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ORIGINAL CONTRIBUTION

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Oxidation-induced micellization of a diblock copolymer containing stable nitroxyl radicals

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Abstract Oxidation-induced micellization was attained for a diblock copolymer containing 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO). Poly(4-vinylbenzyloxy-TEMPO)-*block*-polystyrene (PVTEMPO-*b*-PSt) showed no self-assembly in carbon tetrachloride, a nonselective solvent. Dynamic light scattering demonstrated that the copolymer self-assembled into micelles of 49.5-nm hydrodynamic diameter when chlorine gas was added to the copolymer solution. The UV and electron spin resonance (ESR) analyses verified that as TEMPO was oxidized into the one-electron oxidant, that is, oxoaminium chloride (OAC) by the chlorine, the nonamphiphilic block copolymer became amphiphilic in nature, and thus, the polymers underwent micellization. An investigation of the relation between the micellization and the oxidation degree of the TEMPO into the OAC revealed that the micellization was induced by only 16% of the OAC. It was confirmed that the POAC-*b*-PSt micelles were spherical in shape by transmission electron microscopy observation. The micelles served as a two-electron oxidizing agent for benzyl alcohol to quantitatively give benzaldehyde. The micellar structure was maintained after the oxidation of benzyl alcohol without any dissociation into unimers because the OAC was converted into an insoluble hydroxylamine–hydrochloride salt. On the other hand, the micelles reacted with *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD) to produce Wurster's blue chloride by a one-electron transfer from TMPD to the OAC, converting themselves into PVTEMPO-*b*-PSt unimers.

Keywords Poly(4-vinylbenzyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl)-*block*-polystyrene · Oxidation · Chlorine · Oxoaminium chloride · Micelles

Introduction

Induced micellization of block copolymers has received considerable attention in recent years from the viewpoint of reversible control of the self-assembly. The micellization is induced by variation in the surroundings such as temperature [1–4], pressure [5–9], pH [10–14], salt formation [13–18], and noncovalent bond cross-linking [19–21]. The block copolymers are molecularly converted in situ from the nonamphiphilic copolymers completely dissolved in a solvent to amphiphilic copolymers due to these stimuli. Therefore, the association and dissociation of the isolated copolymers are reversibly controlled by such stimuli. The induced micellization has advantages over direct micellization of amphiphilic copolymers in molecular designing. There is no dependence on the balance of solvophilic and solvophobic moieties when designing the copolymers. Thus, a better selection of the driving force can be provided. The advantages also include the fact that a variety of amphiphilic copolymers can be created from one nonamphiphilic copolymer in situ by selecting the stimuli.

We found novel oxidation-induced micellization of a diblock copolymer containing stable nitroxyl radicals on the side chains. The control of the micellization by oxidation is important when it is taken into account that many vital reactions involving electron transfer occur on the surface of or close to a biomembrane, such as mitochondria, formed by vital surfactants [22, 23]. 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO), a stable nitroxyl radical [24] known as a spin trapping reagent [25], a spin label reagent [26], and a mediator in living radical polymerization [27, 28], acts as a redox catalyst. In the redox system, the radical is converted into the oxoaminium salt by a one-electron oxidation, whereas it is converted into the hydroxylamine by a one-electron reduction (Fig. 1) [29]. The oxoaminium salt serves as a one-electron oxidizing agent for amines [24, 29], sulfides [29, 30], and organometallic compounds [31] to produce their radical cation salts or radical intermediates. The oxoaminium salt also acts as a two-electron oxidizing agent for converting an alcohol into an aldehyde or ketone [32]. The salts such as the oxoaminium chloride, nitrate, trifluoroborate, and hexafluoroantimonate are easily prepared by disproportionation of TEMPO in ether by the acids [33]. In particular, the oxoaminium chloride (OAC) is easily obtained through the oxidation of TEMPO by chlorine gas in carbon tetrachloride [32]. This article describes the micellization of a TEMPO-supported diblock copolymer by the redox reaction of the TEMPO and the application of the micelles as an oxidizing agent.

Experimental

Instrumentation ^{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 an RI-8020 refractometer. Two polystyrene gel columns, Tosoh TSK gel α-M, were used with *N,N*-dimethylformamide (DMF) as the eluent at 40 °C. The UV spectra were obtained using a Shimadzu UV-160A UV-Vis recording spectrophotometer. Light-scattering measurements were performed with a Photal Otsuka Electronics ELS-8000 electrophoretic light-scattering spectrophotometer equipped with a system controller, an evaporative light-scattering (ELS) controller, and an He–Ne laser operating at λ=632.8 nm. The ESR spectra were obtained with a JEOL JES-FE1XG ESR spectrometer. Transmission electron microscopy (TEM) measurements were done using a JEOL JEM-2010 electron microscope.

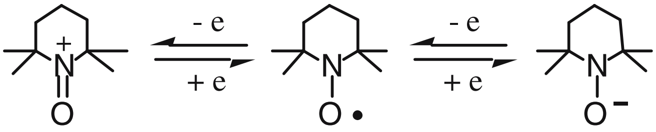


Fig. 1 Redox system of TEMPO

Materials 4-Methoxy-TEMPO [32] and 4-hydroxy-TEMPO [34] were prepared as reported previously. Benzoyl peroxide (BPO) was precipitated from chloroform and crystallized in methanol at 0 °C. Commercial-grade 4-vinylbenzylchloride (VBC) and styrene were washed with aqueous alkaline solution and water and distilled over calcium hydride. DMF was distilled over calcium hydride under reduced pressure. Carbon tetrachloride was purified by refluxing on phosphorus pentaoxide for several hours and distilled over phosphorus pentaoxide. Benzyl alcohol was distilled over calcium hydride in vacuo. Diethyl ether was distilled over sodium. Extrapure *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD) was used without further purification.

Synthesis of a PVBC prepolymer A mixture of VBC (19.5 g, 0.128 mol), BPO (0.390 g, 1.61 mmol), and 4-methoxy-TEMPO (0.360 g, 1.94 mmol) was placed in an ampule. After degassing the contents, the ampule was sealed in vacuo. The polymerization was carried out at 125 °C for 5 h and terminated by cooling with liquid nitrogen. The reaction mixture was dissolved in 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 the prepolymer of poly(4-vinylbenzylchloride) (PVBC, 16.4 g).

