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Encapsulation of polysilane into shell cross-linked micelles

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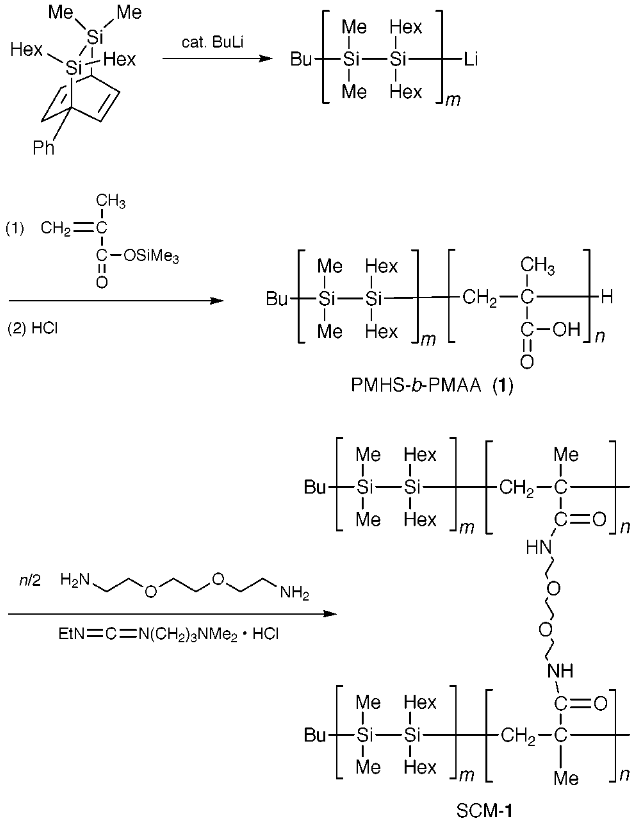
The cross-linking reaction of the poly(methacrylic acid) block of poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(methacrylic acid) with 1,10-diaza-4,7-dioxadecane and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride afforded the first shell cross-linked micelles of polysilane.

Very recently, a vesicle of an amphiphilic multi-block copolymer with poly(phenylmethylsilane) has been reported.[1] We also reported preparation and formation of micelles of an amphiphilic diblock copolymer, poly(1,1 -dimethyl-2,2-dihexyldisilene)-*b*-poly(2-hydroxyethyl methacrylate).[2]

In this area of the chemistry, the formation and properties of shell cross-linked micelles (SCMs) have been investigated actively in recent years.[3,4] The macromolecular architectures of SCMs are nanometer-sized, with amphiphilic core-shell spheres that are prepared by the self-assembly of amphiphilic block copolymers into polymer micelles, followed by cross-linking of the side chains along the block composing the shell of the polymer micelles. Here, polysilane-based shell cross-linked micelles are reported for the first time.

Poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(methacrylic acid) **1** (PMHS-*b*-PMAA) was prepared by the sequential anionic polymerization of masked disilenes[5] and trimethylsilyl methacrylate, followed by hydrolysis of the trimethylsilyl protecting group (Scheme 1).† The copolymer, insoluble in $CHCl_3$, was converted to methyl-esterified copolymer by the reaction with CH_2N_2 and the molecular weight was estimated by size exclusion chromatography with $CHCl_3$ as eluent (M_n = 2.8 × 10^4, M_w/M_n = 1.07, calibrated with polystyrene standards). Then the molecular weight of **1** was estimated to be $M_n = 2.4 \times 10^4$. The ^1H NMR data of **1** in D_2O gave the relative proportion of PMHS to PMAA and the chemical formula of the copolymer was estimated as $(PMHS)_{12}(PMAA)_{240}$. NMR analysis might underestimate the proportion of polymerization of the polysilane block, because the region of the polysilane blocks on the block polymer has a colloidal nature.



Scheme 1

PMHS-*b*-PMAA **1**, which is soluble in water, is expected to self-assemble in water to form polymer aggregates. In fact, dynamic light scattering (DLS) studies indicated the formation of near-monodisperse micelle, with an intensity-averaged micelle diameter of 170 nm in water (0.2 g l^{-1}, 25 °C). Since the calculated length of the stretched copolymer is about 60 nm with an assumption of all *trans* conformation, the micelle may be swollen to some extent. At this stage, the possibility that **1** forms vesicles instead of micelles cannot be excluded, but the formation of spherical SCMs (*vide infra*) supports the formation of micelles. The critical micelle concentration (CMC) was found for **1** to be 8.1 × 10^{-9} mol l^{-1} as studied by the fluorescence probe method with 8-anilinonaphthalene-l-sulfonic acid (ANS) in water. The hydrophobic PMHS block should exist as the core with the hydrophilic PMAA block as the shell, since the PMHS shows UV absorption at λ_{max} 330 nm, similar to the case of PMHS-*b*-poly(2-hydroxyethyl methacrylate).[2]

