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Synthesis of sodium-polystyrenesulfonate-grafted nanoparticles by core-cross-linking of block copolymer micelles

Kozo Matsumoto,* Hirohiko Hasegawa and Hideki Matsuoka

Department of Polymer Chemistry, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

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This paper is dedicated to Professor Robert H. Grubbs on the occasion of his receipt of the 2003 Tetrahedron Prize

Abstract—Sodium poly(styrenesulfonate)(polySSNa)-grafted polymer nanoparticles were synthesized by core-cross-linking of block copolymer micelles and subsequent chemical transformation. Block copolymers, poly(*p*-((1-methyl)silacyclobutyl)styrene-*block*-poly(neopentyl *p*-styrenesulfonate)s, polySBS-*b*-polySSPen, were synthesized by nitroxy-mediated living radical polymerization. The block copolymers formed micelles (R_h=15–23 nm, where R_h represents the hydrodynamic radius) with a polySBS core and polySSPen shell in acetone. The micelle core was cross-linked by ring-opening polymerization of silacyclobutyl groups in polySBS. Hydrolysis of the neopentyl groups provided polySSNa-grafted nanoparticles. The R_h of the particles before the hydrolysis ranged from 12 to 21 nm in acetone, while they varied to the range from 50 to 110 nm in water after the hydrolysis.

1. Introduction

Block copolymers self-assemble to form micelles in solvents selective for one of the blocks. The core of the micelle consists of an insoluble block, and the shell, which is often called corona, consists of both a soluble block and the solvent.[1,2] Such micelle formation has attracted much attention for industrial and biomedical applications. Consequently, many block copolymer micelles have been studied not only for use as surfactants such as lubricant, dispersant, and emulsifier, but also as additives in cosmetics or drug carriers for drug delivery systems.[3,4] Compared with the micelles of low molecular weight surfactants, the block copolymer micelles are generally larger, ranging from several nanometers to tens of nanometers. Additionally, they are more stable due to their slow exchange between associated and non-associated molecules (micelle-unimer exchange). These properties are quite advantageous in constructing nano-scale materials. By cross-linking the core of the micelle, we can obtain nanoparticles with shell-forming polymers grafted from the particle surface.[5–20] In this study, we synthesized strong-ionic-polymer-grafted nanoparticles, using a styrene-based block copolymer, in which one segment has cross-linkable silacyclobutyl groups and the other has potentially ionic surfonate ester groups. The precursor block copolymer was prepared by nitroxy-radical-mediated living polymerization, and its micelle was formed in acetone. Then, the core of the micelle was cross-linked by ring-opening polymerization of silacyclobutyl groups, and finally the ester groups on the grafting polymers were hydrolyzed to obtain sodium poly(styrene sulfonate)-grafted nanoparticles. The outline of this study is shown in Figure 1. The particles synthesized here are expected as new materials in wide variety of applications from industrial surfactants to nano-capsules for biomedical usage. They may also attract fundamental scientific attention as academic samples, since the particle has a well-defined strong polyelectrolyte brush layer on the surface with high grafting density.

2. Experimental

2.1. Materials

Neopentyl *p*-styrenesulfonate (SSPen)[21] and *N*-*t*-butyl-1-diethylphosphono-2,2-dimethylnitroxyl radical (DEPN)[22] were prepared as reported. Benzoyl peroxide (BPO) was purchased from Nacalai Tesque (Kyoto, Japan), 2,2′-azobisisobutyronitrile (AIBN) and chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$) were purchased from Wako Pure Chemicals (Osaka, Japan), iodotrimethylsilane was purchased from Tokyo Chemical Industries (Tokyo, Japan), and they were used as delivered. Tetrahydrofuran (THF) and benzene was distilled over sodium benzophenone ketyl under an argon atmosphere. Acetone was purified by distillation over MS-4A. Carbon tetrachloride was distilled over CaH_2. Water used for dialysis and polymer sample

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* Corresponding author. Tel.: +81-75-383-2597; fax: +81-75-383-2599; e-mail address: matsumo@star.polym.kyoto-u.ac.jp