Synthesis of PVBC-b-PSt The PVBC (2.39 g) and styrene (8.18 g) were placed in an ampule. After degassing the contents, the ampule was sealed in vacuo. Subsequent polymerization was carried out at 125 °C for 18 h. The reaction mixture was dissolved in dichloromethane and then poured into methanol to precipitate the polymer. The polymer was subjected to flash column chromatography, with benzene/cyclohexane = 10/1 (vol/vol) as an eluent to remove the unreacted PVBC, then precipitated into methanol, and dried in vacuo for several hours. PVBC-*b*-PSt (9.45 g) was thus obtained.

Synthesis of poly(4-vinylbenzyloxy-TEMPO)-block-polystyrene A solution of 4-hydroxy-TEMPO (0.543 g, 3.16 mmol) in DMF (5 ml) was added at 0 °C to a suspension of sodium hydride (0.153 g, 6.38 mmol) in DMF (5 ml). The mixture was stirred at 0 °C for 10 min. A solution of the PVBC-*b*-PSt (1.00 g) in DMF (7 ml) at 0 °C under N_2 was added to the mixture. The mixture was stirred at 0 °C for 10 min then allowed to stand at room temperature for 15 h. The resulting mixture was 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 the poly(4-vinylbenzyloxy-TEMPO)-*block*-polystyrene (PVTEMPO-*b*-PSt) (0.893 g).

Light-scattering measurements of POAC-b-PSt micelles PVTEMPO-*b*-PSt (6 mg, 8.06×10^{-3} mmol of the VTEMPO unit) was dissolved in 3.5 ml of carbon tetrachloride degassed with nitrogen, and using a syringe, the solution was injected through a microporous filter into a cell. Chlorine gas (0.18 ml, 8.04×10^{-3} mmol) was added to the solution with a syringe at room temperature. The solution was allowed to stand at room temperature for 5 min then subjected to light scattering at θ=90° at 20 °C.

Reaction of the POAC-b-PSt micelles with benzyl alcohol Ten microliters (8.12×10^{-3} mmol of benzyl alcohol) of a solution (84 μl of benzyl alcohol in 1 ml of carbon tetrachloride) at room temperature was added to the micellar solution prepared by the method described above. Ten microliters (7.93×10^{-3} mmol of diethyl ether) of a solution (83 μl of diethyl ether in 1 ml of carbon tetrachloride) for estimation of the conversion of benzyl alcohol into benzaldehyde by ^{1}H-NMR with diethyl ether as the standard was added to the mixture. The mixture was subjected to ^{1}H-NMR, UV, and light-scattering measurements at 20 °C.

Reaction of the POAC-b-PSt micelles with TMPD A solution (30 μl, 8.04×10^{-3} mmol of TMPD) of TMPD (88 mg, 0.536 mmol) in carbon tetrachloride (2 ml) at room temperature was added to the micellar solution prepared by the method described above. The mixture was subjected to light scattering, UV, and ESR analyses at 20 °C.

Synthesis of Wurster's blue chloride Carbon tetrachloride (3.5 ml) was degassed with nitrogen, and using a syringe, it was injected through a microporous filter into a cell. Chlorine gas (0.18 ml, 8.04×10^{-3} mmol) was added to the solution with a syringe at room temperature. A solution (30 μl, 8.04×10^{-3} mmol of TMPD) of TMPD (88 mg, 0.536 mmol) in carbon tetrachloride (2 ml) was then added to it at room temperature. The black suspension was subjected to ESR analyses.

Transmission electron microscopy observation A drop of the micellar solution 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.

Results and discussion

We prepared a PVTEMPO-*b*-PSt diblock copolymer by the reaction of 4-hydroxy-TEMPO and PVBC-*b*-PSt (Fig. 2). PVBC-*b*-PSt was obtained through the sequential living radical polymerization of styrene (St) by the PVBC prepolymer as an initiator using 4-methoxy-TEMPO as a mediator. The degree of polymerization (DP) of the PVBC prepolymer was estimated to be 108 based on the signal intensities of the benzyl protons at 4.50 ppm and the methoxy protons at 3.25 ppm for the 4-methoxy-TEMPO attached to the polymer chain end [35]. The absolute molecular weight of the PVBC was 16,500. The molecular weight (Mn) and molecular weight distribution (Mw/Mn) estimated by SEC with polystyrene standards were Mn=10,600 and Mw/Mn=1.47, respectively. Figure 3 shows an ^{1}H-NMR spectrum of the PVBC-*b*-PSt. The molar ratio of the VBC unit to the St was estimated to be VBC/St=0.186/0.814 using the intensity ratio of the benzyl protons at 4.2–4.8 ppm to the aromatic protons at 6.1–7.9 ppm. The molecular weight of the PVBC-*b*-PSt was determined to be Mn(PVBC-*b*-PSt)=16,500-*b*-49,400 based on the molar ratio of the VBC and St units and the DP of the PVBC prepolymer. The molecular weight and molecular weight distribution by SEC were Mn=36,900 and Mw/Mn=1.90, respectively. A ^{1}H-NMR spectrum of the PVTEMPO-*b*-PSt copolymer is also shown in Fig. 3. The spectrum was obtained by the reduction of the TEMPO to the hydroxylamine by phenylhydrazine in $CDCl_3$. The signals at 1.18 and 1.26 ppm are attributed to the

