Synthesis of Shell Cross-Linked Block Copolymer Micelles with Poly(*p*-styrenesulfonic acid) in the Micelle Core

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ABSTRACT: Fine particles having poly(*p*-styrenesulfonic acid) (polySS) in the core and a polystyrene (polySt) shell were synthesized by cross-linking and successive chemical transformation of triblock copolymer micelles. A triblock copolymer, polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySSPen, was synthesized by nitroxide-mediated living radical polymerization, where SBS and SSPen denote *p*-(1-methylsilacyclobutyl)-styrene and neopentyl *p*-styrensulfonate, respectively. Block copolymer micelles carrying a polySSPen core and polySt shell with cross-linkable silacyclobutyl groups in the shell were prepared by dissolving the triblock copolymer in cyclohexane. Cross-linking of the shell by Pt-catalyzed ring-opening of silacyclobutane followed by thermolysis of the neopentyl esters in polySSPen in tetralin in the presence of *p*-toluenesulfonic acid gave the cross-linked micellar particles with polySS in the micelle core. The obtained particles showed unique environmentally responsive solubility due to the core−shell structure with a moderately cross-linked shell.

Introduction

Sulfonic-acid-containing polymers have attracted much attention in industrial applications such as ion-exchange resins,[1] membrane separation,[2] and membranes for polymer electrolyte fuel cells (PEFC)[3−10] due to their high ionic dissociation and proton conductivity. In addition, these polymers are attractive from more academic and fundamental point of views, concerning their unique physicochemical properties derived from complex electrostatic interactions between the ionized groups in the presence of surrounding small counterions, which usual nonionic polymers do not possess.[11] We have been studying the properties of amphiphilic block copolymers containing sulfonic acid and found that they show anomalous self-assembling behavior such as micelle formation without absorption at the water surface[12−14] and carpet/brush double-layer formation in the monolayer at the air/water interface.[15]

On the other hand, it is becoming more and more important to control the micro- and/or nanostructure of polymeric materials in order to achieve high performance and special functionality. The aim of this study is to create novel functional materials by controlling the nanostructure of the polymeric materials having strong ionic segments.

Synthesis of well-defined polymers with sulfonic acid groups is not an easy task by ionic polymerization because the sulfonic groups are usually intolerant to conventional ionic polymerization conditions or because harsh reaction conditions are normally required in the introduction of sulfonic groups to precursor polymers after polymerization. However, recent development of radical polymerization techniques has enabled researchers to synthesize polymers with various functional groups in a well-controlled manner.[16−18] Okamura and co-workers reported an efficient method to prepare a block copolymer bearing poly(*p*-styrenesulfonic acid) (polySS) segment by nitroxy-mediated living radical polymerization of styrene (St) and neopentyl *p*-styrenesulfonate (SSPen) with successive chemical transformation of polySSPen to sodium poly(*p*-styrenesulfonate) (polySSNa).[19] Previously, we applied this technique to synthesize nanoparticles having a polySSNa hairy shell by core cross-linking and hydrolysis of block copolymer micelles having a polySSPen segment[20] and developed a cross-linkable monomer, *p*-(1-methylsilacyclobutyl)styrene (SBS), to cross-link the micelle under mild conditions. A vinyl group of SBS can be polymerized in a living fashion by nitroxy-mediated radical polymerization, leaving the four-membered silacyclobutyl group intact, while the silacyclobutyl moiety can readily be polymerized by platinum catalyst after the vinyl polymerization. The polySSNa-grafted particles thus synthesized show high dispersion stability in salted water due to the electrostatic and steric repulsion between grafted polyelectrolyte chains.

