

Oligosilane-Nanofibers Can Be Prepared through Fabrication of Permethyldecasilane within a Helical Superstructure of Schizophyllan

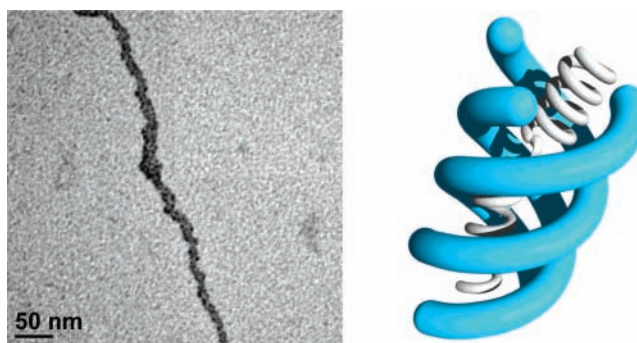
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ABSTRACT



Schizophyllan can interact with permethyldecasilane to produce the corresponding decasilane-nanofiber, in which the decasilane adopts helical conformations in a tubular hollow created by the helical superstructure of schizophyllan.

Schizophyllan (SPG, Figure 1a),¹ a natural β -1,3-glucan produced by the fungus *Schizophyllum commune*, has interesting structural features, including a reversible and solvent-induced structural transition between a triple-stranded helical structure (t-SPG) in neutral aqueous solution and individual single-stranded random coils (s-SPG) in aqueous sodium hydroxide (pH > 13).² In a series of our studies on SPG,³ we found that SPG has a one-dimensional (1D) cavity

inside its helical superstructure (Figure 1b) and accommodates various hydrophobic guests, such as π -conjugated polymers,⁴ inorganic nanoparticles,⁵ small monomers,⁶ etc.⁷ within this 1D cavity through the structural renaturation

(2) (a) Yanaki, T.; Norisuye, T.; Fujita, H. *Macromolecules* **1980**, *13*, 1462. (b) Norisuye, T.; Yanaki, T.; Fujita, H. *J. Polym. Sci. Polym. Phys. Ed.* **1980**, *18*, 547. (c) Chuah, C. T.; Sarko, A.; Deslandes, Y.; Marchessault, R. H. *Macromolecules* **1983**, *16*, 1375.

(3) Sakurai, K.; Uezu, K.; Numata, M.; Hasegawa, T.; Li, C.; Kaneko, K.; Shinkai, S. *Chem. Commun.* **2005**, *35*, 4383.

(4) (a) Numata, M.; Asai, M.; Kaneko, K.; Bae, A.-H.; Hasegawa, T.; Sakurai, K.; Shinkai, S. *J. Am. Chem. Soc.* **2005**, *127*, 5875. (b) Numata, M.; Hasegawa, T.; Fujisawa, T.; Sakurai, K.; Shinkai, S. *Org. Lett.* **2004**, *6*, 4447. (c) Li, C.; Numata, M.; Bae, A.-H.; Sakurai, K.; Shinkai, S. *J. Am. Chem. Soc.* **2005**, *127*, 4548.

(5) Bae, A.-H.; Numata, M.; Hasegawa, T.; Li, C.; Kaneko, K.; Sakurai, K.; Shinkai, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2030.

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(1) (a) Bot, A.; Smorenburg, H. E.; Vreeker, R.; Paques, M.; Clark, A. H. *Carbohydr. Polym.* **2001**, *45*, 363. (b) Saito, H.; Yoshioka, Y.; Uehara, N.; Aketagawa, J.; Tanaka, S.; Shibata, Y. *Carbohydr. Res.* **1991**, *217*, 181.

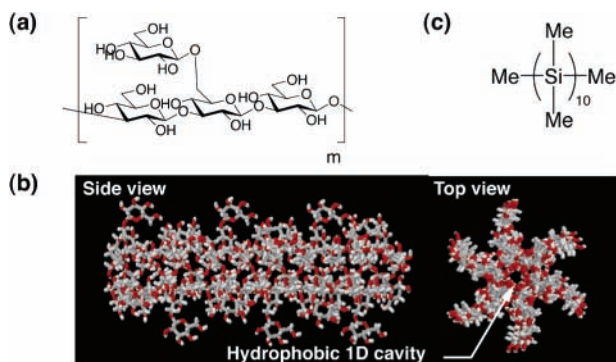


Figure 1. (a) Chemical and (b) spatial structure of t-SPG and (c) chemical structure of PMDS.

process from s-SPG to t-SPG to produce their fibrous composite superstructures. It should be noted that the renaturation process is indispensable for the guest inclusion; in fact, no composite formation is observed by direct mixing of t-SPG with the guest molecules since the hydrophobic 1D cavity of t-SPG is quite narrow (~ 0.3 nm) and entirely shielded from the solvent because of the stability and the rigidity of the t-SPG scaffold (Figure 1b). Once SPG takes the random-coiled structure (s-SPG), the 1D cavity is exposed to the solvent and the inclusion can occur during the renaturation process according to an induced-fit-type mechanism.