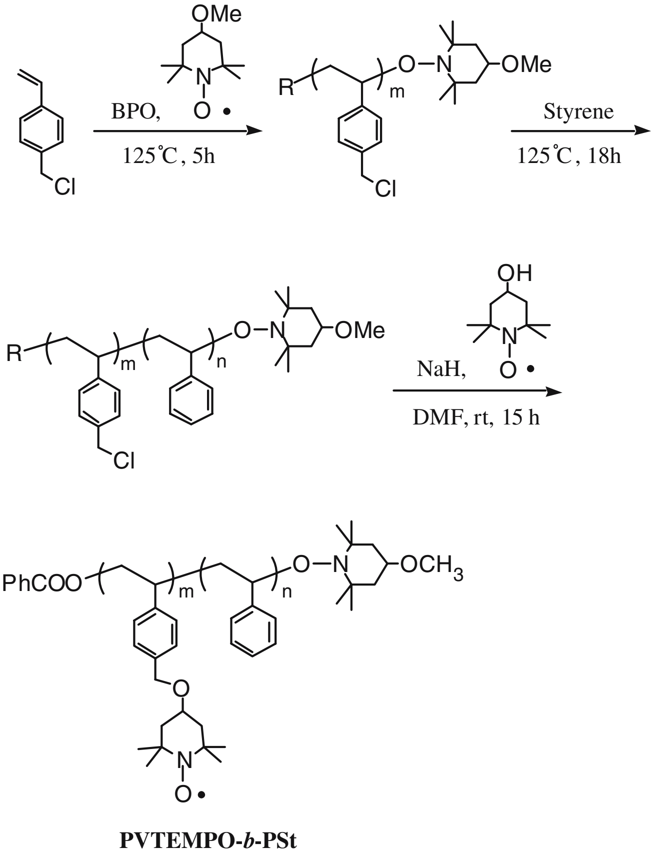


Fig. 2 Synthesis of the PVTEMPO-*b*-PSt diblock copolymer

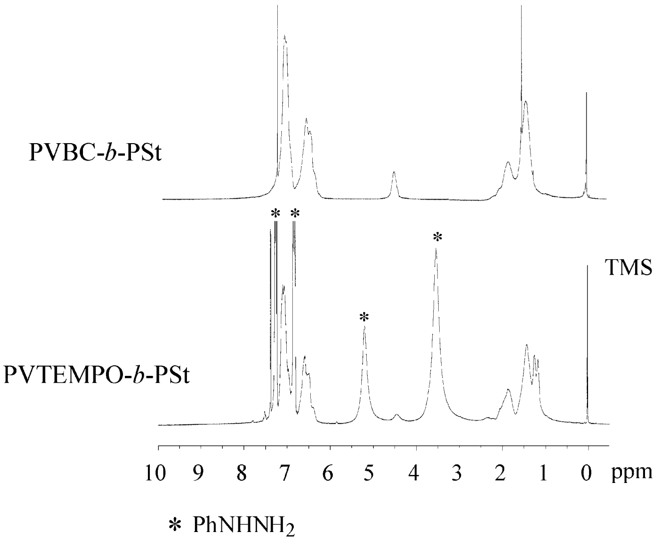


Fig. 3 ^{1}H-NMR spectra of PVBC-*b*-PSt and PVTEMPO-*b*-PSt in the presence of $PhNHNH_2$. Solvent, $CDCl_3$

tetramethyl protons of the TEMPO. The signal for the benzyl attached to the TEMPO is discerned at 4.2–4.7 ppm. The degree of introduction of the TEMPO was estimated based on the intensity ratio of the signals at 1.18 and 1.26 ppm relative to that at 4.2–4.8 ppm because the benzyl protons attached to the chloride of the PVBC-*b*-PSt copolymer are also observed in this range. It was found that the TEMPO was quantitatively introduced to the polymer. The absolute molecular weight of the PVTEMPO-*b*-PSt copolymer was determined to be Mn(PVTEMPO-*b*-PSt) = 31,200-*b*-49,400 based on that of PVBC-*b*-PSt. The Mn and Mw/Mn of PVTEMPO-*b*-PSt by SEC were 58,000 and 1.88, respectively.

The PVTEMPO-*b*-PSt diblock copolymer showed no self-assembly in carbon tetrachloride, a nonselective solvent. Dynamic light scattering demonstrated that the copolymer self-assembled into micelles when chlorine gas was added to the copolymer solution. An excess of chlorine (1.94 eq relative to the TEMPO) was added to complete the reaction with the TEMPO when it was taken into consideration that part of the chlorine gas would escape. The hydrodynamic diameter (D_H) of the micelles was estimated to be 49.5 nm by cumulant analysis, whereas the D_H of the isolated copolymer was 15.6 nm. Figure 4 shows the scattering intensity distribution vs the hydrodynamic diameter of the copolymer before and after the reaction. The scattering intensity distribution was obtained by the Marquadt analysis [36]. The Marquadt method is much better than the cumulant in analyzing the intensity distribution of the hydrodynamic diameter for polymers with comparatively narrow molecular weight distribution. The scattering intensity distribution of the micelles completely took the place of the unimer distribution by the reaction with chlorine.

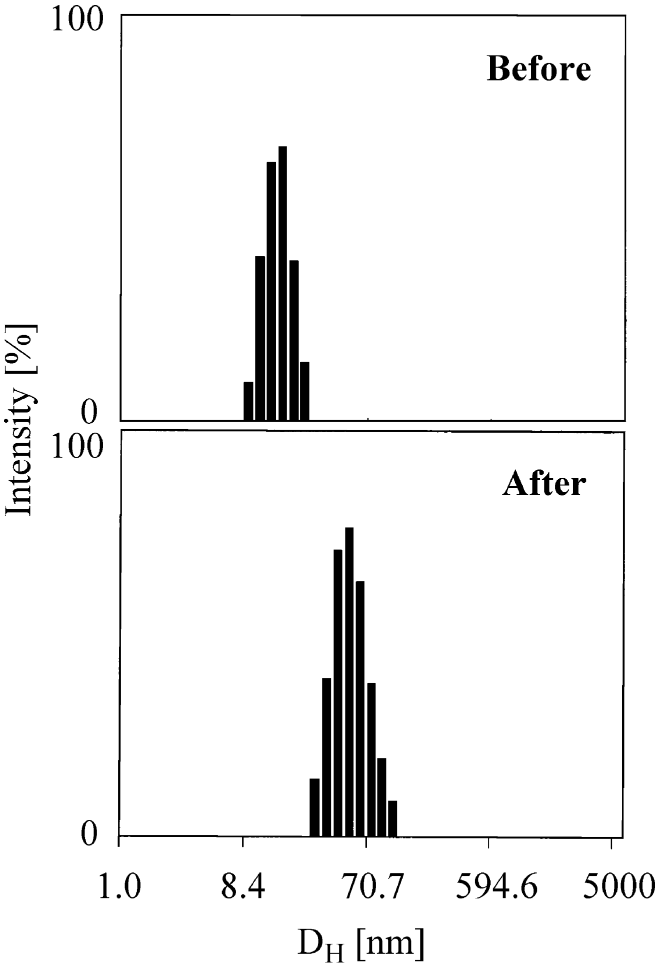


Fig. 4 Scattering intensity distribution of the hydrodynamic diameter before and after the reaction with the chlorine. (PVTEMPO-*b*-PSt)=1.71×10^{-3} g/ml

