Polyrotaxane Hexagonal Microfiber

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How can we prepare a polymer with a well-defined three-dimensional structure on a micrometer scale? We are reporting a method of inclusion complex formation followed by slow recrystallization of the complex. Polyrotaxanes are self-assembled supramacromolecules consisting of host molecules and threaded guest molecules. Cyclodextrins, cucurbiturils, and porphyrines are extensively investigated as host molecules for their specific assembled structure and potential applications such as molecular motors, molecular wires, molecular electronics, and catalysts and for separation purposes.[1−5] In particular, inclusion complexes of poly(ethylene glycol)s (PEGs) and α-cyclodextrin (α-CD) have been attracting attention as a microtubule mimicking system.[6] However, the main issue has been one-dimensional so far; that is, the threading process and threading materials focused on the size of guest molecules to match to the pore of cyclodextrin (CD).[7] Even though a channel-type crystal structure has been suggested for α-CD/polymer inclusion complexes due to the large molecular weight of the polymeric guest,[8] there is no report to show such a channel structure on a micrometer scale. Here, we report the proliferation of α-CD/PEG hexagonal unit cells on a micrometer scale by recrystallizing the α-CD/PEG inclusion complex in water.

The inclusion complex of cyclodextrins with polymers was reported for the first time on the PEG and α-CD in 1990.[9] There are three types of cyclodextrins with different pore sizes. α-CD, β-CD, and γ-CD have pore radii of 0.49, 0.62, and 0.79 nm, respectively. Considering the pore size, α-CD forms inclusion complexes with PEG, polycaprolactone, polyethylene, poly(tetramethylene glycol), and poly(ϵ-lysine).[7] β-CD can form inclusion complexes with polymers with large pendant groups such as poly(propylene glycol) and poly(*N*-isopropylacrylamide), whereas γ-CD can form inclusion complexes with polyisobutylene and double strands of PEG due to their larger pore size.[6,7] The main driving forces are the hydrophobic interactions and hydrogen bonding between host and guest molecules. In the inclusion complex, the 3- and 5-hydroxyl groups of the α-CD are oriented toward the guest molecules inside of the cavity, whereas 1-, 2-, and 4-hydroxyl groups oriented outside the cavity. The yield of an inclusion complex formation between PEG and α-CD depends on the molecular weight of the PEG. As for the short PEG length, the inclusion−exclusion equilibrium is fast, and the net result is the small yield of inclusion complex formation. At the high molecular weight of PEG, the probability for α-CD to find PEG ends is low, and the yield of inclusion complex formation is small in a given time. Therefore, the intermediate molecular weight of PEG of about 1000−3000 Da can form an inclusion complex with α-CD with a high yield in a given time.

We prepared a well-defined three-dimensional structure of α-CD and PEG complex by recrystallizing the inclusion complex. The inclusion complex is prepared by adding the PEG (molecular weight 2000 Da) aqueous solution (5.0 wt %, 2.0 mL) to the saturated aqueous solution (14.5 wt %, 2.0 mL) of α-CD under sonication for 3 min by a homogenizer. The inclusion complex was separated by centrifugation, followed by a freeze-drying process. The inclusion complex was recrystallized in water at room temperature. Before the recrystallization, inclusion complex showed a plate-to-needle shape (IC-1 in Figure 1). After the recrystallization, hexagonal fibers with 2 μm in side and larger than 5 μm in height were formed. The hexagonal microfiber formation was pronounced when the recrystallization was carried out at room temperature in phosphate buffer (10 mM) (IC-2 in Figure 1). The hexagonal microfiber was also confirmed for the inclusion complex recrystallized in the deionized water (Supporting Information: SEM image (Figure S-1)).

The X-ray diffraction (XRD) pattern (Figure 2) of IC-2 is the same as that of IC-1, except for additional reflections due to the crystalline phase of phosphate buffer used in recrystallization of the inclusion complex. The X-ray patterns of IC-1 and IC-2 phase are the same as previously reported.[10] The strong reflection at $2\Theta \approx 20.0$ is characteristic of α-CD molecules representing a channel-type structure with a radius of about 5 Å. The common reflections of IC-1 and IC-2 phase could be indexed corresponding to a hexagonal unit cell with $a = 13.17 \pm 0.02$ Å, $c = 15.27 \pm 0.02$ Å for IC-1 and $a = 13.90 \pm 0.02$ Å, $c = 17.85 \pm 0.02$ Å for IC-2.