Oligosilanes have been investigated as attractive functional materials, since these oligosilanes have unique σ -conjugated helical structures and show unique optoelectric properties.⁸ Their fabrication using the 1D cavity of SPG would be useful for various applications, such as (1) preparation of water-soluble oligosilane composites, (2) regulation of their helical conformation, (3) fabrication of their fibrous superstructures, etc. Herein we demonstrate our successful procedure to prepare a s-SPG/PMDS composite, in which PMDS is included inside the 1D cavity of SPG.⁹ Several lines of evidence, including UV-vis, circular dichroism (CD), and fluorescence (FL) spectroscopic data along with observations using a transmission electron microscope (TEM) and an atomic force microscope (AFM), have clearly revealed that water-soluble, helically ordered oligosilane-nanofibers are formed with s-SPG through the renaturation process but definitely not with t-SPG itself.¹⁰

Because permethyldecasilane (PMDS, Figure 1c) is soluble in nonpolar organic solvents only (e.g., hexane), the simple sonication of an aqueous solution containing t-SPG and PMDS-precipitate did not induce any CD signal due to

PMDS in the UV region.¹⁰ We thus established a new biphasic procedure, based on the renaturation process of SPG, to prepare highly ordered s-SPG/PMDS composites with excellent reproducibility. In this procedure, a hexane layer containing PMDS and an aqueous NaOH layer containing s-SPG were well homogenized by sonication for 5 min. Aqueous acetic acid was then added to the resultant mixture to retrieve t-SPG. After standing at 25 °C, the two layers were separated. The hexane layer showed a broad UV absorption band with a full-width-half-maximum (fwhm) of 40 nm around 280 nm, which is characteristic of the σ - σ^* transition of flexible, random-coiled PMDS. The intensity of the 280-nm band was significantly diminished after the biphasic procedure. Detailed investigation on the concentration dependency of s-SPG indicated that the 280-nm band intensity in the hexane layer is diminished with increasing s-SPG concentration in the aqueous layer (Figure 2a).

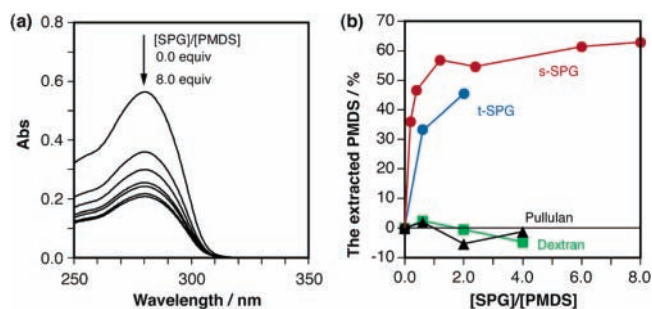


Figure 2. (a) UV absorption spectra of the hexane layer after the treatment with aqueous layers containing different amounts of s-SPG and (b) estimated percentages of PMDS extracted from the hexane layer into the aqueous one: path length 5 mm, 25 °C, [PMDS] = 0.431 mM (an original concentration in the hexane layers), [s-SPG] = 0.0–3.5 mM (0.0–8.0 equiv, an original concentration in the aqueous layers) based on their repeating units (four glucoside units for SPG and one dimethylsilane unit for PMDS).