Since **1** has a reactive methacrylic acid block, the shell cross-linking reaction of the polymer micelles was examined. A solution of the polymer micelles was prepared in water at a concentration high enough to allow the formation of micelles. The shell cross-linking of the carboxylic acid on the poly(methacrylic acid) block of **1** was achieved by the reaction with 1,10-diaza-4,7-dioxadecane and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride to the solution.[6]‡ After the cross-linking reaction, ^1H NMR signals of the cross linked block copolymer could not be detected in D_2O solution because of very long relaxation times due to its colloidal nature, despite the apparent solubility. Although an amount of cross-linking reagent equivalent to the methacrylic acid units was used, the proportion of the cross-linked methacrylic acid units on the block copolymer to the uncross-linked was *ca.* 50% as estimated by ^1H NMR in D_2O–THF-d_8. However, it is difficult to estimate the ratio of the cross-linking accurately. Upon addition of an excess of THF-d_8 to the solution, however, signals of the PMHS core part became observable, indicating that the PMHS block was solvated under these conditions. Interestingly, DLS studies indicated that SCM-**1** in THF was monodispersed, the intensity-averaged diameter of the particles being 230 nm. The (uncross-linked) block copolymer **1** in THF does not form particles. This fact indicates clearly the formation of SCM-**1**. These significant changes in particle size must result from the solvation of the PMHS blocks under these conditions.

Further studies supported the formation of SCMs. In the solid state CP-MAS ^{29}Si NMR of SCM-**1**, two signals were observed at δ_{Si} −27.6 and −35.7, assignable to dihexylsilylene and

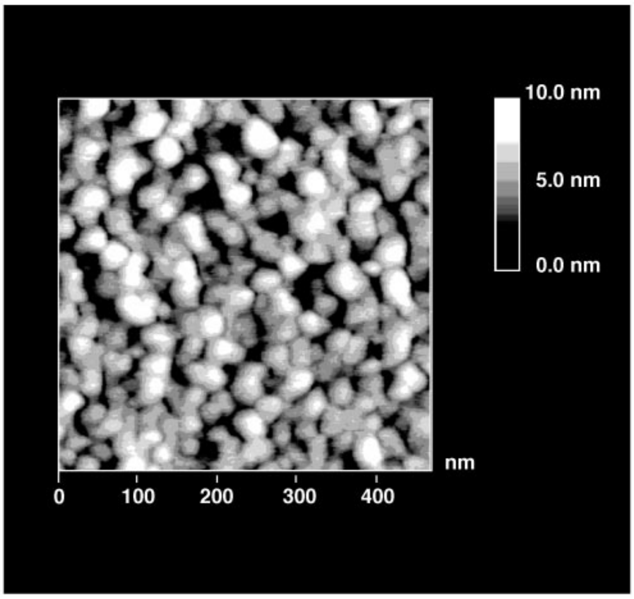


Fig. 1 AFM image of SCM-**1** film of Pyrex glass plate.

dimethylsilylene units, respectively. The IR spectrum of SCM-**1** shows absorption bands for both the carboxylic acid and the amide groups at 1710, 1631 and 1569 cm^{-1}, although that of **1** shows only the absorption band for the carboxylic acid at 1702 cm^{-1}. The DLS studies indicated the intensity-averaged diameter of the particles to be 160 nm with monodispersed spheres, which agreed very closely with the size of the original micelles composed of the block copolymer **1**.

An atomic force microscopy (AFM) image of SCM-**1** provided information on the size and shape of the shell cross-linked spheres.[7] Samples for AFM measurement were prepared by placing a drop of SCM-**1** solution in water (0.045 mg ml^{-1}) on the surface of a Pyrex glass plate and allowing it to dry in air. Fig. 1 shows the AFM image of SCM-**1** film on a Pyrex glass plate operating in the contact mode. Spherical particles of *ca.* 25 nm diameter in the dry state are clearly observed. Under the conditions, the cross-linked corona will eventually shrink onto the glassy PMHS core as the film dries. The measured radius of the dry sphere may fit the molecular length of **1**.

