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Self-Assembled Micelles of Amphiphilic Polysilane Block Copolymers[1]

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Polysilanes[2] have been widely investigated in the past decades because of their potential use in the field of materials science. Applications of these materials require the ability to tailor the structure and composition at the nanometer level. In particular, the ability to generate systems of higher order structures such as supramolecular assemblies is very important.[3,4] Therefore, it is highly desirable to design polysilanes with such an ability to self-assemble. Very recently, a vesicle of an amphiphilic multiblock copolymer with poly(phenylmethylsilane) has been reported.[5] In this paper, we report polysilane-based micelles of amphiphilic diblock copolymer. It is extremely intriguing to examine the electronic properties of hydrophobic polysilanes in the form of core inside a hydrophilic enclosure (corona), since polysilanes exhibit unique electronic spectra depending upon their conformation, which changes with the environment.[6]

Recently, we have developed a novel method of polysilane synthesis based on anionic polymerization of masked disilenes (i.e., 1-phenyl-7,8-disilabicyclo[2.2.2]-octa-2,5-diene derivatives) to obtain polysilanes with highly controlled structures.[7] The polymer we report in this paper is poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(2-hydroxyethyl methacrylate) (PMHS-*b*-PHEMA). Poly(1,1-dimethyl-2,2-dihexyldisilene) (PMHS) was selected as the polysilane block, since this polysilane shows abrupt thermochromism in solution and also in the solid state.

First, two samples of diblock copolymers, which differ in the relative lengths of their blocks, were prepared by the anionic polymerization of the masked disilenes, followed by the second polymerization with 2-(trimethylsilyloxy)ethyl methacrylate.[8] Hydrolysis of the trimethylsilyl protecting groups gave the block copolymers, PMHS-*b*-PHEMA (Scheme 1).[9]

The copolymer **1** with a longer PHEMA, insoluble in both hexane and toluene, appears to be soluble in methanol, but forms a colloidal solution. Dynamic light-scattering (DLS) experiments of **1** in methanol indicated a monodispersed particle size distribution, the *Z*-average hydrodynamic diameter (D_h) being estimated as 50−80 nm in the concentration range of 10^{-3}−10^{-1} g/L at 20 °C. Since the calculated molecular length of **1** is about 35 nm, the copolymer should form spherelike aggregates (micelles). Indeed, static light-scattering (SLS) experiments demonstrated the shape of the aggregates to be ellipsoidal. In contrast, the copolymer **2** with longer PMHS chains dissolves in toluene but also forms aggregates. Light-scattering studies indicate **2** should form aggregates with D_h of 150 nm having a rodlike anisotropic shape at the polymer concentration of 0.046 g/L under the conditions.

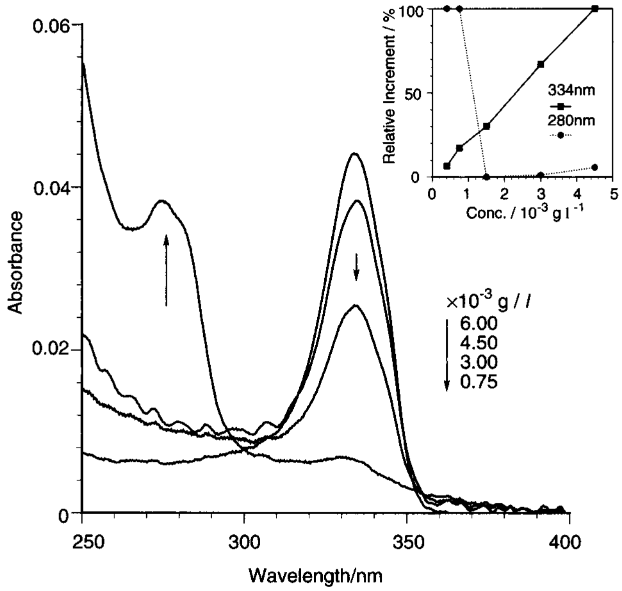
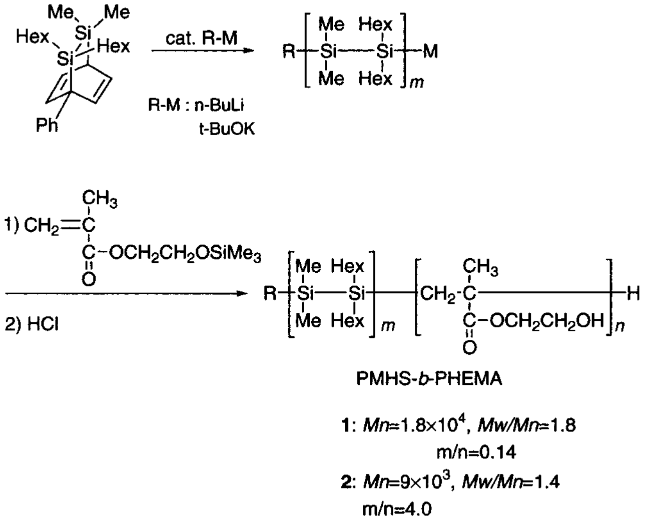


