering intensity to obtain an intensity distribution. The intensity distribution was shifted to the higher side of the hydrodynamic diameter over time during the irradiation. The irradiation in the absence of the photoacid generator did not change the hydrodynamic diameter and scattering intensity of the copolymer. Furthermore, the dark reaction of the copolymer in the presence of the photoacid generator also produced no changes in them. These two control experiments indicated that the micellization occurred by the photolysis of PBSt-*b*-PSt.

The  $^1\text{H}$  NMR analysis revealed that the PBSt blocks decomposed into insoluble poly(vinyl phenol) blocks by the photoacid generator, resulting in the copolymer self-assembling into micelles. Figure 3 shows the  $^1\text{H}$  NMR spectra of the PBSt-*b*-PSt copolymer during the irradiation. The  $^1\text{H}$  NMR measurements were performed in 1,4-dioxane-*d*<sub>8</sub>. PBSt-*b*-PSt coupled with poly(vinyl phenol)-*b*-PSt showed no self-assembly in 1,4-dioxane because this is a good solvent for the PBSt, PSt, and poly(vinyl phenol) blocks. Signals of the *tert*-butyl groups of the PBSt blocks were observed at 1.29 ppm. The signal intensity decreased over time and almost disappeared after 5.5 h. A signal for the hydroxyl groups of the poly(vinyl phenol) blocks could not be discerned due to the fact that it was overlapped with the signals from the aromatic protons and had too low an intensity. Based on the signal intensity of the *tert*-butyl protons and the aromatic protons, the degrees of the photolysis were estimated. Figure 4 shows the plots of the

degree of the photolysis, coupled with the scattering intensity vs the reaction time. The micellization was not initiated below 50% of the photolysis degree. It was found that the micellization rapidly proceeded over 50% and was completed at 90%.

## Conclusion

We found the photolysis-induced micellization of PBSt-*b*-PSt due to irradiation in the presence of an acid generator. The copolymer produced micelles with a 63.0-nm hydrodynamic diameter by irradiation in the presence of a photoacid generator. The micellization resulted from the photodecomposition of the PBSt blocks into the insoluble poly(vinyl phenol) blocks. The micellization rapidly proceeded as the degree of the photolysis reached over 50% and was completed at 90%. This study is the first attempt demonstrating that the micellization occurred due to photolysis of the diblock copolymer. This micellization has the potential to produce new applications for optical devices using the self-assembly induced by photolysis.

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