Electron spin resonance studies verified that the radical concentration of the TEMPO in the copolymer decreased due to the reaction with chlorine. Figure 5 shows the ESR spectra of the copolymer before and after the reaction. Before the reaction with chlorine, a broad signal was observed due to the random orientation probably caused by the restriction of the mobility of the TEMPO supported on the side chains. They should undergo a strong interaction with each other. After the reaction, the broad signal changed to a characteristic triplet attributed to the isotropy along with a decrease in the signal intensity. The *g* values of the radicals before and after the reaction were 2.0066 and 2.0064, respectively. This negligible difference in the *g* values indicates that they are identical radicals originating from the TEMPO. The initial concentration of the TEMPO radical was estimated to be 2.30 mM based on the molar ratio of the VTEMPO unit to the St (VTEMPO/St=0.186/0.814). The radical concentration after the reaction with 1.94 eq

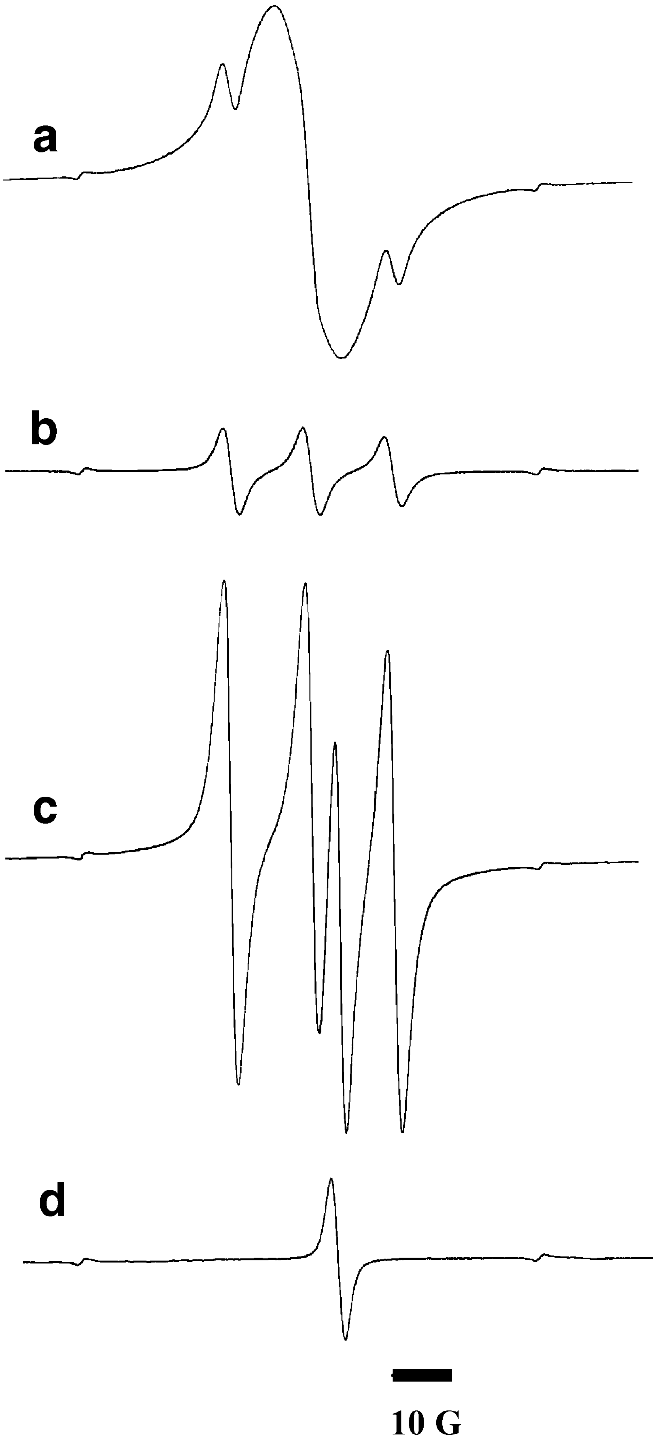


Fig. 5 ESR spectra of PVTEMPO-*b*-PSt in CCl_4 before (**a**) and after (**b**) the reaction with the chlorine, and after the reaction with TMPD (**c**) and of separately prepared Wurster's blue chloride (**d**)

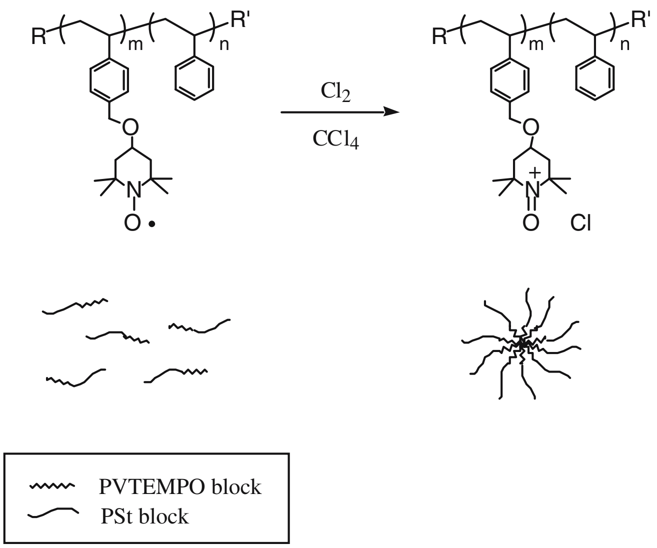


Fig. 6 Micellization of PVTEMPO-*b*-PSt by the chlorine

of chlorine was estimated to be 6.76×10^{-2} mM on the basis of the integral curves obtained from the differential curves of the radicals. Ninety-seven percent of the TEMPO was consumed by 1.94 eq of the chlorine, and only 3% of the TEMPO remained unreacted.

