

Synthesis of Ionic-Polymer-Grafted Nanoparticles by Core-Cross-Linking of Silicon-Containing Block Copolymer Micelles

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Sodium poly(styrenesulfonate)(polySSNa)-grafted polymer nanoparticles were synthesized by core-cross-linking of block copolymer micelles and subsequent chemical transformation. A block copolymer composed of a cross-linkable polySBS segment and ester-protected polySSPen segment was prepared by nitroxyl-mediated living radical polymerization of SBS and SSPen monomers, where SBS and SSPen represent *p*-((1-methyl)silacyclobutyl)styrene and neopentyl *p*-styrenesulfonate. The block copolymer formed micelles 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 fine polymer particles. The hydrodynamic radius (R_h) of each particle was estimated by dynamic light scattering (DLS). The R_h value of the hydrolyzed polymer particle ($R_h = 34\sim 51$ nm) in 0.1 mol/L NaClaq, was much larger than that of the particle in acetone before hydrolysis ($R_h = 6\sim 14$ nm). This increase in R_h is due to stretching of ionic polySSNa chains by electrostatic repulsion. The size and shape of each particle was also determined by atomic force microscopy (AFM).

Key words: micelle, cross-linking, nanoparticle, surface-graft, sodium polystyrenesulfonate

1. INTRODUCTION

Block copolymers form micelles in solvents selective for one of the blocks. The core of the micelle consists of an insoluble block, and the shell consists of both a soluble block and the solvent. Much interest has recently been focused on such micelles from both academic and industrial points of view [1-3]. Compared with the micelles of low molecular weight surfactants, the block copolymer micelles are larger, ranging from several nanometers to tens of nanometers. In addition, they are generally more stable due to their slow kinetics of exchange between associated and non-associated molecules (micelle-unimer exchange). These characteristics are quite advantageous in synthesizing nano-scale polymer particles. By cross-linking the core of the micelle inside the domain, we can obtain nanoparticles with shell-forming polymers grafted from the particle surface. In this study, we prepared a styrene-based block copolymer, consisting of a non-polar block with cross-linkable silacyclobutyl groups and a polar block with surfonate ester groups by nitroxyl-mediated "living" radical polymerization [4], and synthesized nanoparticles bearing anionically charged poly(styrene sulfonate) chains grafted from the surface by the core-cross-linking of the block copolymer micelle.

2. EXPERIMENTAL

2.1 Materials

p-(1-Methylsilacyclobutyl)-styrene (SBS) was prepared by treatment of 1-chloro-1-methylsilacyclobutane with *p*-vinylphenylmagnesium bromide in tetrahydrofuran (THF) and purified by silica-gel column chromatography. Neopentyl *p*-

styrenesulfonate (SSPen) [5] and *N*-*t*-butyl-1-diethylphosphono-2,2-dimethylnitroxyl radical (DEPN) [6] were prepared as reported.

2.2 Polymerization

DEPN-capped polySBS was prepared as follows. A mixture of SBS (3.1 g, 16.5 mmol), BPO (27 mg, 0.21 mmol), DEPN (61 mg, 0.21 mmol), and benzene (5.0 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 h. Reprecipitation with a toluene/methanol system, followed by vacuum drying gave DEPN-capped polySBS (1.56 g). $M_n = 8600$, $M_w/M_n = 1.17$

The block copolymer, polySBS-*b*-polySSPen, was prepared as follows. A mixture of SSPen (5.0 g, 20 mmol), DEPN-capped polySBS ($M_n = 8600$, 1.45 g), 10 mg of DEPN, and benzene (10 mL) was charged in a glass tube equipped with a Teflon cock, degassed, and sealed under argon. The mixture was kept at 110 °C for 6 h. Reprecipitation with a chloroform/hexane system, followed by vacuum drying gave SBS-*b*-SSPen-₇₉ (3.2 g). $M_n = 24400$, $M_w/M_n = 1.17$

2.3 Core-cross-linking of the block copolymer micelle

About 20 mg of $H_2PtCl_6 \cdot 6H_2O$ 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 (240 mL) solution of SBS-*b*-SSPen-₇₉ (2.0 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 core-cross-linked

polymer CCL-(SBS₄₃-*b*-SSPen₇₉) (1.5 g) in 80% yield.

