Schizophyllan Can Act as a One-dimensional Host to Construct Poly(diacetylene) Nanofibers

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Schizophyllan binds 1,4-bis(*p*-amidophenyl)butadiyne and acts as a one-dimensional host to produce fibrous polydiacetylene assemblies through UV-irradiation.

π-Conjugated polymers (poly(acetylene)s, poly(diacetylene)s, poly(phenylenethynylene)s, etc.) have received increasing interests because of their potential utility as conductive wires in nanoscale electric circuits of comming age.[1] Especially, poly(diacetylene)s are of quite interest, since it is readily produced through UV-irradiations without any additives such as catalysts. However, simple polymerization of the corresponding monomers usually results in amorphous, morphologically uninteresting polymer aggregates. It is therefore strongly desired to establish easy and general strategies to construct their morphologically controlled assemblies, e.g., fibrous ones, in which individual polymers are aligned in a parallel fasion. Such fibers are expected to have an excellent conductivity through the long axis and should be therefore useful as molecular wires. Many reseach groups have placed their intense researh efforts on producing such fibrous assemblies of poly(diacetylene)s, mainly utilizing rod-like self-assemblies of the amphiphilic monomers.[2]

Schizophyllan (SPG, Chart 1a) is a β-1,3-glucan having a β-1,6-glucoside-appendage at every three repeating units. The most interesting features of SPG include a reversible transition between a triple-straded helix (t-SPG) in water and a single-stranded random coil (s-SPG) in dimethylsulfoxide (DMSO).[3] Recently, we found that SPG interacts with various hydrophobic polymers (single-walled carbon nanotube,[4] polyaniline,[5] etc.) by mixing s-SPG (in DMSO) with these polymers (in water) to form unique macromolecular complexes, in which the hydrophobic polymers are encapsulated within a tubular hollow constructed by the helical superstructure of SPG. We expected, therefore, that SPG would accommodate not only aforementioned polymers but also small hydrophobic monomers and would act as a "one-dimensional (1-D) host" to produce fibrous polymer assemblies. Herein, we report one of such examples that SPG accommodates amido-functionalized 1,4-diphenylbutadiyne (**1**,[6] Chart 1b) to produce nanofibers composed of the corresponding π-conjugated polymers through UV-irradiation (Figure 1).

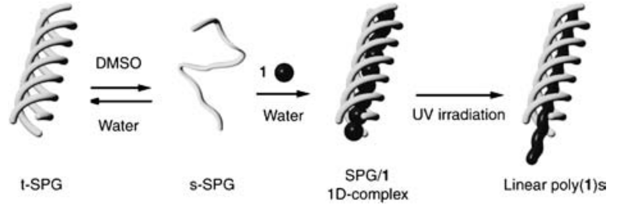

Figure 1. Schematic illustration of our concept to use SPG as a 1-D host to construct poly(diacetylene) nanofibers.

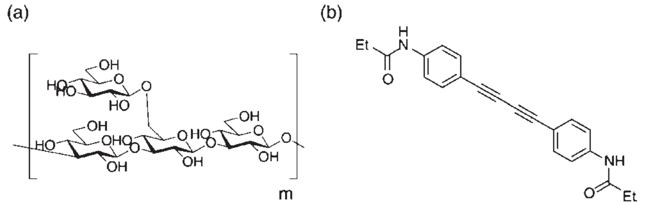

Chart 1. Chemical structures of (a) SPG and (b) **1**.

A DMSO solution containing s-SPG ($M_w = 150\,\text{kDa}$) and **1** was diluted with water to regenerate a t-SPG helical structure ($[H_2O] = 70\,\text{v/v}\,\%$). Although **1** was hardly soluble by itself in this solution system, the resultant slightly-turbid solution showed a clear circular dichroism (CD) spectrum, in which a negative CD exciton-coupling (260–600 nm) assignable to an absorption band of **1** was observed (Figure 2a). Together with the fact that SPG or **1** themselves gave no CD signal at this wavelength region, this negative CD exciton coupling is indicative of twisted conformations or packings of **1** arising from the strong interaction with SPG.

To clarify the detailed mechanism of the interaction, we carried out some referential experiments as follows. 1) DMSO contents of the resultant solution have a critical impact on the CD spectrum (Figure 2b). The CD signal was observed only under water-rich conditions ($[H_2O] = 60\text{–}99\,\text{v/v}\,\%$), suggesting that not hydrogen-bonding but hydrophobic interactions play major roles for the complexation. 2) Furthermore, no or negligibly weak CD signal is observed in our referential experiments using other polysaccharides (amylose, pullulan, and dextran), also supporting our assumption that hydrogen bondings are not main driving force for the interaction (Figure 2a). 3) Finally, when we mixed t-SPG (in water) with **1** (in DMSO), the resultant solution gave no CD signal, indicating that the structural transition from s-SPG to t-SPG is essential for the interaction. This last finding is of quite interest since it implies that **1** locates inside the helical structure of renascent t-SPG (if **1** interacts with the outer surface, the structural transition is unnecessary for the interaction), although we can not exclude a possibility that **1** locates at grooves of the helical structure of SPG.