In addition, the hexagonal unit cell structure coincides with the information from electron diffraction (Supporting Information: Figure S-2).

The infrared spectra of the inclusion complex (Supporting Information: Figure S-3) show the O−H stretching mode at 3320 cm^{-1} of α-CD shifted to 3330 cm^{-1} of the α-CD/PEG complex. The decrease in the broad band intensity at 3300 cm^{-1} (O−H stretching) relative to 2890 cm^{-1} (C−H stretching) and the new band generated at 2883 cm^{-1} (C−H stretching) as a shoulder also indicate the inclusion complex formation.[11] The differential scanning calorimeter (DSC) thermogram (data not shown) shows the melting peak of PEG at 60 °C. However, there is no melting peak of PEG over 180 °C for inclusion complex of IC-1 and IC-2. This fact indicates that the PEG is included in the pore of α-CD by the complex formation.

The change in the resolved peaks of α-CD at about 100 ppm to a single peak in cross-polarization/magic angle spinning (CP/MAS) NMR spectra also confirms the complex formation (Figure 3).[7] The single peak of α-CD that appeared in the inclusion complex indicates the symmetrical conformation of each glucose unit in the IC with a similar magnetochemical environment.[12] Compared with α-CD, the shoulder peak at 76 ppm increased by complex formation.

Using hyperbranched polyether, rectangular parallelepipeds IC were reported.[13] Because of the hyperbranched geometrical constraint, the complexation be-

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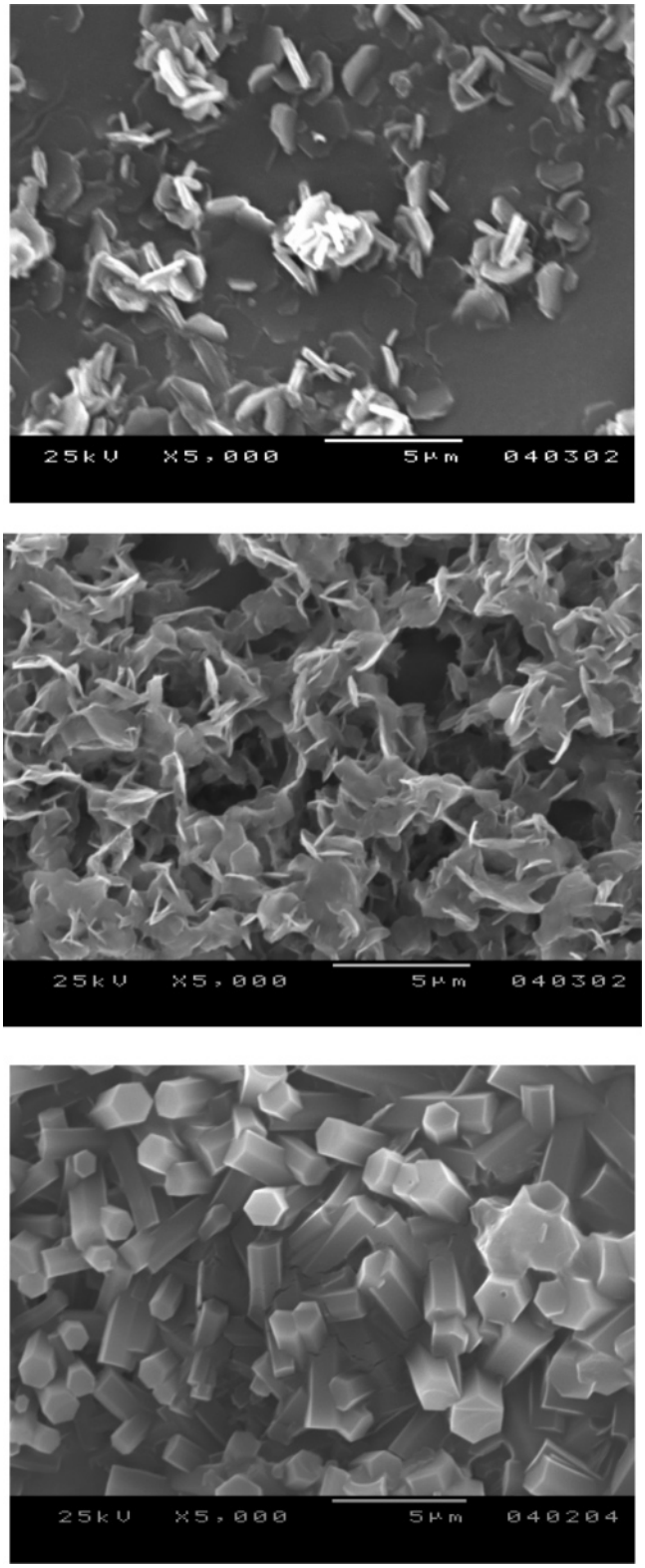