UV analysis revealed that as the TEMPO units were oxidized into the OAC units, the block copolymer became amphiphilic in nature, and thus, the polymers underwent micellization (Fig. 6). Oxoaminium salts are insoluble in carbon tetrachloride; however, in good solvents such as acetonitrile, the salts show absorption at 360 nm. As can be seen in Fig. 7, the absorption at 360 nm increased as a result of increasing the chlorine. The increase in the absorption at 360 nm indicates an increase in the oxoaminium salt. Figure 8 shows the plots of the absorbance at this wavelength, the relative scattering intensity (I/I_0), and the hydrodynamic diameter of the copolymer vs

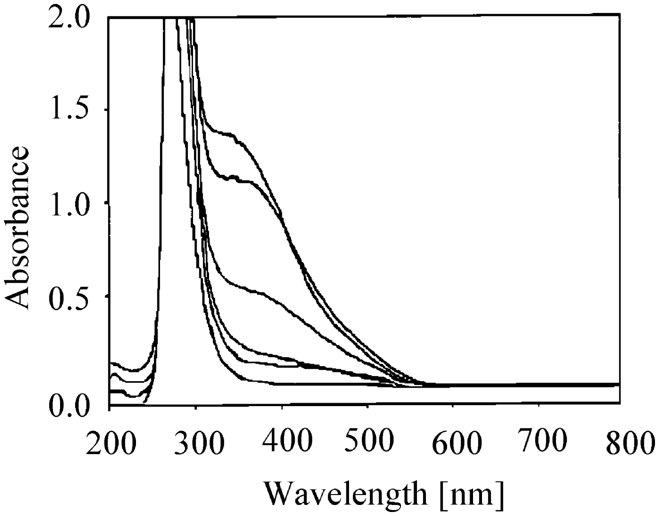


Fig. 7 Variation in the UV absorbance of the PVTEMPO-*b*-PSt copolymer during the micellization. The chlorine to the VTEMPO unit was 0, 0.13, 0.28, 0.58, 1.11, and 1.94 eq from the bottom

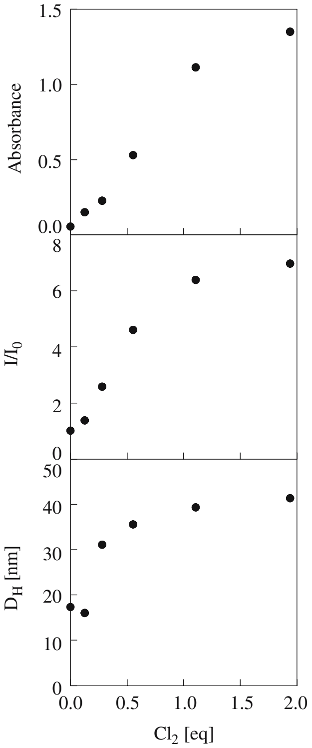


Fig. 8 The variation in UV absorbance at 360 nm, relative scattering intensity (I/I_0), and hydrodynamic diameter (D_H) of PVTEMPO-*b*-PSt vs amount of the chlorine

the amount of chlorine. The absorbance increased with an increase in the amount of chlorine, whereas the scattering intensity and hydrodynamic diameter remained almost constant over 1.11 eq of chlorine. It was assumed that no reaction except for the oxidation of the TEMPO by chlorine to the OAC occurred, and the degrees of oxidation of the TEMPO to the OAC were estimated at each amount of chlorine. The oxidation degrees were determined based on the UV absorbance and the conversion at 1.94 eq by the ESR analysis. Figure 9 shows the variation in the scattering intensity and hydrodynamic diameter of the copolymer vs the oxidation degree. The hydrodynamic diameter rapidly increased at a 16% oxidation degree. Only 16% of the OAC induced the micellization. The scattering intensity also rapidly increased at the 16% oxidation degree; however, it increased almost proportionally with an increase in the oxidation degree. The continuous increase in the scattering intensity over 16% should be based on increases in the aggregation number or the number of micelles. This consequence was supported by the results for the dependence of the scattering intensity on the copolymer concentration. Figure 10 shows the plots of the scattering intensity and hydrodynamic diameter of the micelles vs the copolymer concentration. Whereas the micellar size was almost independent of the copolymer concentration, the scattering intensity increased with increasing copolymer concentration. The number of micelles increased as a result of increasing copolymer concentration, causing an increase in the scattering intensity.

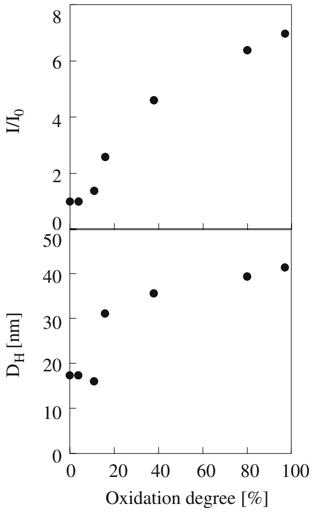


Fig. 9 The plots of relative scattering intensity and hydrodynamic diameter of PVTEMPO-*b*-PSt vs the degree of oxidation

Transmission electron microscopy observations confirmed that the POAC-*b*-PSt copolymer self-assembled into spherical micelles (Fig. 11). The size of the micelles was almost equal to that estimated by the dynamic light scattering. In common cases, some micelles show a smaller size in the TEM image than in light scattering due to swelling of the micelles in solution. The POAC-*b*-PSt micelles may have difficulty swelling in carbon tetrachloride because the micelles have the salts with low affinity for the solvent in the micellar cores, resulting in a slight difference in micellar size between that in light scattering and that in TEM.

The POAC-*b*-PSt copolymer did not seem to be very thermally stable because the orange color of the OAC gradually faded out over room temperature, although the micellar structure was maintained even after the color disappeared. However, below 0 °C, the micellar solution retained the orange color for several hours.