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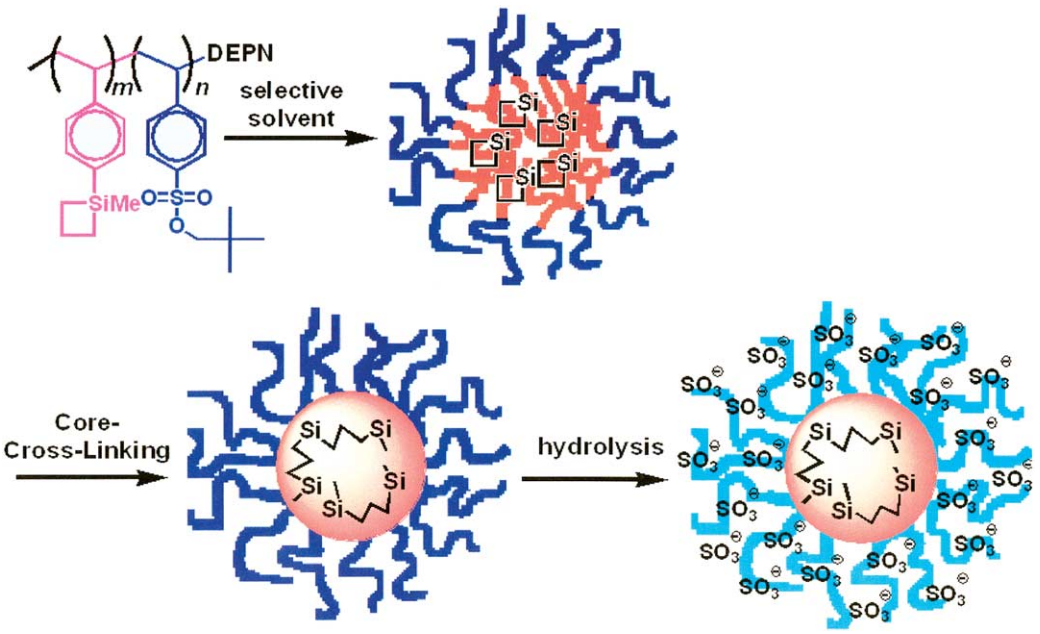


Figure 1. Schematic explanation of synthesis of sodium-polystyrenesulfonate-grafted nanoparticle.

preparation was obtained by a Milli-Q system (Millipore, Pittsburgh, PA) whose resistance was more than 18 MΩ cm.

2.1.1. Synthesis of *p*-(1-methylsilacyclobutyl)styrene (SBS). A THF solution of 1-chloro-1-methylsilacyclobutane was prepared as follows. First, 1,2-dibromoethane (0.3 mL) was added to a suspension of magnesium (1.9 g, 80 mmol) in THF (5 mL) to activate the magnesium. Then a THF solution (45 mL) of 3-chloropropylmethyldichlorosilane (9.5 mL, 60 mmol) was added dropwise over a period of 10 min. Then, the reaction mixture was heated at 50 °C for 2 h. A THF solution of *p*-styrylmagnesium bromide was prepared as follows. First, 1,2-dibromoethane (0.3 mL) was added to a suspension of magnesium (1.5 g, 60 mmol) in THF (5 mL) to activate the magnesium. Then a THF (50 mL) solution of *p*-bromostyrene (6.5 mL, 50 mmol) was added dropwise over a period of 10 min, and the solution was stirred for 2 more hours. The *p*-styrylmagnesium bromide solution thus prepared was slowly added to the 1-chloro-1-methylsilacyclobutane solution prepared above at an ambient temperature over a period of 10 min. Then the mixture was heated at 40 °C over night. The resulting solution was poured into 1 M aq. HCl, and the product was extracted with hexane. The organic layer was washed twice with water, dried with anhydrous Na_2SO_4, and concentrated. The residual oil was purified by silica-gel column chromatography to give the title compound (29 mmol, 5.4 g) in 57% yield. IR (neat) 3062, 2927, 2855, 1629, 1597, 1543, 1389, 1249, 1105, 1028, 989, 907, 866, 828, 770, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.58 (s, 3H), 1.21 (dt, J=8.4, 8.4 Hz, 2H), 1.33 (dt, J=8.4, 8.4 Hz, 2H), 2.22 (tt, J=8.4, 8.4 Hz, 2H), 5.30 (d, J=10.8 Hz, 1H), 5.83 (d, J=17.6 Hz, 1H), 6.75 (dd, J=10.8, 17.6 Hz, 1H), 7.46 (d, J=12.0 Hz, 2H), 7.62 (d, J=12.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −1.68, 14.46, 18.31, 114.38, 125.61, 133.67, 136.70, 138.16, 138.45. Found: C, 76.74; H, 8.72%. Calcd for $C_{12}H_{16}Si$: C, 76.51; H, 8.58%.