Shell cross-linked micelles,[21−23] first reported by Wooley and co-workers, are expected as novel nanoparticles useful for various applications such as solubilization, catalysis, fillers, coatings, delivery, and controlled release. Furthermore, Liu et al. and Armes et al. independently developed a more efficient method to prepare shell cross-linked micelles, by cross-linking the central segment of triblock copolymers in their micelles.[24−30]

In the present study, we synthesized a triblock copolymer, polySt-*b*-poly(St-*co*-SBS)-*b*-polySSPen, which have a cross-linkable central segment composed of St and SBS random copolymer. Then we prepared micelles having a polySSPen core and a polySt shell with cross-linkable silacyclobutane groups in the shell. Cross-linking of the shell in the micelle and thermolysis of sulfonic ester group provided nanoparticles, having an electrolyte polySS core (Figure 1). To describe the cross-linked particle here, we use a term “shell cross-linked micelle”. The shell cross-linked micelle showed switchable solubility, which was drastically altered according to the nature of a solvent to which the particle was exposed. This environmentally responsive property is analogous to the surface property changes already

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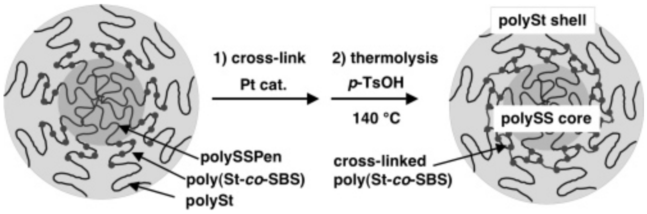


Figure 1. Schematic illustration of this work.

reported in some block copolymer or mixed homopolymer brushes on solid surfaces.[31−34]

Experimental Section

Materials. *p*-(1-Methylsilacyclobutyl)styrene (SBS),[20] neopentyl *p*-styrenesulfonate (SSPen),[19] and *N*-*tert*-butyl-1-diethylphosphono-2,2-dimethylnitroxyl radical (DEPN)[35] were prepared as reported. Benzene was freshly distilled over sodium benzophenone ketyl in argon before use. Azobis(isobutyronitrile) (AIBN) from Nacalai Tesque (Kyoto, Japan), the platinum(0)−1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylenes from Aldrich (Milwaukee, WI), *p*-toluenesulfonic acid (*p*-TsOH) monohydrate, toluene, cyclohexane, 1,4-dioxane, and tetralin (1,2,3,4-tetrahydronaphthalene) from Wako Pure Chemicals Industry (Osaka, Japan) were purchased and used as delivered. Styrene (St) was washed three times with 1 M $NaOH_{aq}$ and three times with H_2O. Then it was distilled twice over CaH_2 under reduced pressure.

Synthesis of PolySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySSPen. DEPN-capped polySt was prepared as follows. A mixture of AIBN (32.3 mg, 0.197 mmol), St (4.01 g, 38.5 mmol), and DEPN (130 mg, 0.443 mmol) was charged in a glass tube reactor equipped with a Teflon screw cock and a magnetic stirring bar, degassed by three freeze−thaw cycles, and sealed under argon. The mixture was kept at 110 °C for 2 h. After the polymerization a portion of the resulting mixture was taken for ^{1}H NMR measurement to check the monomer conversion (46% St conversion). Precipitation with toluene/methanol system (three times), followed by freeze-drying in 1,4-dioxane, gave 1.68 g of DEPN-capped polySt. $M_n = 4500$, $M_w/M_n = 1.07$ (determined by GPC relative to polystyrene standard).

The diblock copolymer, DEPN-capped polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$), was synthesized as follows. A mixture of the above-prepared DEPN-capped polySt ($M_n = 4500$, $M_w/M_n = 1.07$, 1.20 g), St (2.23 g, 21.4 mmol), SBS (1.01 g, 5.39 mmol), DEPN (39.5 mg, 0.134 mmol), and benzene (3 mL) was charged in a glass tube reactor equipped with a Teflon screw cock and a magnetic stirring bar, degassed by three freeze−thaw cycles, and sealed under argon. The mixture was kept at 120 °C for 50 min. After the polymerization a portion of the resulting mixture was taken for ^{1}H NMR measurement to check the monomer conversion (32% monomer conversion). Precipitation with toluene/methanol system (three times), followed by freeze-drying in 1,4-dioxane, gave 1.82 g of DEPN-capped polySt-*b*-($St_{0.8}$-*co*-$SBS_{0.2}$). $M_n = 7900$, $M_w/M_n = 1.11$ (determined by GPC relative to polystyrene standard).