2.4 Hydrolysis of neopentyl sulfonate

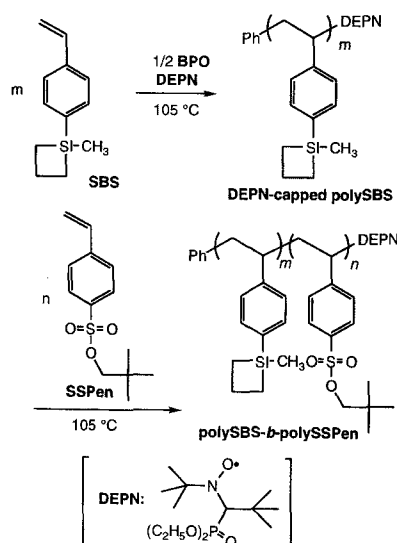
To a solution of CCL-(SBS₄₃-*b*-SSPen₇₉) (1.5 g) in carbon tetrachloride (40 mL), trimethylsilyl iodide (2.4 mL, 17 mmol) was added, and the mixture was stirred under reflux for 10 h. The mixture was concentrated, and the resulting residue was dissolved in 250 mL of methanol/HCl (1 mol/L) mixture, then aqueous NaOH (1 mol/L, 100 mL) was added. The solution was filtered, and dialyzed against deionized water. Freeze-drying of the solution gave a CCL-(SBS₄₃-*b*-SSNa₇₉) powder, (1.2 g) in 87% yield.

2.5 Measurements

Gel permeation chromatography was carried out in THF on a JASCO PU-980 chromatograph equipped with two polystyrene gel columns (Shodex KF-804L) and JASCO RI-930 reflective index detector. Number-averaged molecular weight (M_n) and weight-averaged molecular weight (M_w) were determined by GPC with a polystyrene standard calibration. Proton NMR spectra were recorded on JEOL GSX-270. IR spectra were measured on a Shimadzu FTIR-8400 spectrometer. DLS experiments were carried out with an ELS-800 (He-Ne laser), (Otsuka Electric). The decay rate Γ was evaluated by double-exponential fitting of the time correlation function. After the translational nature of Γ was confirmed by angler dependence, the translational diffusion coefficient D was calculated by $\Gamma = Dq^2$, where q is the scattering vector, and then the hydrodynamic radius R_h was calculated by using the Stokes-Einstein equation. AFM was performed on SPI3800 probe station and SPA300 unit system (Seiko Instruments) in Dynamic Force Mode (non-contact mode). The cantilever was made of silicon (Olympus, Tokyo, Japan) and its spring constant was 20 N/m. For sample preparation, aqueous solutions of the CCL-(polySBS-*b*-polySSNa) was spread on a micro slide glass (IWAKI), and dried in a desiccator with silica-gel.

3. RESULTS AND DISCUSSIONS

3.1 Block copolymer synthesis



Scheme 1. Synthetic route to polySBS-*b*-polySSPen

We chose SBS and SSPen as monomers for the diblock copolymer synthesis, because the silacyclobutyl and sulfonate ester functionalities are tolerant to nitroxyl-mediated radical polymerization, the four-membered silacyclobutyl can act as a cross-linking moiety [7], and the sulfonate ester can be further transformed into a strong ionic sulfonate group [5]. The synthetic route is shown in Scheme 1. First we prepared a nitroxyl-capped polySBS with narrow molecular weight distributions by polymerization of SBS using benzoyl peroxide (BPO) as a radical initiator and DEPNa as a radical mediator. Then SSPen was polymerized using polySBS as a macro initiator. The ¹H-NMR spectrum of the product indicates the existence of polySBS and polySSPen as shown in Figure 1.

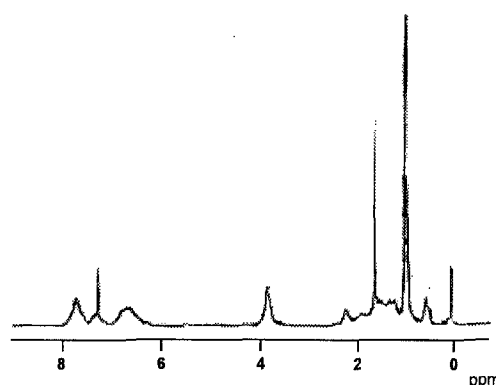


Figure 1. ¹H NMR spectrum of SBS₄₄-*b*-SSPen₁₃₇ in CDCl₃

Figure 2 shows GPC curves for polySBS and the product after polymerization of SSPen. The GPC chart shifted to the higher molecular weight region keeping the narrow molecular weight distributions, clearly indicating a formation of the block copolymer.