2.1.2. Synthesis of 1-methyl-1-phenylsilacyclobutane. A THF solution of 1-chloro-1-methylsilacyclobutane was prepared from 22.3 mL of 1-chloro-1-methylsilacyclobutane (140 mmol) and magnesium (4.13 g, 170 mmol) as described above. Then the solution was cooled to 0 °C and a phenylmagnesium bromide (1.0 mol/L THF solution, 200 mmol, 200 mL) was slowly added. The mixture was stirred at room temperature over night. The resulting solution was poured into 1 M aq. HCl, and the product was extracted with hexane. The organic layer was washed twice with water, dried with anhydrous Na_2SO_4, and concentrated. Distillation of the residual oil over calcium hydride under reduced pressure gave the title compound (15.2 g, 94 mmol) in 67% yield. Bp, 87–89 °C/15 Torr; IR (neat) 3067, 3050, 2927, 2855, 1589, 1487, 1428, 1396, 1300, 1249, 1184, 1112, 998, 925, 899, 866, 772, 732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.55 (s, 3 H), 1.16 (dt, J=8.4, 8.4 Hz, 2H), 1.30 (dt, J=8.4 Hz, 2H), 2.19 (tt J=8.4 Hz, 2H), 7.33–7.43 (m, 3H), 7.57–7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −1.69, 14.42, 18.31, 127.83, 129.32, 133.39, 138.57. Found: C, 73.90; H, 8.91%. Calcd for $C_{10}H_{14}Si$: C, 73.99; H, 8.71%.

2.2. Polymerization

DEPN-capped SBS_{113} was prepared as follows. A mixture of SBS (3.80 g, 20.1 mmol), BPO (13.6 mg, 0.04 mmol), DEPN (30.1 mg, 0.10 mmol), and benzene (3 mL) was charged in a glass tube equipped with a Teflon screw cock, degassed, and sealed under argon. The Teflon screw cock was used to seal the tube easily and surely. The mixture was kept at 115 °C for 2.5 h. Reprecipitation with a toluene/methanol system, followed by vacuum drying gave DEPN-capped polySBS (2.96 g, 78% SBS conversion) in quantitative yield. M_n=21,700, M_w/M_n=1.31.

The block copolymer, SBS_{113}-*b*-$SSPen_{208}$, was prepared as follows. A mixture of SSPen (2.21 g, 8.70 mmol), DEPN-capped SBS_{113} (M_n=21,700, 0.65 g) prepared above, 1.5 mg of DEPN, and benzene (2.5 mL) was charged in a

glass tube equipped with a Teflon cock, degassed, and sealed under argon. The mixture was kept at 115 °C for 2.0 h. Reprecipitation with a chloroform/hexane system, followed by vacuum drying gave SBS_{113}-*b*-$SSPen_{208}$ (1.08 g, 62% SSPen conversion) in 54 wt% yield. M_n=50,500, M_w/M_n=1.59.

2.3. Core-cross-linking of the block copolymer micelle

A core-cross-linked (CCL) block copolymer, CCL-(SBS_{113}-*b*-$SSPen_{208}$), was synthesized. About 20 mg of $H_2PtCl_6{\cdot}6$-H_2O was placed in a two-necked 500 mL-round bottomed flask equipped with a reflux condenser, and the flask was filled with argon. Then an acetone (100 mL) solution of SBS_{113}-*b*-$SSPen_{208}$ (1.0 g) was added, and the mixture was heated at 55 °C for 3 h. The resulting solution was filtrated and concentrated to about 1/5 in volume by evaporation. Then 1,4-dioxane (200 mL) was added and the solution was freeze-dried to give a powdered CCL polymer CCL-(SBS_{113}-*b*-$SSPen_{208}$) (1.0 g) in quantitative yield.[23]

2.4. Hydrolysis of neopentyl sulfonate

A CCL SBS_{113}-*b*-(sodium styrenesurfonate)$_{208}$ (CCL-(SBS_{113}-*b*-$SSNa_{208}$)) was synthesized. Trimethylsilyl iodide (1.5 mL, 10 mmol) was added to a solution of CCL-(SBS_{113}-*b*-$SSPen_{208}$) (900 mg) in carbon tetrachloride (30 mL), and the mixture was stirred at 50 °C for 15 h. The mixture was concentrated, and the neopentyl and the resulting residue was dissolved in 200 mL of methanol/HCl (1 mol/L) mixture, then aqueous NaOH (1 mol/L) was added to neutralize the solution. The solution was filtrated and dialyzed against deionized water for a week. The dialysate was diluted with water to afford 0.1 wt% aqueous solution of CCL-(SBS_{113}-*b*-$SSNa_{208}$) (780 mL).