The triblock copolymer, polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySSPen, was synthesized as follows. A mixture of the above-prepared DEPN-capped polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$) (M_n = 7900, $M_w/M_n = 1.11$, 1.70 g), SSPen (4.97 g, 19.5 mmol), DEPN (14.9 mg, 0.0507 mmol), and benzene (12.0 mL) was charged in a glass tube reactor equipped with a Teflon screw cock and a magnetic stirring bar, degassed by three freeze−thaw cycles, and sealed under argon. The mixture was kept at 115 °C for 45 min. After the polymerization a portion of the resulting mixture was taken for ^{1}H NMR measurement to check the monomer conversion (42% SSPen conversion). Precipitation with the toluene/methanol system (three times), followed by freeze-drying in 1,4-dioxane, gave 3.68 g of polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySSPen. M_n = 15 200, M_w/M_n = 1.23 (determined by GPC relative to polystyrene standard).

Cross-Linking of the Triblock Copolymer Micelle. The above-prepared polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySSPen (0.50 g) was dissolved in 2.0 g of toluene. Then 14.2 g of cyclohexane was slowly added to the copolymer solution. Thus, the prepared block copolymer micelle solution was charged in a two-necked 100 mL round-bottomed flask equipped with a three-way stopcock, rubber balloon, a stirring bar, and a rubber septum in an argon atmosphere. Then 0.1 mL of xylene solution of platinum(0)−1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst was added, and the mixture was stirred for 3 h. The resulting mixture was poured in methanol, and the precipitate was collected by filtration and dried in vacuo. By these procedures, we obtained shell cross-linked polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySSPen micelle (0.50 g).

Thermolysis of Sulfonic Esters in the Cross-Linked Micelle. The above-prepared shell cross-linked polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySSPen micelle (50 mg) and *p*-TsOH (3 mg) were dissolved in Tetralin (5 mL). The mixture was stirred for 6 h at 140 °C. The resulting mixture was cooled to room temperature and poured in excess hexane. Precipitated products were collected by filtration and dried in vacuo to give the thermolysis product, shell cross-linked polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySS micelle (40 mg).

Measurement. Gel permeation chromatography (GPC) was carried out in THF on a JASCO PU-980 chromatograph (JASCO Engineering, Tokyo, Japan) equipped with two polystyrene gel columns (Shodex KF804L; separation range in molecular weight of polystyrene: $100-4 \times 10^5$) and JASCO RI-930 refractive index detector. The average molecular weight and molecular weight distributions of samples were evaluated relative to polystyrene standards. Proton NMR spectra were recorded with a JEOL AL-400 spectrometer in $CDCl_3$ or D_2O. IR spectra were measured with a Shimadzu FTIR-8400 spectrometer equipped with a total reflection attachment MIRacle (Ge prism). The dynamic light scattering (DLS) was measured on an Otsuka Photal SLS-6000HL equipped with a correlator (Photal GC-1000) and He−Ne laser (wavelength, 632.8 nm). The measurements were performed at 20 °C. The time correlation functions were analyzed by cumulant or double-exponential fitting. The measurements were performed at scattering angles of 60°, 75°, 90°, and 105°. The diffusion coefficient was calculated from the slope of the straight line in the decay rate Γ vs q^2 plot, where q is the scattering vector. Atomic force microscopy (AFM) measurements were performed by Seiko SPI3800 probe station and SPA300 unit system of scanning probe microscopy system SPI3900 series using a dynamic force mode (noncontact mode). The micro-cantilever (SI-DF-A, Seiko) was made of silicon, and its spring constant was 2 N/m. For sample preparation, the 1,4-dioxane solution of polymer particle was dropped on a micro-slide glass (IWAKI, Japan) and air-dried. Thermal gravimetric analysis (TGA) was performed on a Mac Science TG-DTA 2000S using an aluminum pan under N_2 flow of 50 mL/min at a heating rate of 2 °C/min. Titration of a polymer aqueous solution was performed with 0.05 mol/L $NaOH_{aq}$ with monitoring the electric conductivity by HORIBA conductivity meter DS-8M.