Furthermore, a broad UV absorption band with fwhm of 37 nm at 290 nm due to random-coiled PMDS newly appears in the aqueous layers (ESI), revealing that PMDS is efficiently extracted into the aqueous layer through the interaction with s-SPG. By analyzing the 280-nm band intensity of PMDS in the hexane layer, ca. 60% of PMDS

(10) Very recently, Tanaka et al. reported a preliminary communication about formation of supramolecular structures of permethyldecasilane bearing an end-capping naphthyl group (napPMDS) by direct mixing with t-SPG: Sanji, T.; Kato, N.; Tanaka, M. *Chem. Lett.* **2005**, 34, 1114. In this case, the supramolecules afforded a narrow negative Cotton CD signal at 282 nm and a very broad UV band around 280 nm. They assigned the negative 282-nm CD band to helical napPMDS included in the 1D cavity of t-SPG. This CD band is, however, also assignable to the CD and UV bands arising from the end-capped naphthyl groups. The overlapping of π - π^* band of the naphthyl group with the σ - σ^* band of the PMDS moiety makes the discussion difficult. In addition, their data clearly conflict with our data using PMDS without the naphthyl group: in our system, no detectable CD-signal in UV region was observed for PMDS through simple sonication with t-SPG in water. Furthermore, it has been confirmed by us that the inside cavity of t-SPG is only ~ 0.3 nm, and even D₂O molecules cannot enter into this 1D cavity without the renaturation process. These data clearly indicate that the renaturation process is indispensable for the guest inclusion.

(6) Hasegawa, T.; Haraguchi, S.; Numata, M.; Fujisawa, T.; Li, C.; Kaneko, K.; Sakurai, K.; Shinkai, S. *Chem. Lett.* **2005**, 34, 40.

(7) Hasegawa, T.; Fujisawa, T.; Numata, M.; Li, C.; Bae, A.-H.; Haraguchi, S.; Sakurai, K.; Shinkai, S. *Chem. Lett.* **2005**, 34, 1118.

(8) (a) Ichino, Y.; Minami, N.; Yatabe, T.; Obata, K.; Kira, M. *J. Phys. Chem.* **2001**, 105, 4111. (b) Nakashima, H.; Fujiki, M.; Koe, J. R.; Motonaga, M. *J. Am. Chem. Soc.* **2001**, 123, 1963. (c) Peng, W.; Motonaga, M.; Koe, J. R. *J. Am. Chem. Soc.* **2004**, 126, 13822.

(9) Shinkai, S. 11th Asian Chemical Congress, Seoul, August 22–25, 2005.

was efficiently extracted into the aqueous layer at the high s-SPG concentration (Figure 2b). It should be noted that the similar extraction efficiency is already attained with a comparable s-SPG molar concentration to PMDS ([s-SPG]/[PMDS] = 1.2, based on their repeating units), suggesting formation of a composite with 1:1 stoichiometry (s-SPG/PMDS). The 1:1 stoichiometry was also confirmed through a much detailed stoichiometric analysis of the composite, as described in ESI.

To clarify the detailed mechanism of the SPG–oligosilane interaction, additional experiments using other polysaccharides (pullulan and dextran, Figure 2b) were carried out. No detectable extraction of PMDS into the aqueous layer was observed for other polysaccharides, indicating that the specific structural feature (the 1D cavity) of SPG rather than the general polyol structure plays indispensable roles in the extraction. The fact that t-SPG extracted a small amount of PMDS into the aqueous layer compared to s-SPG suggests the presence of the minimal intermolecular interaction between PMDS and t-SPG. This interaction mechanism, however, appears to be much different from that of the s-SPG/PMDS composite, because no detectable CD-signal was observed for the t-SPG/PMDS composite (see the following paragraph).

Although the resultant aqueous layer containing s-SPG/PMDS composites showed a broad UV absorption band with fwhm of 37 nm around 290 nm, no detectable CD signal was observed at this wavelength. These spectral features suggest that PMDS adopts a flexible, random-coiled conformation in the 1D cavity of SPG. From ^1H NMR analysis of the aqueous layer (in D_2O), a large amount of hexane was found to be extracted into the aqueous layer by s-SPG. Combined with the tolerance of s-SPG toward various hydrophobic guest molecules, PMDS and hexane are assumed to be co-included within the 1D cavity of SPG. The co-included hexane molecules should (1) give sufficient space for random coiled PMDS and (2) greatly reduce certain chiral interaction between PMDS and SPG (Figure 3). To confirm

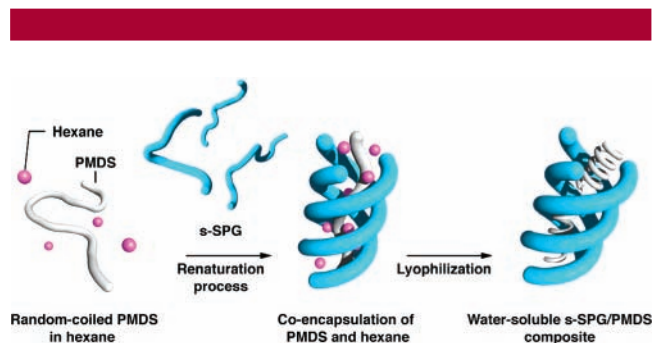


Figure 3. Schematic illustration of the composite formation of s-SPG with PMDS.