It is worthwhile to examine the electronic properties of the polysilanes encapsulated as the core and protected by the cross-linked hydrophilic corona, since polysilanes exhibit unique electronic spectra depending upon their conformation, which is sensitive to the environment around the chain.[8] SCM-**1** shows an absorption maximum at 333 nm, which is almost identical to those observed both in the solid state and in micelle **1**, where the PMHS block takes the *trans* conformation.[9] This indicates that the PMHS blocks form the unsolvated micelle core, with the cross-linked PMMA forming the solvated corona. In a water–THF mixed solvent, however, the absorption maximum of SCM-**1** undergoes an abrupt shift from 333 to 305 nm (Fig. 2). In THF, SCM-**1** shows an absorption maximum at 305 nm, indicating that the PMHS block takes a random-coil conformation. The (uncross-linked) block copolymer **1** in THF also shows absorption maximum at 305 nm.

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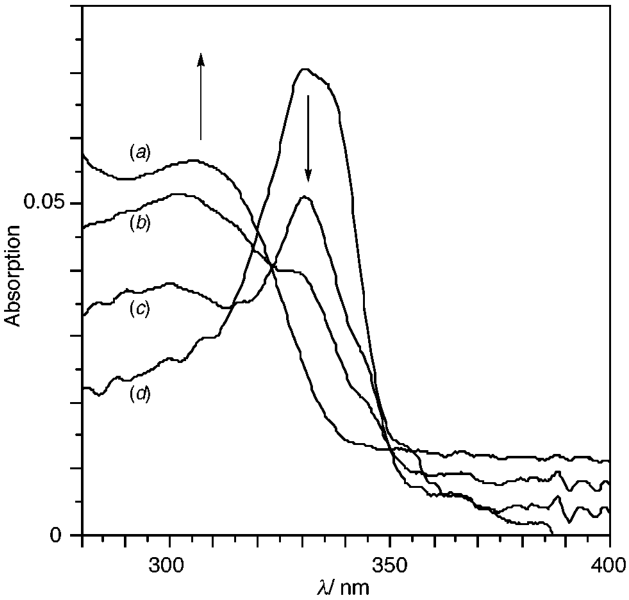

Fig. 2 UV absorption of SCM-**1** in H_2O: (*a*) 0, (*b*) 10, (*c*) 20 and (*d*) 100% H_2O.

Notes and references

† A hexane solution of BuLi (0.72 mmol) was added to 1-phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (masked disilene, 2.0 g, 4.9 mmol) and THF (20 ml) at −78 °C. The mixture was stirred for 20 min after removal of the cooling bath. After complete polymerization of the masked disilenes, trimethylsilyl methacrylate (0.77 g, 4.9 mmol) was added to the reaction mixture at −78 °C. The mixture was stirring for 2 h at −78 °C and then a few drops of 1.5 M HCl solution were added to the mixture. After removal of the solvent, fractional precipitation followed by drying *in vacuo* gave water-soluble polymer **1** as a white powder (270 mg, 15.2%). *Spectral data* for **1**: δ_{H}(D_2O, 300 MHz) 0.08 (br s), 0.87–1.26 (br), 1.78 (br s); δ_{C}(D_2O, 75.5 MHz) 17.2, 45.4, 49.2, 184.5; ν_{max}(KBr)/cm^{-1} 1702 (COOH).

‡ Synthesis of SCM-**1**: to an aqueous solution of PMHS-*b*-PMAA (100 mg in 22 ml H_2O, 4.5 mg ml^{-1}), 1,10-diaza-4,7-dioxadecane (0.18 mg, 0.21 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.23 mg, 1.20 mmol) were added at room temperature. The amount of the cross-linking reagents corresponds to 100% of the total amount of methacrylic acid units. The mixture was stirred for 1 h at room temperature and then transferred to a dialysis bag followed by dialysis against distilled water for 2 days. After drying *in vacuo*, a solid sample of SCM-**1** was obtained (90 mg, 90%). *Selected data* for SCM-**1**: δ_{H}(D_2O–THF-d_8, 300 MHz) 0.4–0.5 (br s, $SiMe_2$), 1.15–1.68 (br, $SiHex_2$, CH_3), 2.08 (br s, CH_2C); δ_{C}(D_2O–THF-d_8, 75.5 MHz) 18.6, 44.8, 54.3, 166, 177; δ_{Si}(Solid-state CP-MAS) −35.7, −27.6; ν_{max}(KBr)/cm^{-1} 3600–2500 (OH), 1710 (COOH), 1631, 1569 (NHC=O).

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