Results and Discussion

Synthesis of the Triblock Copolymer. The triblock copolymer, polySt-*b*-poly(St-*co*-SBS)-*b*-polySSPen, was synthesized by a three-step DEPN-mediated living radical polymerization,[36,37] as shown in Scheme 1. The first polymer, DEPN-capped polySt ($M_n = 4500$, $M_w/M_n = 1.07$), was prepared using AIBN as an initiator and DEPN as a radical mediator. Then the second polymer, DEPN-capped polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$) ($M_n = 7900$, $M_w/M_n = 1.11$), was prepared by random copolymerization of a mixture of St and SBS (initial molar ratio of [St]/[SBS] = 4/1) using the above-prepared DEPN-capped polySt as a macroinitiator. The desired triblock copolymer was finally obtained by radical polymerization of SSPen using the DEPN-capped polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$) as a macroinitiator again. ^{1}H NMR

Scheme 1

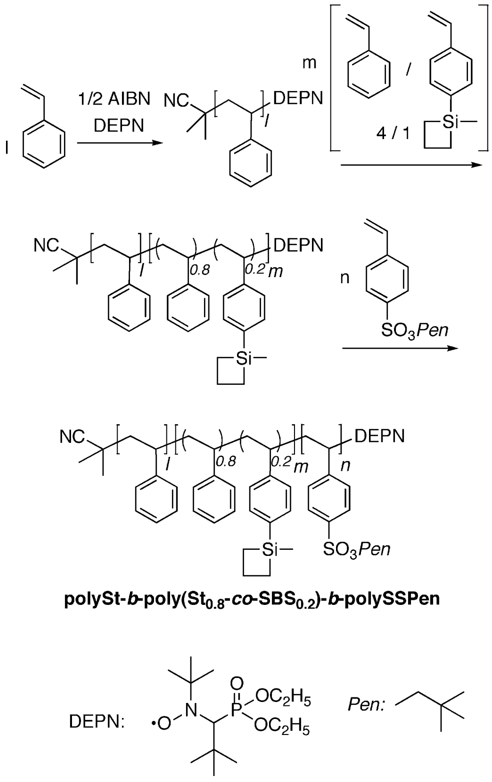


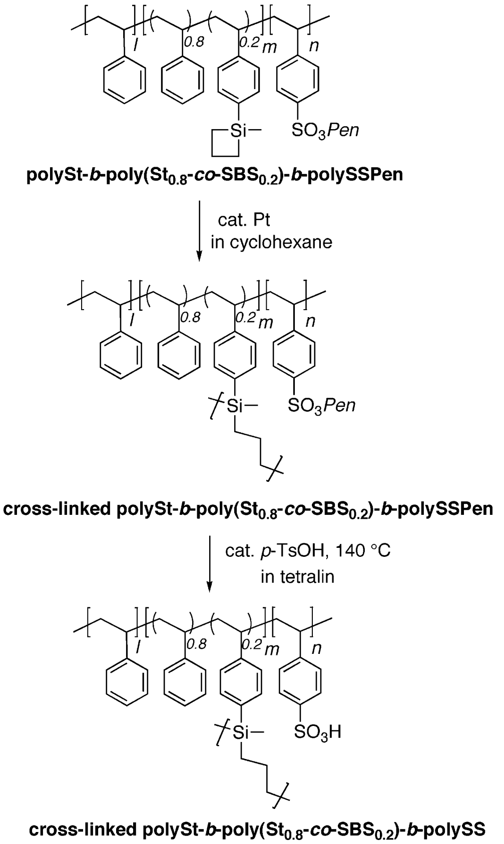
Table 1. Characteristics of the Polymers Synthesized in This Study[a]

polymer	l	m	n	x	M_n	M_w/M_n
St_l	43				4500	1.07
St_l-b-$(St_{1-x}$-co-$SBS_x)_m$	43	28		0.20	7900	1.11
St_l-b-$(St_{1-x}$-co-$SBS_x)_m$-b-$SSPen_n$	43	28	29	0.20	15200	1.23

