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β-1,3-Glucan (Schizophyllan) Can Act as a One-Dimensional Host for Creation of Novel Poly(aniline) Nanofiber Structures

Munenori Numata,[†] Teruaki Hasegawa,[†] Tomohisa Fujisawa,[†] Kazuo Sakurai,[‡] and Seiji Shinkai*,[†]

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, 812-8581, and Department of Chemical Processes and Environments, Faculty of Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Wakamatu-ku, Kitakyushu, Fukuoka, 808-0315.

seijitcm@mbox.nc.kyushu-u.ac.jp

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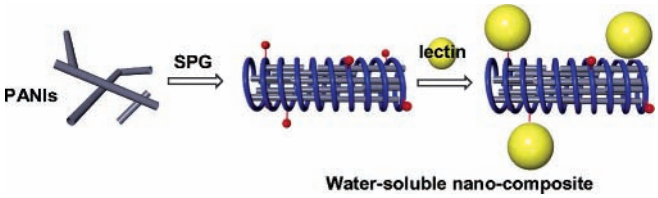
ABSTRACT



We here demonstrate the creation of novel poly(aniline) (PANI) nanofiber structures by a polymer wrapping method using schizophyllan (SPG). Mannose-modified SPG can also wrap PANIs to give nanofibers having a lectin affinity. This interaction is applicable to designing novel PANI/protein composites. The results establish that SPG can act as a novel "host" to assemble PANIs into one-dimensional superstructures.

Schizophyllan (SPG) is a natural polysaccharide produced by the fungus *Schizophyllum commune*, and its repeating unit consists of three β-(1−3) glucoses and one β-(1−6) glucose side chain linked at every third main-chain glucose. SPG adopts a triple helix (t-SPG) in nature, which is stabilized by the hydrogen-bonding interaction among 2-OH groups, but can be dissociated into a single chain (s-SPG) by dissolving in dimethyl sulfoxide (DMSO).[1] The s-SPG chain can retrieve the original triple helix by exchanging DMSO for water. It is already known that the 2-OH side along the main-chain glucoses is more hydrophobic, whereas the 6-OH or the side glucose face is more hydrophilic (Figure 1).[2] Therefore, when s-SPG retrieves its original triple helix, the hydrophobic surface is always located inside the triple helix and the resultant t-SPG is covered by the hydrophilic surface. Considering the structural characteristics of the SPG chain, one may imagine that the one-dimensional hydrophobic cavity is created inside the SPG triple helix, like a one-dimensional cyclodextrin array.[3] It thus occurred to us that when the renaturating process from s-SPG to t-SPG is carried out in the presence of hydrophobic polymers, they may be entrapped in the cavity with the aid of hydrophobic force to give a novel nanocomposite that has a unique one-dimensional structure. Recently, we applied this idea to single-walled carbon nanotubes and found that SPG can include them inside the helical structure during the renaturating process.[4]

Poly(aniline) (PANI) is one of the most promising conducting polymers due to its chemical stability, low cost, high conductivity, and unique redox properties.[5,6] The recent research focus on PANIs has been directed toward the construction of PANI-based nanofibers because they are readily applicable to electronic nanowires or sensors. In

[†] Kyushu University.
[‡] The University of Kitakyushu.

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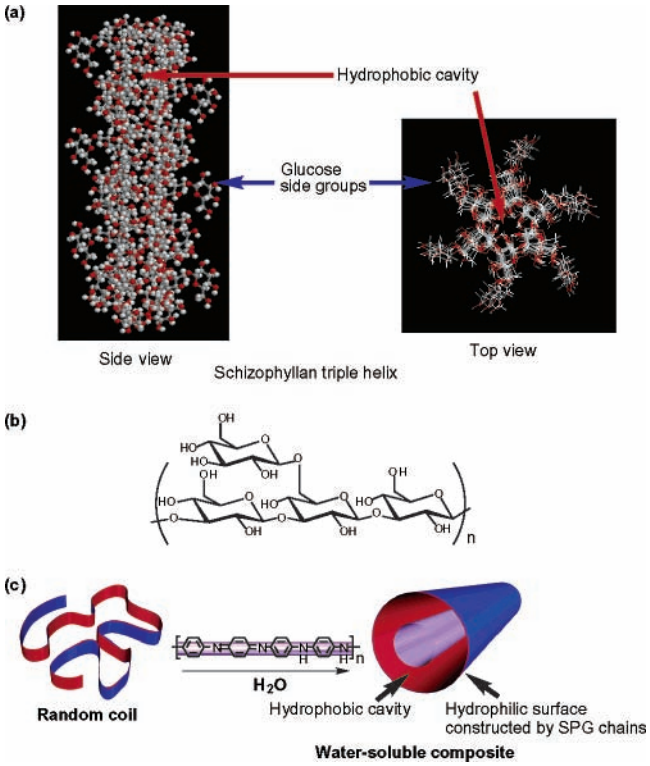

Figure 1. (a) Representive models of SPG triple helix, (b) repeating unit of SPG, and (c) entrapping of PANIs into SPG hydrophobic cavity during the renaturating process.

particular, the water-soluble nanofibers sustaining molecular recognition groups have been expected to become a new potential source of biological sensors because most biological interactions occur in aqueous solution.[7,8] A few groups have demonstrated chemical modification of PANIs such as grafting of water-soluble groups,[9,10] but few examples have so far been reported for the creation of PANI-based water-soluble nanofibers and introduction of molecular recognition groups into them.