The micelles served as an oxidizing agent for converting benzyl alcohol into benzaldehyde. When 1 eq of benzyl

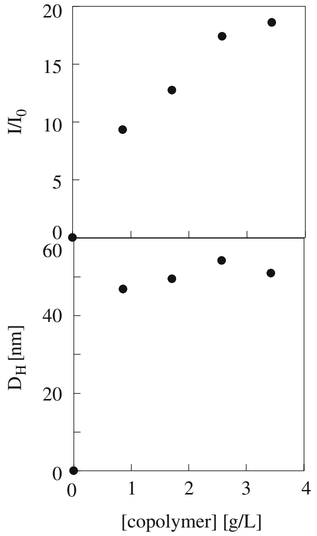


Fig. 10 The plots of the relative scattering intensity and hydrodynamic diameter of PVTEMPO-*b*-PSt vs copolymer concentration

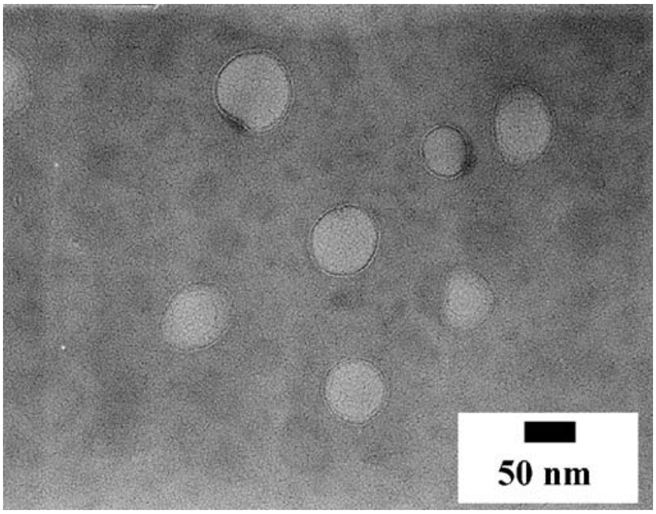


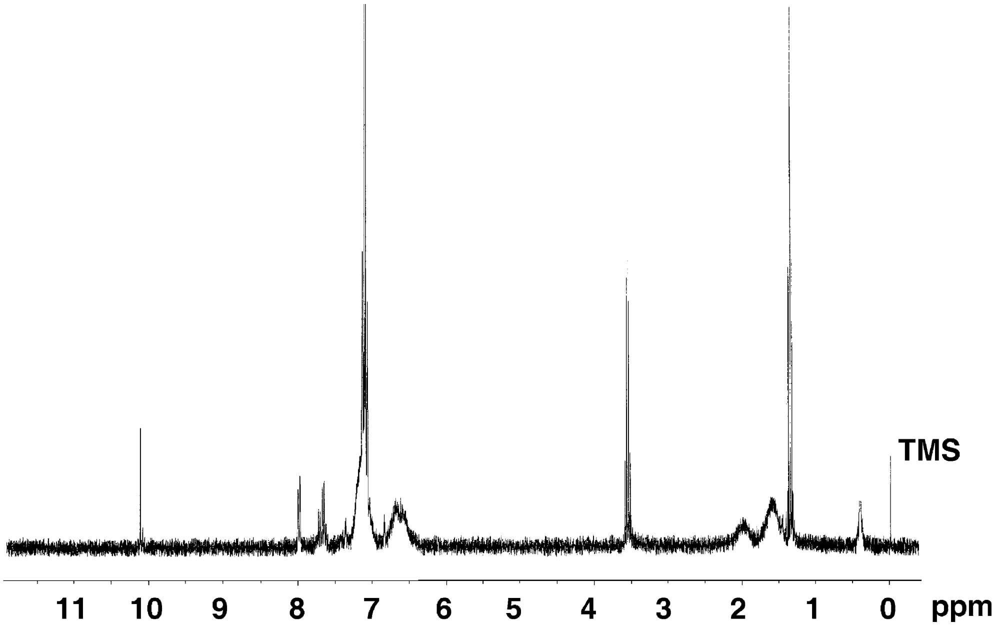
Fig. 11 A TEM image of the POAC-*b*-PSt micelles

alcohol relative to the VTEMPO unit was added to the POAC-*b*-PSt micellar solution in carbon tetrachloride, the orange solution became colorless. ^{1}H-NMR demonstrated the quantitative formation of benzaldehyde. Figure 12 shows the ^{1}H-NMR spectrum of the reaction mixture. Signals originating from benzaldehyde are observed at 7.72, 8.00, and 10.13 ppm. The signals at 1.30 and 3.54 ppm are attributed to diethyl ether added as a standard to estimate the conversion into benzaldehyde. The conversions were determined from the ratio of the signal intensity at 10.13 ppm to that at 3.54 ppm, with the results after 20 and 45 min being 91 and 97%, respectively. The 97% conversion of benzyl alcohol into benzaldehyde confirms that the VTEMPO units were almost quantitatively converted to the OAC by the chlorine. The signals based on the blocks containing the pendant groups were not observed even after the oxidation of benzyl alcohol, indicating that the copolymer maintains the micellar structure after the reaction. The light scattering revealed that no changes occurred in the micellar size and in the relative scattering intensity after the reaction. The OAC served as a two-electron oxidizing agent for benzyl alcohol, converting to the insoluble hydroxylamine–hydrochloride salt. Consequently, no dissociation of the micelles occurred due to the oxidation. It can be deduced that the micelles oxidized benzyl alcohol in the cores and released soluble benzaldehyde from the cores maintaining the micellar structure (Fig. 13).

The POAC-*b*-PSt micelles also oxidized TMPD to produce Wurster's blue chloride. As 1 eq of TMPD relative to the VTEMPO unit was added to the micellar solution prepared by 1.94 eq of chlorine, the solution with orange-colored micelles immediately turned purple. Figure 14 shows the UV spectrum of the micellar solution after the reaction. The characteristic absorption of Wurster's blue [37] was confirmed at 536, 574, and 624 nm. It was suggested that the Wurster's blue chloride was generated in the micellar cores by a one-electron transfer from TMPD to the OAC because the insoluble Wurster's blue chloride was dissolved into carbon tetrachloride.