[a] l = polymerization degree of polySt segment; m = polymerization degree of poly(St_{1-x}-*co*-SBS_x) segment; n = polymerization degree of polySSPen segment; x = mole fraction of SBS unit in the poly(St-*co*-SBS) segment; l, m, n, M_n, and M_w were determined by GPC relative to polySt standards; x was determined by ^{1}H NMR.

signal at 0.5 ppm of a methyl group at the 1-position and a signal at 2.3 ppm of a methylene group at the 3-position of the silacyclobutyl group clearly indicated that SBS was incorporated into the polymer chain, leaving the four-membered silacyclobutane ring completely unchanged.[38] GPC curves of the obtained polymers in each step clearly shifted to the higher molecular weight region, keeping narrow molecular weight distributions in both second and third polymerization steps, indicating the formation of the block copolymers.[39] It should be noted here that the polymerization should be quenched at conversions around 50% or less; otherwise, polymers with broader molecular weight distributions were obtained due to the occurrence of bimolecular radical coupling termination. Table 1 summarizes the molecular characteristics of the polymer obtained in each polymerization step. Estimating the polymerization degree of each component from the molecular weight of the copolymer determined by polySt-calibrated GPC measurements, the obtained copolymer can be described as St_{43}-b-$(St_{23}$-co-$SBS_6)$-b-$SSPen_{29}$.

Scheme 2



Block Copolymer Micelle Formation and Its Cross-Linking. A low molecular weight polySt and a poly($St_{0.8}$-b-$SBS_{0.2}$) discussed in this study are soluble in cyclohexane at room temperature, while polySSPen is not soluble in cyclohexane at room temperature. Therefore, it is expected that the triblock copolymer can form micelles in cyclohexane, whose core consists of polySSPen and shell consists of poly($St_{0.8}$-b-$SBS_{0.2}$) and polySt. To prepare block copolymer micelle solutions, the triblock copolymer was first dissolved in a small amount of toluene, which is a good solvent for all the segments, and then added a large amount of cyclohexane dropwise to the polymer solution. This is because the cyclohexane-insoluble polySSPen segment is highly glassy so that the triblock copolymer is not directly soluble in cyclohexane. DLS measurement of the copolymer solution thus prepared indicated the existence of the block copolymer micelles. Analyzing the DLS results by cumulant fitting, the hydrodynamic radius (R_h) of the micelle in cyclohexane was estimated to be 16 nm (p.d. = 0.10). This value seems to be reasonable for the R_h of the block copolymer micelle because it is comparable to the contour length of the St_{43}-b-$(St_{23}$-co-$SBS_6)$-b-$SSPen_{29}$, which is estimated to be 25 nm. Taking both the segment solubility and block copolymer sequence into account, one can consider that the micelle consists of a polySSPen core and a polySt shell having some cross-linkable silacyclobutyl groups in the inner shell without distinct boundary of SBS-containing polySt inner shell and polySt only outer shell (Figure 1).

The poly(St-*co*-SBS) segment was cross-linked by addition of platinum catalyst and stirring for 3 h at room temperature, and the product was purified by precipitation in methanol. The ^{1}H NMR signals at 0.5 and 2.3 ppm typical for silacyclobutyl group completely disappeared in the spectrum of the product,[40] indicating the occurrence of the ring opening of the silacyclobutyl group (Scheme 2). In addition, the DLS double-exponential analysis of the products in 1,4-dioxane, which is a good solvent for all of three segments, indicated the