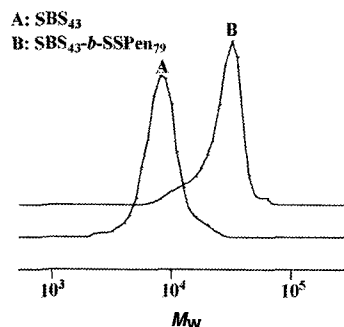


Figure 2. GPC curves for DEPNa-capped SBS₄₃ and SBS₄₃-*b*-SSPen₇₉

m^a	n^b	M_n^c	M_w/M_n^c
43	79	24000	1.17
44	137	32000	1.30
63	182	57000	1.41

^aestimated by polystyrene-calibrated GPC of the polySBS macro initiator, ^bestimated by ¹H NMR of the block copolymer, ^cdetermined by polystyrene-calibrated GPC of the block copolymer

The molecular characteristics of the samples are summarized in Table I.

3.2 Micelle formation

The polySBS-*b*-polySSPen samples were dissolved in acetone, and dynamic light scattering measurement was taken for the 1wt% solutions. In all cases, slow scattering decay was observed, which indicated the existence of multi-molecular assembly. The time-correlation functions of the block copolymer solutions analyzed by double exponential fitting suggested the existence of two kinds of scattering particles. Table II summarizes the R_h values for the block copolymer solutions. Smaller particles ($R_h = 5\sim 6$ nm) were considered to be micelles, while larger particles ($R_h = 24\sim 117$ nm) might be complex aggregates, which were in a very small volume fraction. The core of the micelle consists of polySBS, which is insoluble, and the shell consists of swollen polySSPen, which is soluble in acetone.

Table II. DLS results of polySBS-*b*-polySSPen in acetone

polymer	$R_{h\text{-micelle}}$ (nm)	$R_{h\text{-aggregate}}$ (nm)	Φ_{micelle}
SBS ₄₃ - <i>b</i> -SSPen ₇₉	5	24	0.92
SBS ₄₄ - <i>b</i> -SSPen ₁₃₇	5	117	0.99
SBS ₆₃ - <i>b</i> -SSPen ₁₈₂	6	29	0.98

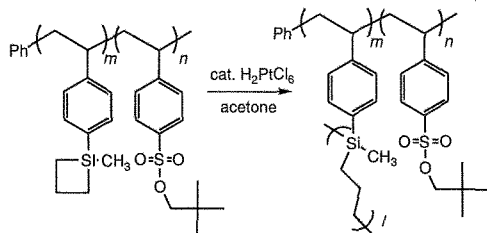
$R_{h\text{-micelle}}$: hydrodynamic radius of micelles

$R_{h\text{-aggregate}}$: hydrodynamic radius of aggregates

Φ_{micelle} : volume fraction of micelles in the all assembly

3.3 Micelle core cross-linking

Ring-opening polymerization of silacyclobutane can be readily induced by a transition metal catalyst [8]. We applied this reaction to a core-cross-linking of the block copolymer micelle. The micelle solution was heated at 55 °C in the presence of H_2PtCl_6 (Scheme 2).



Scheme 2. Cross-linking reaction of polySBS-*b*-polySSPen

Figure 3 shows the 1H NMR spectrum of the crude reaction mixture 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 3, indicating the occurrence of ring-opening reactions. Particle size in the resulting solution was examined by DLS measurement. The evaluated R_h values are summarized in Table III. Particles of R_h ranging from 6~14 nm were considered to be core-cross-linked (CCL) micelles, and particles of R_h ranging from 31~176 nm

were assumed to be cross-linked aggregates, whose volume fractions can be almost negligible. The hydrodynamic sizes of the major products obtained after the ring-opening polymerization were slightly larger than those of the micelles before the polymerization, but they were comparable in size, which suggested that cross-linking had proceeded in the micelle.