UV-irradiation using a high pressure Hg lamp induced a gradual color change of the solution containing SPG/**1** complex from colorless to pale blue (It is visibly detectable as shown in our graphical abstract).[9] The UV–vis spectrum of the resultant solution shows an absorption band at around 720 nm which is characteristic of poly(diacetylene)s with extremely long π-conjugated length and/or tight interstranded packings.[8,9] UV-mediated polymerization of **1** was also confirmed by Raman spectra

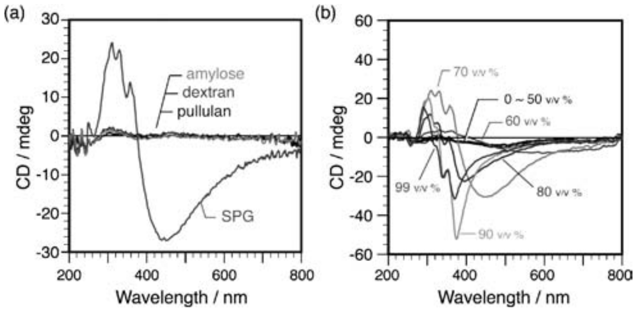

Figure 2. (a) CD spectra of **1** in the presence of SPG, amylose, dextran, or pullulan, and (b) CD spectra of **1** in the presence of SPG under various aqueous DMSO solutions with different water contents: $d = 1.0\,\mathrm{cm}$, 20 °C, $[\mathrm{H_2O}] = 70\,\mathrm{v/v}\,\%$, $[\mathbf{1}] = 25\,\mu\mathrm{g\,mL^{-1}}$, $[\mathrm{SPG}] = 25\,\mu\mathrm{g\,mL^{-1}}$, 24 h after sample preparation.

(Figure 3b), in which SPG/**1** complex shows a clear peak at $2000\,\mathrm{cm^{-1}}$ assignable to poly(diacetylene)s (–CH=CH– streching vibration) after 16-h UV irradiation.[9] On the contrary, no such Raman peak appeared without SPG. Together with the fact that UV-mediated polymerization of diacetylenes proceeds in a topochemical manner, these data suggest that SPG accommodates **1** to align them in a packing suitable for such topochemical polymerization.[10] It should be noted that *p*-amido-functionalities of **1** are essential for the UV-mediated polymerization. 1,4-Diphenylbutadiyne with SPG showed a CD spectrum with much small intensity (ca. 1/4 times in comparison to that of **1**) and no UV-mediated polymerization was induced. We assume that the *p*-amido-functionalities should form supporting hydrogen bonds with SPG and/or neigboring monomers to orientate the monomers in the suitable packing for the polymerization.

Transmittance electron microscopic (TEM) observations showed that the resultant SPG/poly(**1**)s complex has a fibrous structure (Figure 4a) with diameters ranging from 2 to 20 nm. On the other hand, no such fibrous assembly was observed without SPG (data not shown). We also confirmed that neither carbohydrate-based surfactant (dodecyl-β-D-glucoside) nor other single-stranded polysaccharides (amylose, dextran, pullulan, etc.) can produce such nanofibers (Figures 4b and 4c, respectively). These data clearly emphasize an advantage of SPG as a 1-D host to produce the nanofibers. Energy dispersive X-ray (EDX) spectroscopic analysis of the nanofibers also showed a large amount of oxygen, suggesting that SPG still coexists around poly(**1**) nanofibers (Figure 4d).

In conclusion, *p*-amido-functionalized 1,4-diphenylbutadiyne (**1**) can be polymerized in the presence of SPG to produce fibrous assemblies of the corresponding polymers through UV irradiation, in which SPG acts as a 1-D host. Our research efforts are now focused on the assessment of the conductivity through these fibers.

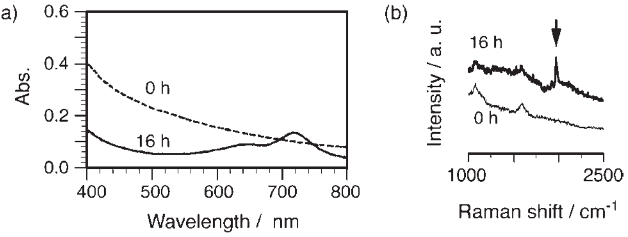

Figure 3. (a) UV–vis spectra of **1** in the presence of SPG before (0 h) and after (16 h) UV irradiation: $[\mathbf{1}] = 25\,\mu\mathrm{g\,mL^{-1}}$, $[\mathrm{SPG}] = 25\,\mu\mathrm{g\,mL^{-1}}$, aqueous DMSO ($[\mathrm{H_2O}] = 70\,\mathrm{v/v}\,\%$), and (b) Raman spectra of **1** in the presence of SPG before and after UV irradiation: cast films.

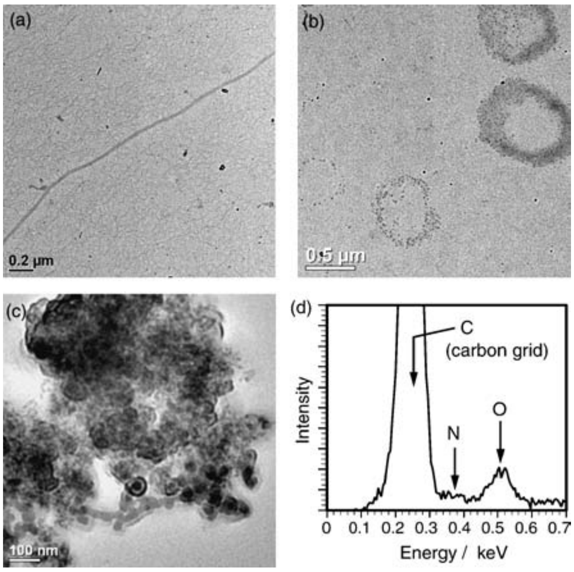

Figure 4. TEM images of poly(**1**)s in the presence of (a) SPG, (b) dodecyl-β-D-glucoside, or (c) amylose and (d) EDX spectrum of the nanofiber.

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