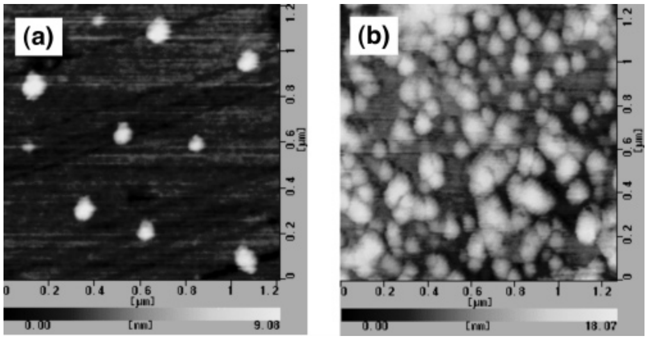


Figure 2. AFM image of (a) shell cross-linked polySt-*b*-poly(St$_{0.8}$-*co*-SBS$_{0.2}$)-*b*-polySSPen and (b) shell cross-linked polySt-*b*-poly(St$_{0.8}$-*co*-SBS$_{0.2}$)-*b*-polySS dried on glass substrate.

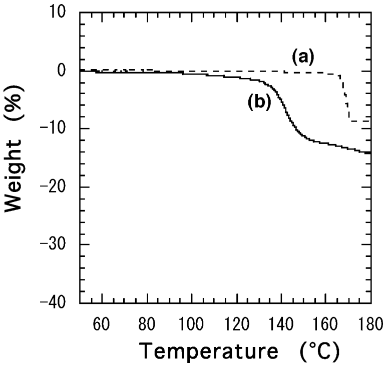


Figure 3. TGA results of (a) shell cross-linked polySt-*b*-poly(St$_{0.8}$-*co*-SBS$_{0.2}$)-*b*-polySSPen and (b) shell cross-linked polySt-*b*-poly(St$_{0.8}$-*co*-SBS$_{0.2}$)-*b*-polySSPen in the presence of 5 wt % *p*-TsOH.

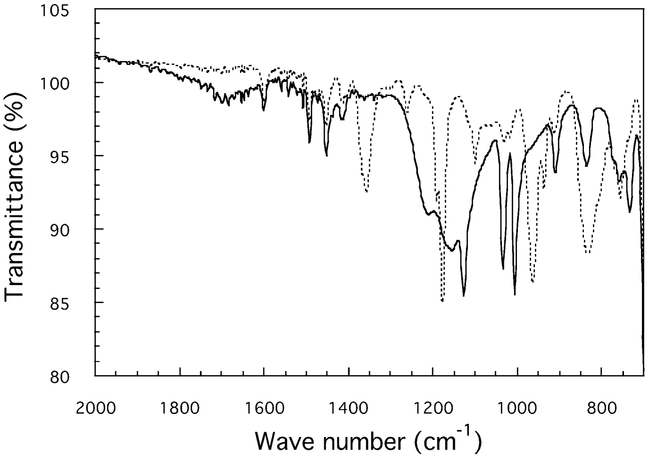


Figure 4. IR spectra of shell cross-linked polySt-*b*-poly(St$_{0.8}$-*co*-SBS$_{0.2}$)-*b*-polySSPen (dotted line) and shell cross-linked polySt-*b*-poly(St$_{0.8}$-*co*-SBS$_{0.2}$)-*b*-polySS (solid line).

existence of particles with R_h of 17 nm (98.7% volume fraction) along with a trace amount of larger aggregate (73 nm, 1.3% volume fraction), which are presumably multimicellar aggregates. The smaller R_h value (17 nm) in 1,4-dioxane is very close to the R_h (16 nm) in cyclohexane before Pt treatment. This indicated that the cross-linking proceeded within one micelle with sufficiently high efficiency so that the cross-linked particles did not swell even in a good solvent for all the segments. Furthermore, spherical objects with diameter of around 80 nm were observed by AFM measurements of the product dried on a glass substrate from a dilute 1,4-dioxane solution (Figure 4a). The shell cross-linked micelles may be somehow flattened when the product was dried on the glass substrate. This might be the reason why the diameters and heights of the particles obtained by AFM were larger and smaller, respectively, than the hydrodynamic dimensions obtained by DLS. However, both DLS and AFM results clearly indicated that cross-linking of the block copolymer micelles proceeded inside the individual micelles to give particles with structures derived from precursor micelles (Figure 1). It should be noted here that the polySt segment is necessary for preparation of fine particles. Exposure of diblock copolymer micelles without polySt segment, micelles of polySSPen-*b*-poly(SBS$_{0.8}$-*co*-SBS$_{0.2}$), to the same reaction conditions resulted in macrogel formation, which was presumably generated through cross-linking between micelles. Thus, the polySt outer shell has an important steric effect to avoid intermicellar cross-linking. A similar effect in the shell cross-linking of micelles has been already reported.[29,30]