The one-electron transfer mechanism from TMPD to the oxoaminium salt was supported by the ESR analysis. As can be seen in Fig. 5c, the signal intensity of the TEMPO increased due to the reaction with TMPD. The *g* value of the signal was 2.0063, showing good agreement with that before the reaction (g=2.0064). In the triplet signal, another sharp signal was discerned. This singlet signal had a *g* value of 2.0034. We separately prepared Wurster's

Fig. 12 A ^{1}H-NMR spectrum of the POAC-*b*-PSt micelles after the reaction with benzyl alcohol. Solvent, CCl_4 with benzene-d_6 as the lock solvent and diethyl ether as the standard to estimate the conversion



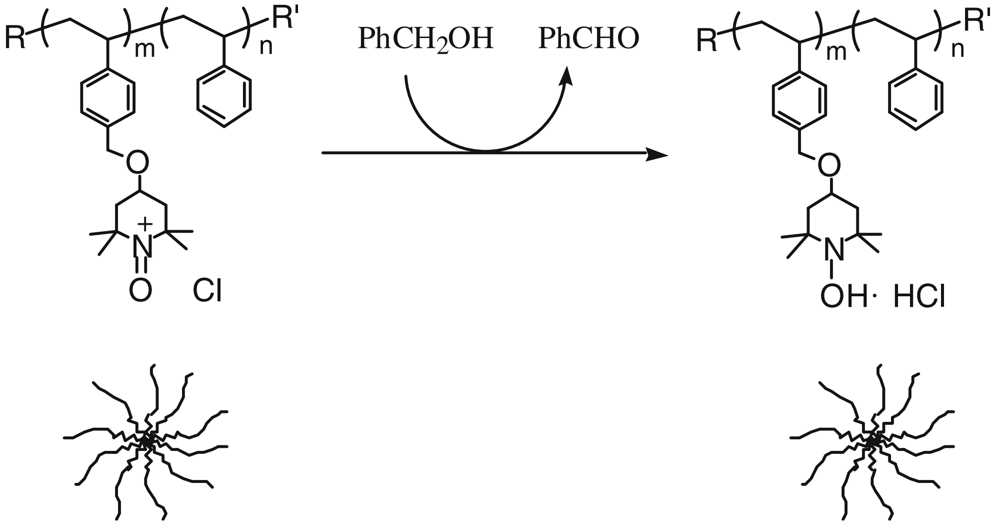


Fig. 13 Oxidation of benzyl alcohol into benzaldehyde by the POAC-*b*-PSt micelles

blue chloride in carbon tetrachloride by the reaction of TMPD with chlorine. Wurster's blue chloride was obtained as an insoluble black precipitate by the direct oxidation of TMPD by chlorine in carbon tetrachloride; however, the radical salt was unstable by itself and was rapidly decomposed, thus losing its radical nature. Figure 5d shows the ESR spectrum of Wurster's blue chloride. Wurster's blue chloride alone showed a singlet signal with g=2.0034 in carbon tetrachloride. The identification of g values verified that Wurster's blue chloride was produced from the reaction of TMPD and the POAC-*b*-PSt micelles and was solubilized within the micellar cores.

The Marquadt analysis also revealed that the POAC-*b*-PSt micelles were dissociated into the PVTEMPO-*b*-PSt copolymer by the reaction with TMPD. Figure 15 shows three different distributions of the hydrodynamic diameter of the copolymer: the scattering intensity distribution, weight exchange distribution, and number exchange distribution. The scattering intensity distribution showed the formation of huge particles over 500 nm in addition to particles with a size similar to that of the POAC-*b*-PSt micelles. The huge particles should be attributed to the insoluble Wurster's blue dropped from the micelles because the resulting solution gradually became a white suspension, thus losing the purple color. However, there were not many huge particles because the distribution of the huge particles was not seen in the weight exchange

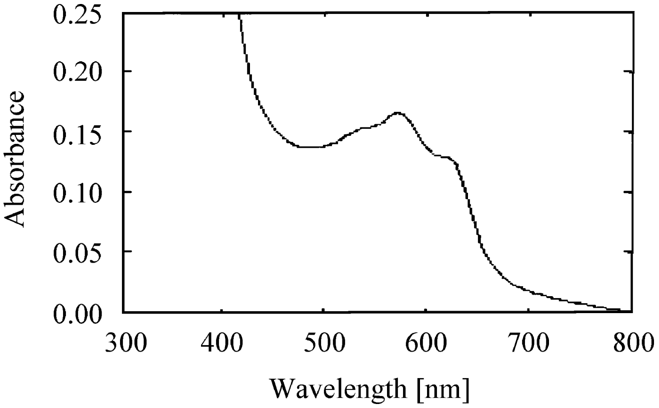


Fig. 14 The UV spectrum of Wurster's blue chloride produced through the oxidation of TMPD by the POAC-*b*-PSt micelles

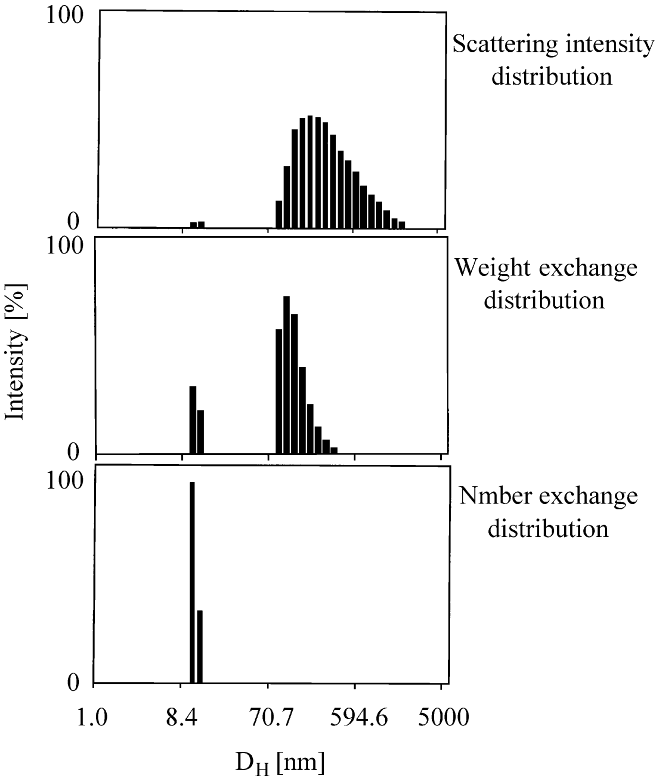


Fig. 15 Scattering intensity distribution, weight exchange distribution, and number exchange distribution of the hydrodynamic diameter of the copolymer after the reaction with TMPD