Here, we report our new findings that the polymer wrapping by SPG can be an alternative approach toward creation of water-soluble and functionalized PANI nanofibers, where SPG acts not only as a solubilizer into water but also as a one-dimensional aligner for PANIs.

To differentiate the ability of SPG over others, several kinds of polysaccharides were tested for the reference experiments. A DMSO solution of PANIs (1.0 g L^{-1}, emerardine base, MW = 10 000) was mixed with a DMSO solution containing polysaccharide (5.0 g L^{-1}, MW = 150 000 for s-SPG, 15 000 for amylose, 70 000 for dextran, and 200 000 for plullan and starch). At this stage, the mixed solution contained 200 μg of PANIs and 1.0 mg of polysaccharide. To the resultant DMSO solution, water was gradually added with stirring to avoid the precipitation of PANIs. The final composition of water/DMSO (v/v) was adjusted to 95/5 (v/v). After the mixture was left for 2 days, it was treated with a centrifuge (7000 rpm) for 1 h and the supernatant, which contains unreacted s-SPG, was pipetted off. The precipitated polysaccharide/PANI complexes were then dispersed into water (200 μL). Repeating this process three times, the excess s-SPG was removed and the solvent was replaced by water. We found that SPG and amylose give a homogeneous aqueous solution, whereas other polysaccharide samples result in precipitation. Moreover, we confirmed that SPG can solubilize PANIs as much as 400 μg mL^{-1}, whereas amylose solubilizes it up to 100 μg mL^{-1}. These results indicate that SPG is the best solubilizer among polysaccharides tested herein. As a reference experiment, we prepared a mixed solution containing PANIs and t-SPG instead of s-SPG. However, the mixture resulted in the PANI precipitation. These findings imply that the renaturating process from s-SPG to t-SPG is a key step in which PANIs are entrapped in the hydrophobic one-dimensional cavity. Furthermore, the obtained SPG/PANI composite was easily doped by the HCl treatment (pH = 2) and the resultant solution was stable for several weeks. On the other hand, the amylose/PANI composite resulted in precipitation after 24 h under the same treatment (Figure S1, Supporting Information).

The SPG/PANI composite was characterized by spectroscopic and microscopic measurements. To differentiate the characteristic feature of the SPG/PANI composite, we always used the amylose/PANI aqueous solution as a reference. Figure 2 shows the UV−vis spectrum of SPG/PANI aqueous solution. In Figure 2a, two characteristic absorption bands are seen at 311.6 and 606.6 nm, which are basically similar to those reported for the water-soluble PANI spectra.[11] The result clearly supports the fact that PANIs are solubilized in water with the aid of SPG. The amylose/PANI solution also gives similar absorption bands at 312.2 and 613.4 nm. Comparison of these two spectra in Figure 2a reveals that blue and hypsochromic shifts are induced in the SPG/PANI composite. The slight but significant shifts are attributed to the intermolecular stacking among PANI fibers.[12] These

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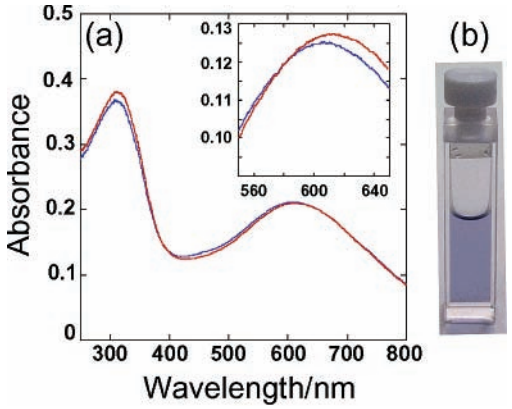

Figure 2. (a) UV−vis spectra of SPG/PANI (blue line) and amylose/PANI (red line) aqueous solution, room temperature, cell length 0.5 cm. (b) Photo image of SPG/PANI aqueous solution.

results suggest that the bundle of PANI fibers is tightly entrapped in the one-dimensional cavity of SPG, resulting in the one-dimensionally aligned PANI fiber structure.