Thermolysis of Neopentyl Esters in PolySSPen Segment. Okamura et al. reported that polySSPen can be converted to polySS by thermolysis at 160 °C.[19] We examined the thermolysis of shell cross-linked micelle in bulk by thermogravimetric analsyis. The results are given in Figure 3. Weight loss due to the decomposition of neopentyl esters was observed at 160 °C. The weight loss was about 9 wt %, which is less than the expected value of 13 wt % when the all the SSPen were converted to SS with losing the neopentyl groups. This is because a portion of the neopentyl groups added again to the phenyl ring in the copolymer via Friedel−Crafts type reactions as Okamura et al. suggested.[19] The sharp weight loss at 160 °C is due to the sulfonic acid generated by the thermolysis self-catalyzing the reaction.[19] Therefore, the thermolysis by TGA was reexamined using sample containing a small amount of *p*-toluenesulfonic acid (*p*-TsOH), which was prepared by addition of *p*-TsOH to the 1,4-dioxane solution of shell cross-linked micelle and freeze-dried. Addition of *p*-TsOH reduced the decomposition temperature to 130 °C. This catalytic reaction enables the thermolysis to occur under milder conditions not only in bulk but also in solution (Scheme 2). In the absence of *p*-TsOH, it was necessary to heat the shell cross-linked micelle solution above 160 °C to convert the sulfonate ester groups to sulfonic acids in tetralin, and the products were colored dark brown, which indicated the occurrence of undesired side reactions. On the other hand, we could completely convert the ester groups to acid forms by heating the tetralin solution at 140 °C for 6 h in the presence of a catalytic amount of *p*-TsOH. Precipitation of the resulting mixture in excess hexane gave colorless thermolyzed products. Figure 4 depicts the FTIR spectra of cross-linked micelles before and after the thermolysis. The absorption at 964 cm^{-1} assigned to S−O−C stretching and 1357 cm^{-1} assigned to S═O stretching of sulfonate ester disappeared after heating, and absorption at 1007 and 1034 cm^{-1} assigned to S−OH stretching and 1153 cm^{-1} assigned to S═O stretching of sulfonic acid appeared.

By DLS analysis of the thermolized product in 1,4-dioxane, which is a good solvent for all the segments, we estimated the R_h of the particles to be 15 nm (cumulant fitting, p.d. = 0.027), which is in agreement with the R_h value of the shell cross-linked micelles before thermolysis. This means that cross-linking networks in the shell were not cleaved, and the micelle structure was maintained during the thermal treat-

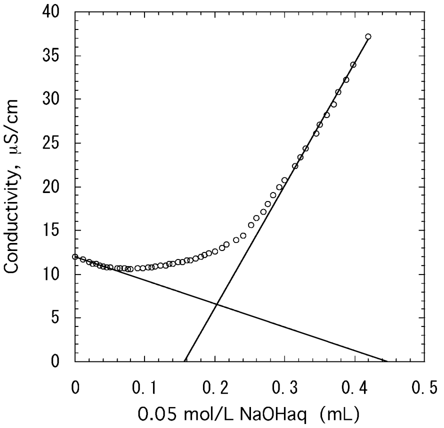


Figure 5. Titration curve of shell cross-linked polySt-*b*-poly-($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySS in water with 0.05 mol/L aqueous NaOH.

ment. Figure 2b shows the AFM images of the thermolyzed product dried on glass substrate from a dilute 1,4-dioxane solution. Many spherical particles with a diameter of around 80 nm and height of less than 15 nm were observed, which indicated again that the particles were flattened on the glass substrate. These observations clearly show that spherical particles of shell cross-linked polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySS were obtained.