2.5. Measurements

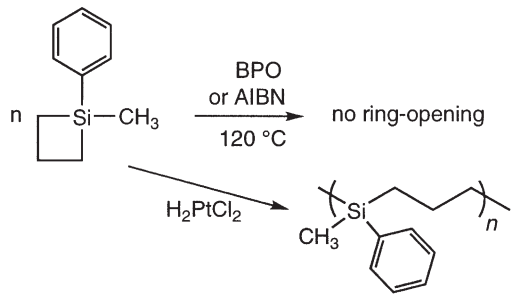
Gel permeation chromatography (GPC) was carried out in THF on a JASCO PU-980 chlomatograph (JASCO Engineering, Tokyo, Japan) equipped with two polystyrene gel columns (Shodex KF804L; separation range in molecular weight of polystyrene: 100 to 4×10^5) and JASCO RI-930 refractive index detector. The averaged polymerization degree of polySBS and molecular weight distributions of both polySBS and polySBS-*b*-polySSPen were determined relative to polystyrene standards. Proton NMR spectra were recorded on a JEOL AL-400 spectrometer in $CDCl_3$, acetone-d_6, and D_2O. The averaged polymerization degree of polySSPen segment in polySBS-*b*-polySSPen was calculated from the polymerization degree of SBS prepolymer (by GPC) and composition of the block copolymer estimated from ^1H NMR measurement. IR spectra were measured on a Shimadzu FTIR-8400 spectrometer. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. The dynamic light scattering (DLS) measurements were performed on a DLS apparatus of Photal SLS-6000HL (Otsuka Electrics, Osaka, Japan) equipped with a correlator (Photal GC-1000). He–Ne laser (the wavelength of 632.8 nm) was used for the measurements. Sample solutions (1–0.1 wt%) were filtrated through a membrane (Millex-HN, Millipore, pore-size of 0.45 μm). The measurements were performed at 20 °C at scattering angle of 90°. AFM measurements were performed by SPI3800 probe station and SPA300 unit system of Scanning Probe Microscopy System SPI3800 series (Seiko Instruments, Tokyo, Japan). The cantilever was made of silicon (Olympus, Tokyo, Japan) and its spring constant was 2 N/m. The measurements were performed in Dynamic Force Mode (non-contact mode). For sample preparation, a THF or aqueous solution (ca.0.1 wt%) of the polymer was dropped on a microslide glass (IWAKI, Japan) and air-dried.

3. Results and discussion

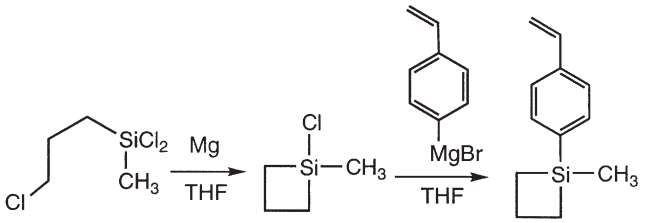
3.1. Block copolymer synthesis

Controlled radical polymerization of vinyl compounds has resulted in a wide variety of well-defined block copolymers.[24–26] Okamura and co-workers reported a quite sophisticated method of synthesizing polystyrene-*block*-polySSNa by a nitroxy-radial-mediated living polymerization of styrene with styrene having neopentyl surfonate group at the *para*-position (SSPen) and a successive hydrolysis of neopentyl ester.[21] On the other hand, it has been well-known for a long time that silacyclobutanes can be readily polymerized in the presence of platinum catalyst,[27] while the four-membered ring is tolerant under radical conditions as shown in Scheme 1. We confirmed that no consumption of 1-methyl-1-phenyl-silacyclobutane occurs in heating a bulk 1-methyl-1-phenylsilacyclobutane in the presence of AIBN or BPO at 120 °C. This suggests that styrene derivatives having silacyclobutanes might be radically polymerized without affecting the cyclic group in one step, whereas the resulting styrenic polymer can be cross-linked by ring-opening polymerization in the later step.