Figure 1. Concentration-dependent UV spectra of **1** in methanol. The inset shows the relative increment of absorbance at 280 and 334 nm.

Scheme 1



In UV spectra of these two copolymers, **1** in methanol exhibits λ_{max} at 334 nm while **2** in toluene shows λ_{max} at 307 nm. The absorption at 334 nm of **1** is identical to the absorption of **1** in the solid state at room temperature, where the PMHS block takes a trans conformation. These spectroscopic characteristics indicate that, in **1**, the PMHS block exists in the hydrophobic core as a solid surrounded by the hydrophilic PHEMA block while, in **2**, the PMHS block exists in a corona being exposed to toluene, a good solvent for PMHS, where the PMHS block takes a random conformation.[10]

It is interesting to examine whether these amphiphilic block copolymers show critical micellization phenomena because it is a fundamental process in colloid forma-

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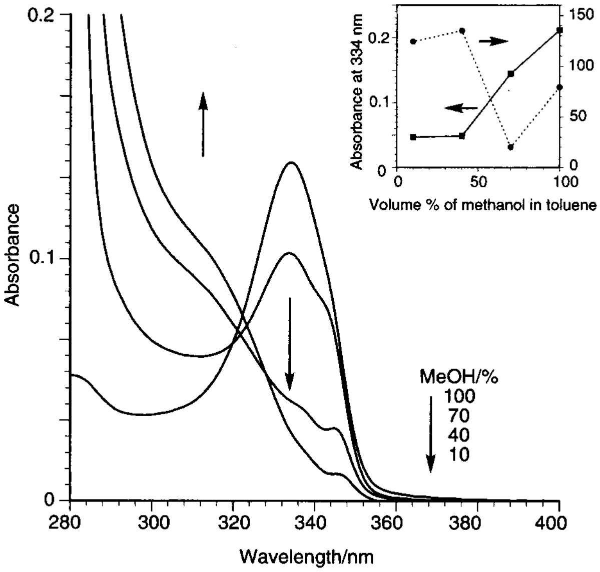

Figure 2. UV spectral change of **1** by solvent compositions of methanol and toluene. The inset shows absorbance at 334 nm and particle sizes depending on solvent composition.

tion.[11] Figure 1 shows the dependence of UV absorption of **1** on concentrations. Absorption at 334 nm due to all-trans solid states decreased upon dilution from 6.00×10^{-3} g/L and disappeared almost completely at 0.75×10^{-3} g/L with evolution of a new absorption at 280 nm due to the random coil structure. These spectral characteristics could be reasonably explained by synchronized conformational changes of the PMHS block with micelle formation. The micelle structures of **1**, with a PMHS block in the core, are maintained at concentrations down to 0.75×10^{-3} g/L and then micelles are destroyed upon further dilution to give a unimer in solution, which adopts random coil structures.[12] This particular concentration should correspond to the critical micelle concentration (cmc) under these conditions.[13]

Next, the dynamic behavior of the copolymer **1** on changing the solvent composition was studied. The absorption maximum of **1** at 334 nm in 100% methanol (0.02 g/L) decreased on addition of toluene while the concentration of the copolymer was kept constant (Figure 2). A new peak at around 310 nm started to grow as a shoulder (methanol/toluene = 70/30) when toluene was added, and then the peak grew constantly. DLS experiments indicated that the average D_h of 80 nm in 100% methanol decreased to 20 nm in a methanol/toluene (70/30) mixed solvent. Then the average D_h increased again to 140 nm on increasing the toluene proportion further (methanol/toluene = 40/60). The observed phenomena could be explained as follows: the micelles with PMHS in the core are destroyed by adding toluene and then form another aggregate with PMHS as corona (reverse micelle).