Properties of Cross-Linked PolySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySS. One of the interesting properties in the particles is their unique solubility. The virgin sample of the shell cross-linked polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySS obtained above is soluble in good solvents for polySt such as THF, 1,4-dioxane, toluene, and chloroform but insoluble in poor solvents for polySt such as methanol and water. However, after the sample was dissolved in 1,4-dioxane and concentrated, they became soluble in toluene, chloroform, THF, 1,4-dioxane, methanol, and even water, both good and poor solvents for polySt. Furthermore, the sample, once dissolved in methanol or water and concentrated, became insoluble in toluene or chloroform. This environmentally responsive solubility may attribute to the polySS existing in the core. In the virgin sample, the particle surface is completely covered with polySt, but after the treatment with 1,4-dioxane, which is a good solvent for both polySt and polySS, a portion of polySS in the core emerges to the surface and the particles become soluble in good solvents for polySS as well as good solvents for polySt. The surface of the sample dissolved in methanol and concentrated may become covered mostly with polySS, and the particles become insoluble in toluene and chloroform, which are good solvents for polySt.

Conductometric titration of the shell cross-linked polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySS aqueous solution was performed by 0.05 mol/L $NaOH_{aq}$. Figure 5 shows the titration curve obtained from 27.0 mg of shell cross-linked polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySS. An interesting feature is that the conductivity once decreased and then slowly increased with the addition of $NaOH_{aq}$, and the end point was indistinct. This is in good contrast to the normal titration curve for linear polySS solutions, in which a very clear titration end point is observed. This is presumably because of the structural restriction of the polySS chains in the shell cross-linked micelles. The intersection of the two tangent lines in the figures should be the end point of the titration, which implied that 17 mol % of sulfonic acid in the cross-linked micelle was titrated.

Finally, the cross-linked polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySS after the treatment with 1,4-dioxane was dissolved in 1 mol/L NaOH aqueous solution, and DLS measurement was carried out. Cumulant analysis of the DLS results indicated that particles of $R_h = 97$ nm (p.d. = 0.17) existed. This R_h value is apparently larger than the contour length of the triblock copolymer (25 nm), suggesting that the shell cross-linked micellar particles may assemble to form multiparticle aggregates in the aqueous media, although they are soluble in water after the treatment with 1,4-dioxane. This aggregation occurred presumably due to a hydrophobic interaction between particles imperfectly covered with polySSNa. On the basis of the above solubility property, titration, and DLS results, we suppose that a portion of the polySS chains in the core escaped to the outside of the cross-linked shell, but most of the polySS was confined to the core of the micelle.

Conclusions

A triblock copolymer with cross-linkable center segment, polySt-*b*-poly(St-*co*-SBS)-*b*-polySSPen, was synthesized by nitroxy-mediated living radical polymerization. The shell of the triblock copolymer micelle formed in cyclohexane was successfully cross-linked by Pt-catalyzed ring-opening of silacyclobutyl moieties. The sulfonate ester groups in the core of the cross-linked micelle were converted to sulfonic acids by acid-catalyzed thermolysis. The obtained particles showed unique environmentally responsive solubility due to the core−shell structure with a moderately cross-linked shell. A small portion of the polySS in the core escaped from the core to the surface of the particle by dissolving in water in the case of this particular sample. However, the mobility of the polySS chain strongly depends on the thickness and cross-linking degree of the intermediate layer. A detailed study on the property of the shell cross-linked micelles is now in progress.

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Supporting Information Available: ^{1}H NMR spectrum of the triblock copolymer, GPC curve for each polymerization step, and ^{1}H NMR spectrum of shell cross-linked polySt-*b*-poly($St_{0.8}$-*co*-$SBS_{0.2}$)-*b*-polySSPen in $CDCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) ^{1}H NMR spectrum of the triblock copolymer is available in the Supporting Information.

(39) GPC curve for each polymerization step is available in the Supporting Information.

(40) ^{1}H NMR spectrum of the cross-linked triblock copolymer is available in the Supporting Information.

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