To obtain further evidence that SPG interacts with PANIs, we carried out CD measurements. From the CD spectra shown in Figure S2 (Supporting Information), we confirmed that the SPG/PANI solution gives a positive Cotton effect at 370 nm and a negative Cotton effect at 330 nm. As a reference experiment, we mixed an aqueous solution containing t-SPG with PANIs. However, the mixture did not give any CD signal around the same wavelength region. This result also supports the view that the renaturating process is indispensable for the effective interaction between SPG and PANIs.

The morphology images of these composites were obtained by TEM and SEM. Figure 3 shows the TEM images of the

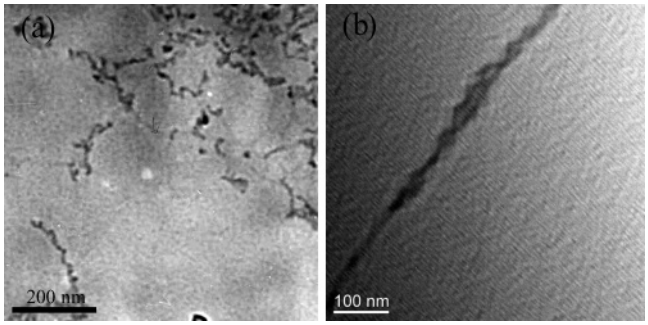

Figure 3. (a) TEM images of SPG/PANI composites and (b) a magnified image of a. The images were taken without staining. PANIs themselves afforded massive, spherical aggregates.

SPG/PANI composite (for SEM, see Figure S3, Supporting Information). Although the pictures were taken without staining, one can recognize many shadowed fibers, the length of which is consistent with that of SPG (200 nm) but the morphology of which is totally different from SPG itself and PANIs themselves. The coincidence supports the view that PANI fibers are arranged one-dimensionally through the SPG wrapping process. The diameter of the composite is estimated to be 10−15 nm, indicating that the PANI bundle consisting of several pieces is included in the SPG tubular cavity. This morphology was scarcely changed by the HCl treatment (pH = 2). In contrast, the amylose/PANI composite did not give any significant specific structure (Figure S4, Supporting Information). From these TEM images, we can conclude that the difference in the higher-order morphology between SPG and amylose determines the final solubility and aggregate structure of the composites.

When the PANI fibers are entrapped in the SPG cavity, one may presume that the 2-OH side of the main-chain glucose would interact with PANIs, whereas the side group glucose does not participate in such an interaction. If this is the case, one would expect that a functional group introduced into the side group glucose would be useful as a recognition target because it should exist on the surface of the composites.[13] To test this idea, we prepared the PANI composite using mannose-modified SPG[13a] and used it as a wrapping reagent. It is known that this mannose group exhibits selective binding to Concanavalin A (ConA). The specific interaction between the composite and ConA was estimated by a confocal laser scanning microscopy (CLSM) using a FITC-labeled ConA. The result (shown in Figure 4) indicates

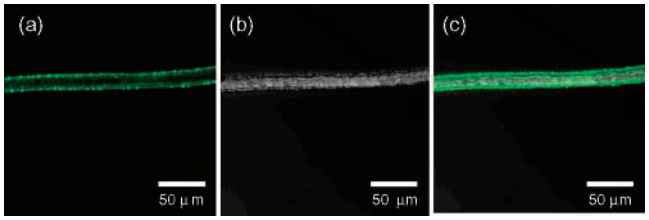

Figure 4. CLSM images of mannose-modified SPG/PANI composite + FITC−ConA: (a) fluorescence image, (b) optical microscope image, and (c) overlap of a and b.

that FITC−ConA gives green fluorescence under UV light irradiation, whereas PANIs appear as black shadow under the optical microscope observation (Figures 4a and 4b, respectively). As shown in Figure 4c, the green fluorescence in Figure 4a and the black shadow in Figure 4b are perfectly overlapped, indicating that PANIs and ConA coexist in the same domain.[14] The results indicate that (1) mannose-modified SPG can also wrap PANIs and (2) the mannose

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(14) Selective interaction was also confirmed by AMF measurements (see Figure S5, Supporting Information).

groups introduced into the side groups would exist on the exterior surface of the composite.

In conclusion, we have demonstrated that creation of the novel water-soluble PANI nanofibers is possible by utilizing the polymer wrapping technique. The findings clearly show that SPG has potential as a one-dimensional host and suggest future applications to arrange PANI bundles in a desired orientation by using a recognition group introduced into SPG. These systems would be readily applicable to sensors, nanocomposites, catalysts, etc.

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Supporting Information Available: UV−vis spectra of SPG/PANI composites after doping, CD spectra and SEM images of SPG/PANI composites, TEM images of amylose/PANI composites, and AFM images of mannose-modified SPG/PANI composites after addition of ConA. This material is available free of charge via the Internet at http://pubs.acs.org.

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