our idea, the hexane was removed by lyophilization of the aqueous layer containing the s-SPG/PMDS composite, followed by redissolution of the resultant s-SPG/PMDS composite into water. The resultant aqueous solution showed a

sharp UV absorption band at 290 nm with a narrow fwhm of 12 nm and bisignate CD signals (positive at 283 nm and negative at 293 nm) (Figure 4a, red lines). The small fwhm

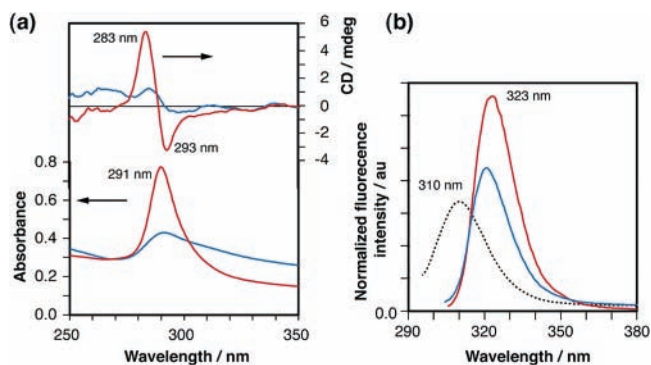


Figure 4. (a) UV (bottom) and CD (top) and (b) FL spectra of the s-SPG/PMDS composite in water (Ex = 290 nm, red solid line), the t-SPG/PMDS composite in water (Ex = 290 nm, blue solid line) and free PMDS in hexane (Ex = 280 nm, black dotted line). [s-SPG]/[PMDS] = 1.2 in molar ratio, path length 5 mm, and 25 °C.

of this UV band suggests a very rigid, extended conformation of PMDS in the s-SPG/PMDS composite.¹¹ The origin of the bisignate CD spectral profile indicates two possibilities: (1) a mixture of two different helices with the opposite (*P* and *M*) screw senses and different pitches and (2) exciton couplet due to chirally twisted PMDS aggregates. Kunn's dissymmetry ratio (defined as $g_{\text{abs}} = \Delta\epsilon/\epsilon = \text{CD (in mdeg)}/32980/\text{Abs}$), which is a dimensionless parameter to semi-quantitatively characterize helical structures of oligosilanes and other chromophoric chiral molecules, excludes the latter case, because the evaluated g_{abs} values at two extrema are $+3.3 \times 10^{-4}$ at 283 nm and -1.7×10^{-4} at 293 nm, respectively. The absolute magnitude in these small g_{abs} values is almost comparable with the g_{abs} value of $(2.0-2.5) \times 10^{-4}$ at 323 nm of rigid rodlike polysilane with a single-screw helix. PMDS incorporated in the helical cavity of s-SPG, therefore, exists as a mixture of diastereomeric helices with the *P*- and *M*-screw senses: the 283-nm CD signal is responsible for a *P*-7₃ helix and the 293-nm CD signal is for an *M*-15₇ helix.¹¹ The inclusion of PMDS in the 1D cavity of SPG is also supported by its UV and CD characteristics, because these spectral features are very similar to those for the γ -cyclodextrin(γCD)/PMDS composite, in which a PMDS molecule threads several γCD molecules to form a necklace-like composite (for detailed discussion, see ESI).¹² On the other hand, the t-SPG/PMDS composite showed a broad UV absorption with fwhm of 26 nm around 290 nm and quite weak CD signals even after lyophilization (Figure 4a, blue lines). The marked difference between t-SPG/PMDS and s-SPG/PMDS indicates that (1)

(11) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 6017.

(12) Okumura, H.; Kawaguchi, Y.; Harada, A. *Macromolecules* **2003**, *36*, 6422.

the t-SPG/PMDS composite still adopts disordered structures and the s-SPG/PMDS composite adopts rodlike helical structures and (2) the formation mechanisms of the composites are much different from each other.