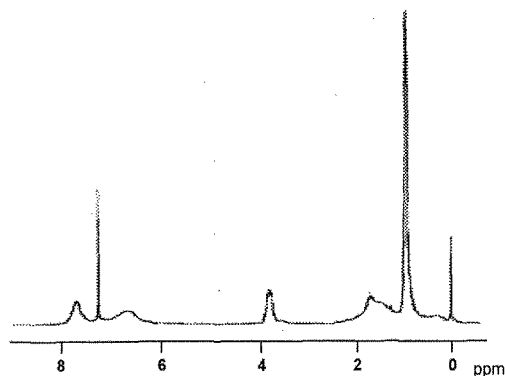


Figure 3. 1H NMR spectrum of CCL-(SBS₄₄-*b*-SSPen₁₃₇) in $CDCl_3$

Table III. DLS results of CCL-(polySBS-*b*-polySSPen) in acetone

polymer	$R_{h\text{-micelle}}$ (nm)	$R_{h\text{-aggregate}}$ (nm)	Φ_{micelle}
CCL-(SBS ₄₃ - <i>b</i> -SSPen ₇₉)	6	31	0.99
CCL-(SBS ₄₄ - <i>b</i> -SSPen ₁₃₇)	8	102	0.99
CCL-(SBS ₆₃ - <i>b</i> -SSPen ₁₈₂)	14	176	0.99

$R_{h\text{-micelle}}$: hydrodynamic radius of CCL-micelles

$R_{h\text{-aggregate}}$: hydrodynamic radius of CL-aggregates

Φ_{micelle} : volume fraction of micelles in the all assembly

Furthermore, the same R_h values were obtained from DLS analysis of the products in THF, which clearly indicated the formation of CCL-micelles. This is because both the SBS and SSPen segments were soluble in THF, and no scattering would be observed if the micelles were not cross-linked. Schematic explanation of the Pt-catalyzed core-cross-linking of the block copolymer micelle is given in Figure 4.

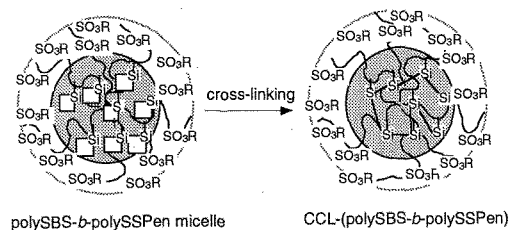


Figure 4. Core-cross-linking of the micelle

3.4 Synthesis and property 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. Completion of the hydrolysis was confirmed by IR measurements. 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.

DLS analysis of the hydrolyzed particles was performed in aqueous solutions. The results are summarized in Table IV. The R_h of the CCL-micelles ranged from 34 nm to 51 nm. The size of these particles was three- to six-fold that of the esterified particles in organic media. This was probably due to 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. A schematic explanation is illustrated in Figure 6.

Table IV. DLS Results of CCL-(polySBS-*b*-polySSNa) in aqueous 0.5 mol/L NaCl

polymer	$R_{h\text{-micelle}}$ (nm)	$R_{h\text{-aggregate}}$ (nm)	Φ_{micelle}
CCL-(SBS ₄₃ - <i>b</i> -SSNa ₇₉)	34	210	0.99
CCL-(SBS ₄₄ - <i>b</i> -SSNa ₁₃₇)	48	181	0.97
CCL-(SBS ₆₃ - <i>b</i> -SSNa ₁₈₂)	51	216	0.95

$R_{h\text{-micelle}}$: hydrodynamic radius of CCL-micelles

$R_{h\text{-aggregate}}$: hydrodynamic radius of CL-aggregates

Φ_{micelle} : volume fraction of micelles in the all assembly

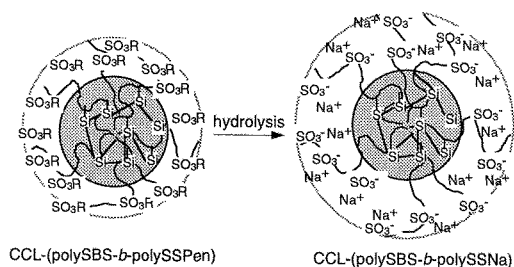


Figure 6. Hydrolysis of CCL-(polySBS-*b*-polySSPen)