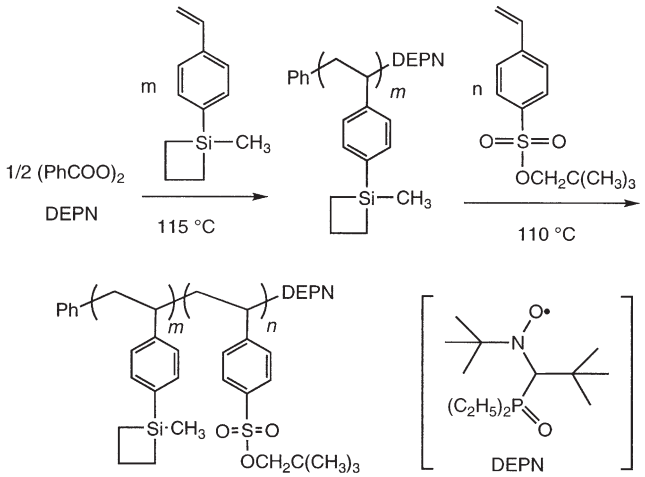
In this study, we used styrenes having a silacyclobutyl group at the *para*-position (SBS) and SSPen as monomers for a



Scheme 1.



Scheme 2.



Scheme 3.

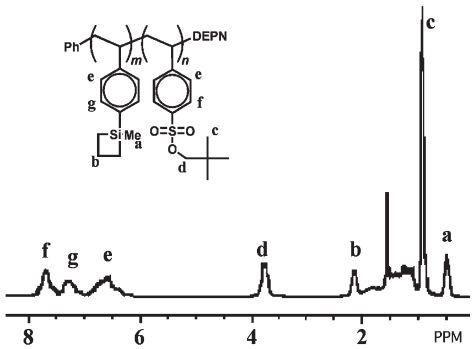


Figure 2. ^{1}H NMR spectrum of SBS_{113}-*b*-$SSPen_{208}$ in $CDCl_3$.

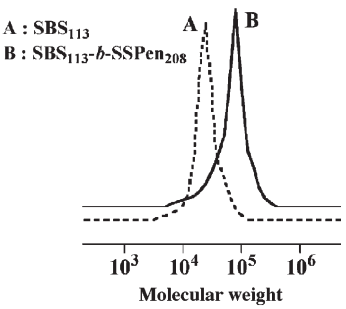


Figure 3. GPC charts for (A) DEPN end-capped SBS_{113} and (B) SBS_{113}-*b*-$SSPen_{208}$.

block copolymer synthesis. The SBS monomer was readily prepared by treatment of 1-chloro-1-methylsilacyclobutane with *p*-styrylmagnesium bromide as shown in Scheme 2.

The desired block copolymer, polySBS-*b*-polySSPen, was synthesized by nitroxy-radical-mediated living polymerization as shown in Scheme 3. In the first step, we prepared a nitroxy-capped polySBS with narrow molecular weight distributions by polymerization of SBS using benzoyl peroxide (BPO) as a radial initiator and DEPN[22] as a radical mediator. Then SSPen was polymerized using polySBS as a macro initiator. A representative ^{1}H NMR spectrum and GPC charts of the obtained polymer are given in Figures 2 and 3. The ^{1}H NMR spectrum indicates the existence of both polySBS and polySSPen. The peak on the GPC charts shifted to the higher molecular weight region after polymerization of SSPen, which indicates formation of a block copolymer. In the first polymerization step, three polySBS samples having different polymerization degrees were synthesized by tuning the molar ratio of BPO and SBS, while the molar ratio of the radical mediator to the radical initiator was kept constant ([DEPN]/[BPO]=2.5) in all cases. In the second polymerization step, five different samples were prepared by tuning the molar ratio of SBS prepolymer and SSPen. The polymerization results are summarized in Table 1. The polymerization degree of the polySBS (*m*) was estimated by GPC measurements relative to polystyrene standard, and the polymerization degree (*n*) of polySSPen was estimated by ^{1}H NMR spectra of the block copolymers, thus the *m* and *n* are not absolute values. It is also true that the products were contaminated with a trace amount of 'dead' polySBS prepolymer as detected by GPC, which broadened the molecular weight distribution, although most of the products were block copolymers. However, we used the crude products in the later experiments without further purification, because the homopolymer was solubilized in the core of the block copolymer micelle and did not pose a crucial problem in the cross-linking step.

3.2. Micelle formation

PolySBS is nonpolar and soluble in nonpolar solvent such as hexane, toluene, chloroform, and THF, while it is insoluble in polar solvent such as acetone, dimethylsulfoxide (DMSO), and *N*, *N*-dimethylformamide (DMF). On the other hand, polySSPen is moderately polar and insoluble in hexane but soluble in all the other solvents described above. Thus the block copolymers were soluble in chloroform, which is a good solvent for both blocks, and we could see ^{1}H NMR signals of both polySBS and polySSPen in $CDCl_3$ as shown in Figure 2. In the meanwhile, the block copolymers were also soluble in acetone, which is a selective solvent for polySSPen. In this case, however, the signals only for polySSPen were observed but the signals for polySBS were