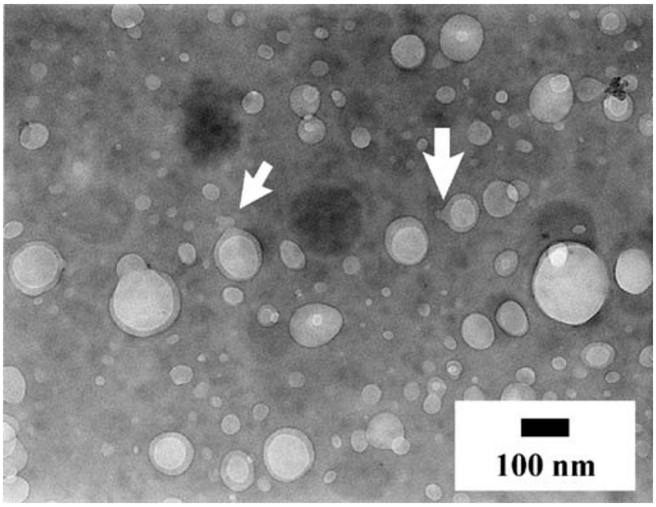


Fig. 16 A TEM image of the POAC-*b*-PSt copolymer after the reaction with TMPD

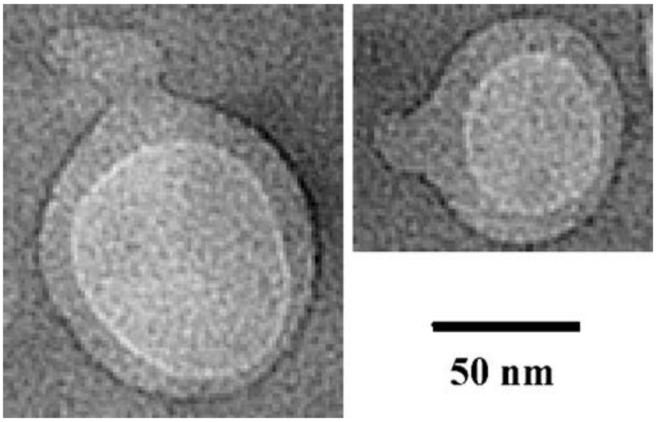


Fig. 17 Transmission electron microscopy images of PVTEMPO-*b*-PSt separating from the micelles

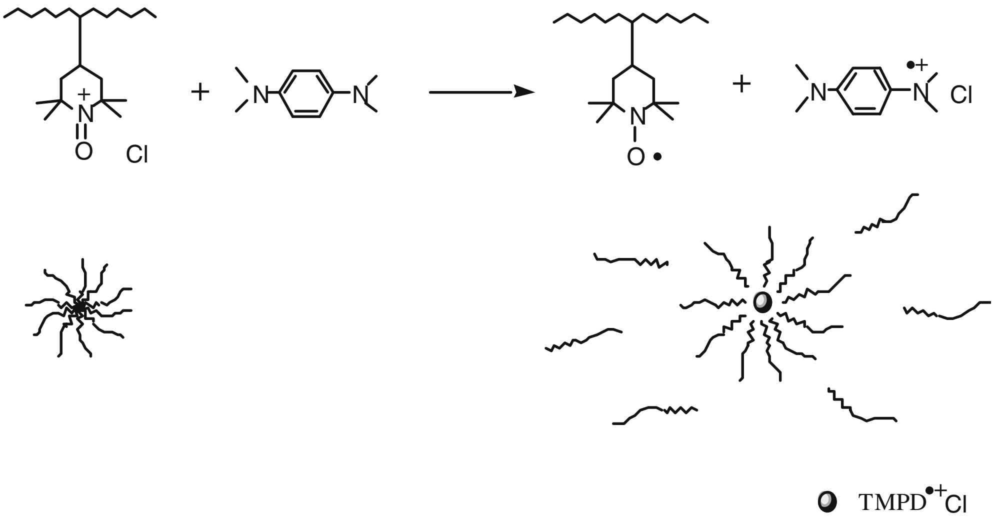
distribution. On the other hand, the unimer distribution slightly discerned in the scattering intensity distribution was clearly observed in the weight exchange distribution. The number exchange distribution showed only the unimer distribution, suggesting that most of the micelles were dissociated into unimers by the reaction with TMPD.

Transmission electron microscopy observations showed that the POAC-*b*-PSt micelles reverted into PVTEMPO-*b*-PSt unimers. Figure 16 shows a TEM image of the copolymer after the reaction with TMPD. It is observed that larger particles with cores and smaller particles almost without cores coexist. The larger particles were expected to originate from the micelles, including Wurster's blue. The larger particles are still bigger than the POAC-*b*-PSt micelles and have a somewhat distorted shape compared with the micelles. The distortion of the shape should be caused by the copolymer associating through a weak force. This weak association of the copolymer is also reflected in the fact that Wurster's blue chloride gradually dropped out of the micelles. The many small particles were considered to be the isolated copolymers because the average size of the particles was 17.0 nm, almost the same size as the unimer determined by light scattering. Furthermore, unimers separating from the large particles were also observed (Fig. 17). It was deduced that the POAC-*b*-PSt micelles oxidized TMPD to the Wurster's blue chloride, reverting into the PVTEMPO-*b*-PSt copolymers (Fig. 18). Most of the copolymers reverted into the isolated copolymers, whereas some of them still surrounded the Wurster's blue particles to solubilize them.

Conclusions

We found the oxidation-induced self-assembly of the TEMPO-containing diblock copolymer into micelles using the redox system of the TEMPO. As the TEMPO units

Fig. 18 The reaction of TMPD and the POAC-*b*-PSt micelles



were oxidized into OAC units, the nonamphiphilic block copolymer became amphiphilic in nature, and thus, the polymers underwent micellization. The POAC-*b*-PSt micelles were spherical in shape. The micelles served as a two-electron oxidizing agent for benzyl alcohol to quantitatively give benzaldehyde. The micellar structure was maintained after the oxidation of benzyl alcohol without any dissociation into unimers because the OAC units were converted into the insoluble hydroxylamine–hydrochloride salt units. The micelles also reacted with TMPD to produce Wurster's blue chloride by a one-electron transfer mechanism. While some micelles solubilized the insoluble Wurster's blue in the cores by a weak aggregation force, most of the micelles reverted into the PVTEMPO-*b*-PSt unimers.

This is the first attempt in demonstrating that the micellization and dissociation of the block copolymer were controlled by the redox reactions of the pendant groups in the diblock copolymer. The concept in this study can be applied to a great variety of reactions to induce the micellization of block copolymers. The reactions include substitution, condensation, addition, rearrangement, polymerization, degradation, and so on. Furthermore, this concept for the micelle formation will provide macromolecular micelles with new ways for their applications and technologies.

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