Since **1** forms kinetically frozen micelles and the component polysilane block has a glass transition temperature (T_g) higher than room temperature, it is expected that the morphology of the copolymer can be observed directly by the technique of atomic force microscopy (AFM) operating in the tapping mode.[14] Structures of the copolymer **1** in the solid film on mica coated from a methanol solution (0.043 g/L) indicated ellipsoidal structures with a size of 50−60 nm (Figure 3) in agreement with SLS experiments.[15]

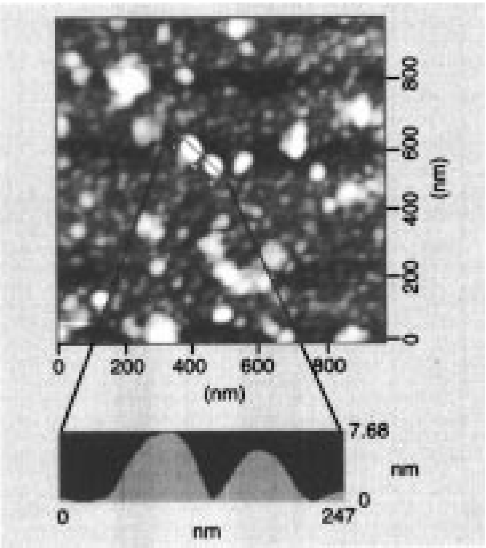

Figure 3. Tapping mode AFM images and vertical profile of **1** in the solid film on mica coated from a methanol solution (0.043 g/L).

The amphiphilic polysilane block copolymers should be important as materials for further applications as a means of controlling the nanoscale molecular organization. Further work is in progress.

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Supporting Information Available: Hydrodynamic diameter distribution in methanol (Figure 1S) and a plot of $\sin^2(\theta/2)$ vs $P^{-1}(\theta)$ in methanol (Figure 2S). These materials are available free of charge via the Internet at http://pubs.acs.org.

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(9) A typical example for synthesis of the block copolymer is as follows. In a 50 mL two-necked flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, the masked disilenes (1.02 g, 2.5 mmol) and THF (5 mL) were placed under dry argon. A hexane solution of *n*-butyllithium (0.29 mmol) was added to the solution at −78 °C. The mixture was stirred for 20 min after removal from the cooling bath. After complete polymerization of the masked disilenes, 2-[(timethylsilyl)oxy]ethyl methacrylate (0.54 g, 2.7 mmol) was added to the reaction mixture. After the reaction mixture was stirred for a day at room temperature, a few drops of 1.5 N hydrogen chloride solution were added to the mixture. After removal of the solvent, fractional precipitation followed by drying under vacuum gave soluble polymer **1** in methanol as a white powder (0.18 mg, 15%). Spectral data: ^{1}H NMR (MeOH-d_4, 300 MHz) δ 0.06 (br s), 0.6−1.7 (br), 1.7−2.2 (br), 3.69 (br s), 3.97 (br s); ^{13}C NMR (MeOH-d_4, 75 MHz) δ −0.3, 14.3, 15.4, 18.6, 24.5, 28.5, 33.6, 35.7, 47.2, 54.4, 61.5, 68.4, 179.6. This copolymer was insoluble in chloroform. We then examined the reaction with benzoyl anhydride to give benzoylated copolymer and estimated the molecular weight of **1** by SEC with polystyrene standards: $M_n = 1.8 \times 10^4$, $M_w/M_n = 1.8$.

(10) **2** shows the same abrupt thermochromism as that of the PMHS homopolymer. The absorption maximum observed for **2** at room temperature disappeared, and a new absorption at 338 nm due to the all-trans structures was generated at a temperature below −30 °C in toluene.

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(13) A referee suggested that the absorption at 334 nm attributed to micelles should extrapolate to zero relative increment at the cmc in the inset of Figure 1. However, the influence of polydispersity on the micellization of block copolymers should be taken into account. In fact, the block copolymer we report here has some relatively wide polydispersity. This fact may cause that the extrapolation did not reach to zero. For relevant discussion, see: (a) Gao, Z.; Eisenberg, A. *Macromolecules* **1993**, *26*, 7353. (b) Linse, P. *Macromolecules* **1994**, *27*, 6404.

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(15) Although the mica surface influences the morphology of aggregates deposited thereon to some extent, the existence of slightly distorted spheres must be evident.

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