Table 1. Polymerization results of SBS and SSPen

$[BPO]_0/[SBS]_0$	Conv. (%) of SBS	*m*	M_w/M_n of polySBS	$[polySBS]_0/[SSPen]_0$	Conv. (%) of SSPen	*n*	M_w/M_n of block copolymer
1/256	75	64	1.36	1/122	50	70	1.38
1/348	82	89	1.23	1/137	57	97	1.62
—	—	89	1.23	1/251	60	163	1.56
1/480	78	113	1.31	1/194	64	134	1.52
—	—	113	1.31	1/290	62	208	1.59

$[BPO]_0/[SBS]_0$: initial molar ratio of BPO and SBS. $[polySBS]_0/[SSPen]_0$: initial molar ratio of SBS prepolymer and SSPen. *m* was determined by GPC relative to polystyrene standard. *n* was determined by ^{1}H NMR using the value of *m*. M_w/M_n was determined by GPC relative to polystyrene standard.

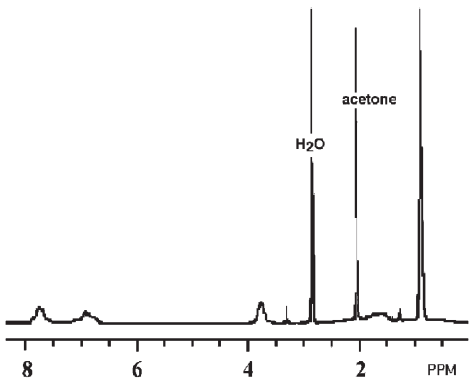


Figure 4. ^{1}H NMR spectrum of SBS_{113}-*b*-$SSPen_{208}$ in acetone-d_6.

acetone-soluble polySSPen and the solvent. To examine more about the micelle formation, we measured the DLS of the block copolymer solutions. In all cases, strong light scattering intensity was observed, which suggested the existence of block copolymer micelles. Hydrodynamic radius (R_h) of the block copolymer micelles in acetone for all the samples examined here are summarized in Table 2. The R_h ranged from 15 to 23 nm, all of which are reasonable values for the block copolymer micelles, and they increased as the total chain length of the block copolymer increased.

3.3. Micelle core cross-linking

It is well-known that silacyclobutanes can be readily polymerized by a hexachloroplatinic acid (H_2PtCl_6).[27] We

Table 2. Hydrodynamic radius of SBS_m-*b*-$SSPen_n$ micelle and CCL-(SBS_m-*b*-$SSPen_n$) evaluated by DLS measurement

n	*m*	Hydrodynamic radius, R_h (nm)				
		SBS_m-*b*-$SSPen_n$ in acetone	CCL-(SBS_m-*b*-$SSPen_n$) in acetone	CCL-(SBS_m-*b*-$SSPen_n$) in THF	CCL-(SBS_m-*b*-$SSNa_n$) in water	CCL-(SBS_m-*b*-$SSNa_n$) in 0.3 M NaCl aq.
64	70	15	12	13	50	40
89	97	17	15	13	82	66
89	163	19	19	19	87	66
113	134	17	21	20	90	63
113	208	23	19	19	110	70

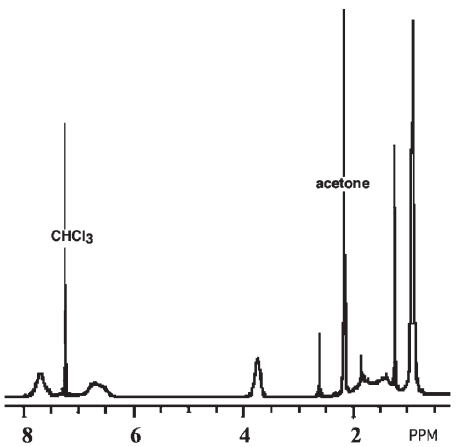
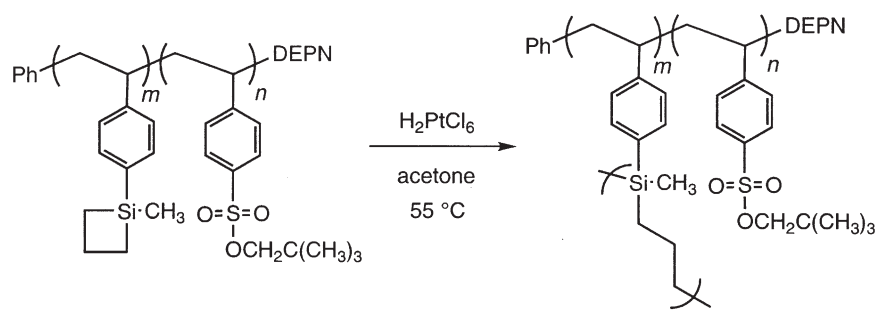