The s-SPG/PMDS composite in neutral aqueous solution showed an intense red-shifted FL band with fwhm of 18 nm at 323 nm when excited at the $\sigma-\sigma^*$ transition band (280 nm), compared to the corresponding FL band at 310 nm of free PMDS in hexane (Figure 4b). Although the similar red shift (~ 13 nm) was also observed for the t-SPG/PMDS composite, the FL intensity of the s-SPG/PMDS composite is much enhanced, suggesting that (1) molecular motion of the included PMDS is greatly restricted in the s-SPG/PMDS composite and (2) the PMDS molecules are highly insulated from each other by fabrication with s-SPG rather than with t-SPG. These UV/CD/FL spectroscopic studies led us to conclude that the renaturation process is inevitable to produce the highly ordered s-SPG/PMDS composite, while direct formation using t-SPG is impossible.

TEM observation of the s-SPG/PMDS composite showed a fibrous architecture (Figure 5a). In this case, the s-SPG/

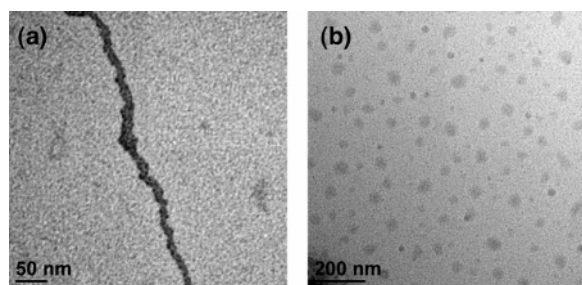


Figure 5. TEM images of (a) SPG/PMDS composite after a treatment with phosphotungstic acid and (b) free PMDS.

PMDS composite was prepared according to the biphasic procedure followed by the purification through centrifugation. This fibrous superstructure of the s-SPG/PMDS composite is in sharp contrast to the small dot-like morphology of free PMDS (Figure 5b). No such fibrous superstructure can be obtained by the same treatment with such polysaccharides as dextran and pullulan.

AFM observation of the s-SPG/PMDS composite on mica showed a network superstructure (Figure 6).¹³ This network

(13) The samples contain s-SPG/PMDS composite and free SPG. Both entities are well-visible in AFM images; however, free SPG gives only low-contrast and barely visible pictures in TEM images. This should be a main reason the TEM and the AFM images look very different from each other.

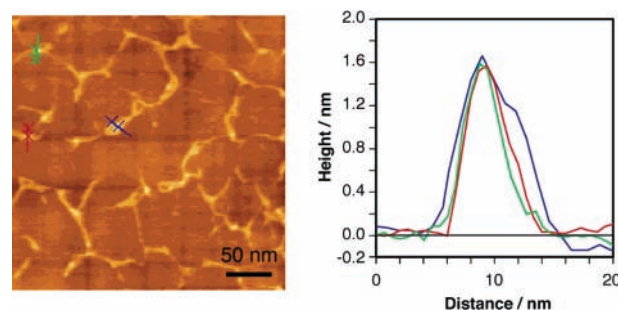


Figure 6. (Left) AFM image and (right) cross sectional profiles along red, blue, and green lines in the AFM image: the s-SPG/PMDS composite on mica substrate.

structure is much different from the dot-like structure of free PMDS (Figure 6). Although the similar network structure was observed for free SPG (ESI), the detailed investigation revealed a clear difference between the two systems: the nanofibers made of the s-SPG/PMDS composite have enhanced height in the AFM image along its network structures. This finding shows a clear contrast to free SPG having the network structure with lower height. From cross-sectional analysis, the s-SPG/PMDS composite was revealed to have ca. 1.6 nm in height, whereas free SPG has 1.0 nm in height. The difference in height of 0.6 nm corresponds to the molecular diameter (ca. 0.6 nm) of PMDS, supporting a PMDS single strand incorporated in the 1D cavity of s-SPG.

In conclusion, we demonstrated formation of insulated PMDS-nanofibers by inclusion of PMDS within the 1D cavity of SPG. In addition, it is evident that the insulated PMDS-nanofibers can be obtained by the renaturation process only and not by direct interaction with t-SPG.¹⁰ Our facile approach has a great advantage to further develop oligosilane-based nanofibers that may serve as a potent optoelectronic material in the forthcoming age.

Acknowledgment. We thank Mitsui Sugar Co. (Tokyo, Japan) for providing SPG samples. This work was supported by Japan Science and Technology Agency, SORST Program.

Supporting Information Available: Detailed description for the biphasic procedure, stoichiometric analysis of the composite, UV spectra of the aqueous layer before the lyophilization, spectral comparison between the SPG/PMDS composite and the γ CD/PMDS composite, and an AFM image of free SPG. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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