The obtained polymer nanoparticles were investigated by AFM. Figure 7 shows typical AFM images. Many particles were ca. 50 nm in diameter and ca. 10 nm in height, suggesting that the obtained CCL-micelles were spherical. The particle size obtained here was in good agreement with the hydrodynamic size obtained by DLS. It is true that the structures of the particles observed by AFM (dry condition) is naturally different from those evaluated by DLS (wet condition), but the AFM clearly revealed the formation of nanoparticles.

4. CONCLUSIONS

A styrene-based block copolymer having the cross-linkable silacyclobutane and sulfonate groups, polySBS-*b*-polySSPen, was synthesized by nitroxide-mediated "living" radical polymerization. The block copolymer formed a micelle in acetone, and the core of the micelle was cross-linked to afford polySSPen-grafted polySBS nanoparticles. Chemical transformation of the polySSPen gave ionic poly(styrene sulfonate)-grafted polySBS nanoparticles. The hydrodynamic radius of the particle with ester-protected graft chains was 10 nm or less in acetone, while that of the particle with ionic polySSNa chains was several ten nm. This size difference is induced by electrostatic repulsion of the

ionic polymer chains. We believe that nanoparticles having a strong ionic brush tethered on the particle surface are very promising candidates for novel functional materials.

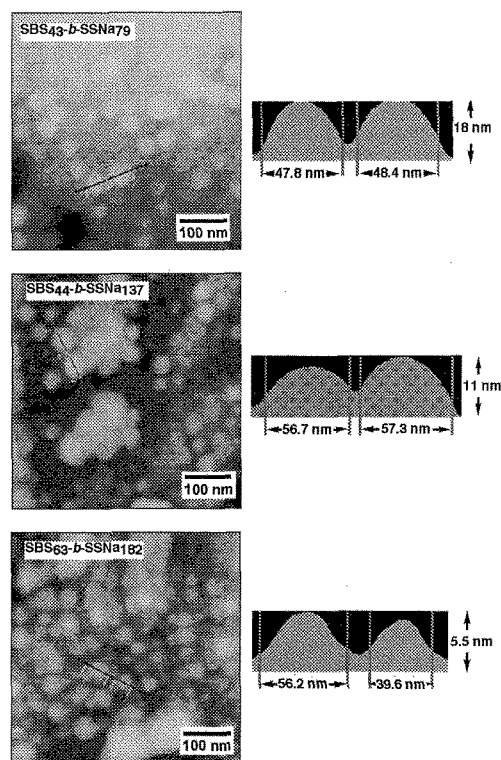


Figure 7. AFM images of CCL-(polySBS-*b*-polySSNa) deposited on a glass plate

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References

- [1] I. W. Hamley, *Encyclopedia of Polymer Science and Technology* third edition, Ed. by H. F. Mark, John Wiley & Sons, New Jersey (2003) vol. 1 pp.457-482.
- [2] N. Hadjichristidis, S. Pispas, and G. Floudas, *Block Copolymers*, John Wiley & Sons, New Jersey (2003) pp. 203-231.
- [3] B. Lindman and P. Alexandridis, *Amphiphilic Block Copolymers*, Ed. by B. Lindman and P. Alexandridis, Elsevier (2000) pp.1-40.
- [4] C. J. Hawker, A. W. Bosman, and E. Harth, *Chem. Rev.*, 101, 3661 (2001).
- [5] H. Okamura, Y. Takatori, M. Tsunooka, and M. Shirai, *Polymer*, 43, 3155 (2002).
- [6] D. Benoit, V. Chaplinski, R. Braslau, and C. J. Hawker, *J. Am. Chem. Soc.*, 121, 3904 (1999).
- [7] E. S. Finkelshtein, E. B. Portnykh, N. V. Ushakov, and B. Marciniec, *Silicon-Containing Polymers*, Ed. by R. G. Jones, the Royal Society of Chemistry, Cambridge (1995), pp. 29-34.
- [8] D. R. Weyenberg and L. E. Nelson, *J. Org. Chem.*, 30, 2618 (1965).