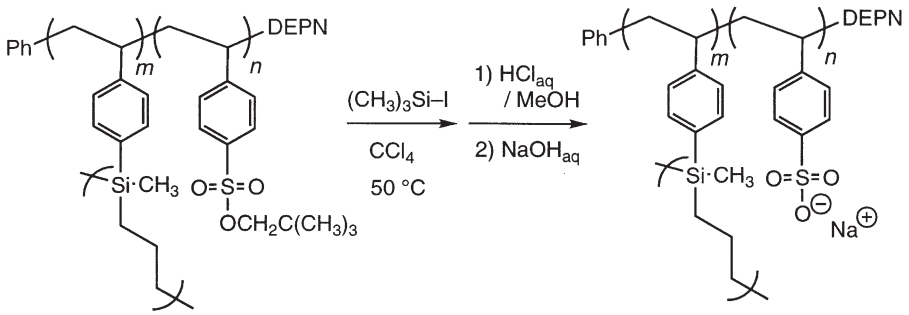
Figure 5. ^{1}H NMR spectrum of CCL-(SBS_{113}-*b*-$SSPen_{208}$) in $CDCl_3$.

not observed as shown in the spectrum of the block copolymer in acetone-d_6 (Fig. 4). This suggested that micelles were formed in acetone, whose core consists of acetone-insoluble polySBS and the shell consists of

utilized this reaction to a CCL of the block copolymer micelle. The micelle solution in acetone was heated at 55 °C in the presence of catalytic amount of H_2PtCl_6. Figure 5 shows ^{1}H NMR spectrum of the products obtained by treatment with Pt catalyst in acetone and redissolved in $CDCl_3$. The four-membered ring methylene signals at 2.2 ppm (observed in Figure 2) completely disappeared and signals of the methyl group on the silicon atom at 0.4 ppm (observed in Figure 2) were detected as significantly broad signals in Figure 5, indicating the occurrence of ring-opening reactions (Scheme 4). Particle size in the acetone solution was examined by DLS measurement. The R_h values for the samples evaluated here are summarized in Table 2. R_h of the obtained particles ranges from 12 to 21 nm in acetone, which are in good agreement with those of the block copolymer micelles before the ring opening reaction. The DLS measurement was also carried out in the THF solution. Light scattering were observed even in THF, which is a good solvent for both polySBS and polySSPen, evidenced the formation of CCL micelles. In addition, the hydrodynamic sizes of the particles evaluated in THF were analogous to those in acetone (Table 2), suggesting that the



Scheme 4.



Scheme 5.

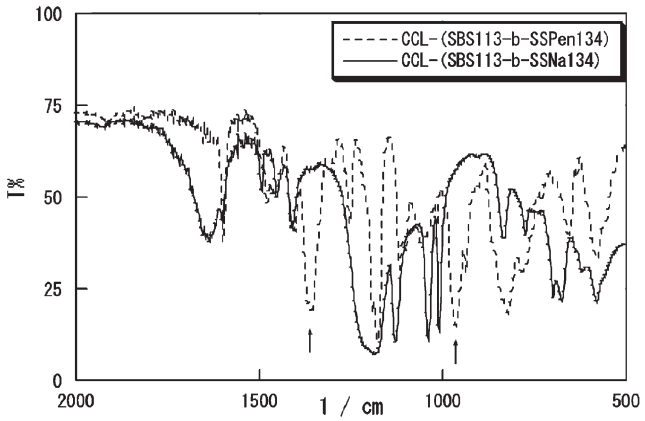


Figure 6. IR-spectra of CCL-(SBS_{113}-*b*-$SSPen_{134}$) and CCL-(SBS_{113}-*b*-$SSNa_{134}$).

cross-linking proceeded so enough that the core was not swollen even by good solvent. These results clearly indicate the formation of the CCL micelles.

3.4. Synthesis of polySSNa-grafted particle

The neopentyl sulfonates of the grafting chains were transformed into trimethylsilyl sulfonates by treatment with trimethylsilyl iodide in carbon tetrachloride, and the silyl sulfonates were further transformed to sodium sulfonates by sequential exposure to HCl_{aq} and $NaOH_{aq}$ (Scheme 5). Completion of the hydrolysis was confirmed by IR measurements (Fig. 6). Absorption at 1350 and 950 cm^{-1} typical for sulfonate ester, which were observed in the case of CCL-(polySBS-*b*-polySSPen), completely disappeared in the spectra for products after hydrolysis.

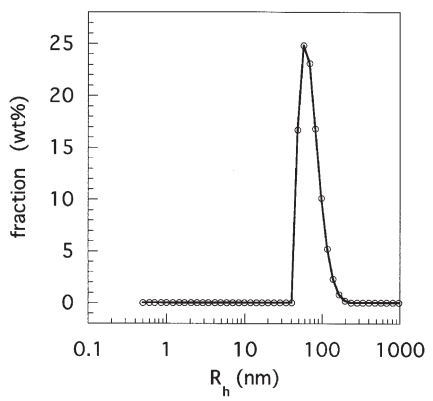


Figure 7. Distribution of hydrodynamic radius (R_h) of CCL-(SBS_{113}-*b*-$SSNa_{134}$) in water evaluated by DLS CONTIN analysis. Scattering angle: 90°.

The hydrolyzed products were soluble in water. DLS analysis of the particles was performed in aqueous solutions. The size distribution of CCL-(SBS_{113}-*b*-$SSNa_{134}$) in water is given in Figure 7, which shows narrow size distribution. The R_h values for all the samples are summarized in Table 2. The R_h of the hydrolyzed CCL-micelles ranged from 50 to 110 nm. The size of these particles was about four times larger than that of the esterified particles in organic media. This increase in R_h is probably caused by the drastic conformation change of the grafted polymer chains. The non-ionic polySSPen chain took a corona conformation in the organic solvent, while the ionic polySSNa chains adopted a stretched conformation due to the electrostatic repulsion between the ionic groups. DLS measurement was carried out in salt-added aqueous solutions to confirm this effect. The R_h values for the hydrolyzed particles in 0.3 M NaCl solutions are given in Table 2. The particle sizes were reduced by salt addition in all cases. We consider this to be because the electrostatic interaction in the polySSNa chains is screened by the added ions. Another significant characteristics of this material is that the CCL-(polySBS-*b*-polySSNa) aqueous solution was very stable even in a salted water, that is no flocculation or precipitation of the polymer particles was observed in 0.5 mol/L NaCl aqueous solution at room temperature even after one week. We consider that a high steric stabilization effect of grafting polySSNa chains might play an important role in this phenomenon.

The obtained polymer nanoparticles before and after the hydrolysis were further investigated by AFM. Figure 8 shows typical AFM images for CCL-(SBS_{113}-*b*-$SSPen_{134}$) and CCL-(SBS_{113}-*b*-$SSNa_{134}$). Many protubances of ca.70 nm in diameter were observed for CCL micelles both before and after hydrolysis, suggesting the existence of spherical particles. The height profiles for the images were also given in the figure. The height of the protubances is ca.6 nm for a particle before hydrolysis, while that for a particle after hydrolysis is ca.30 nm. Because of the convolution effect of a silicon probe used in the AFM measurement, horizontal size is always larger than the real one. Therefore, we estimated the particle size from the height profiles. By AFM analysis, the diameters of the particles were determined at 6 and 30 nm before and after hydrolysis, respectively. These results also suggest that the polySSNa chains in the hydrolyzed particles have a more

stretched conformation than polySSPen in the particles before hydrolysis. However, it should be noted that the particles evaluated here are significantly smaller than those obtained by DLS. This is because the structures of the particles observed by AFM are in a dry state and different from those in a wet state evaluated by DLS. Nevertheless, the AFM observation clearly revealed that spherical nanoparticles could be synthesized by core-cross-linking of block copolymer micelles.

4. Conclusions

A well-defined styrene-based block copolymer having the cross-linkable silacyclobutane and sulfonate groups, polySBS-*b*-polySSPen, was synthesized by nitroxy-mediated 'living' radical polymerization. The block copolymer formed a micelle whose R_h ranged from 15 to 23 nm in acetone, and the core of the micelle was cross-linked to provide polySBS nanoparticles with polySSPen grafting from the surface. Hydrolysis of the neopentyl ester in polySSPen gave ionic poly(styrene sulfonate)-grafted polySBS nanoparticles. The R_h of the particle with ester-protected graft chains was 12–21 nm in acetone, while that of the particle with ionic polySSNa chains was 50–110 nm in water. This size difference is induced by electrostatic repulsion between ions on the polymer chains. The electrostatic interaction in the grafting polySSNa chains is currently being investigated in detail.

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