Figure 1. Scanning electron microscope (SEM) images of the α-CD (top), PEG/α-CD inclusion as prepared (IC-1; middle), and PEG/α-CD inclusion complex recrystallized in phosphate buffer (IC-2; bottom).

tween α-CD and hyperbranched polyether resulted in lamellar morphology in a juxtaposed manner. Similarly, PEGs with multiarms such as 2, 4, and 6 arms can also form an inclusion complex with a channel-type structure.[14] α-CD is an enzymatically degradable and biocompatible polymer.[15] Recently, the α-CD inclusion complex has been reported for a biomedical applications

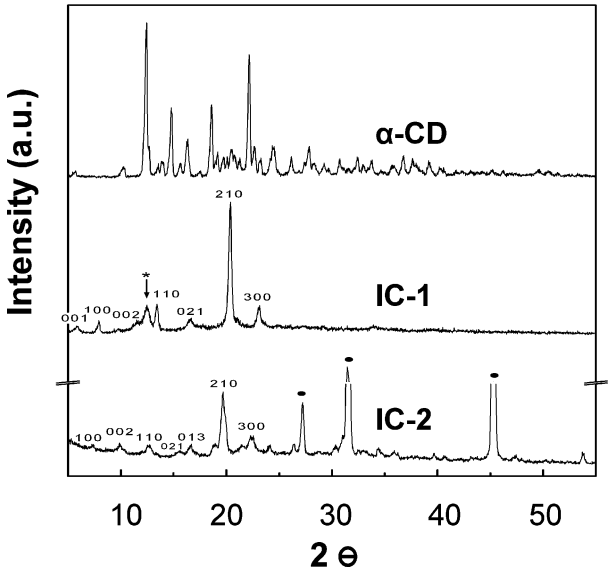

Figure 2. X-ray diffraction patterns of α-CD, IC-1, and IC-2 showing the inclusion complex formation. Asterisk (*) in IC-1: the strongest reflection of α-CD; dark spots in IC-2: cubic phase due to the phosphate buffer. The reflections of the PEG/α-CD inclusion complex are indexed corresponding to a hexagonal unit cell.

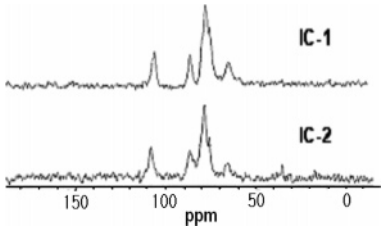

Figure 3. CP/MAS NMR spectra of IC-1 and IC-2 showing the inclusion complex formation.

such as drug delivery and tissue engineering scaffold. Polycaprolactone-*b*-poly(ethylene glycol)-*b*-polycaprolactone (PCL-PEG-PCL)/α-CD, poly(lactic acid)-*b*-poly(ethylene glycol)-*b*-poly(lactic acid) (PLA-PEG-PLA)/α-CD, and chitosan-*g*-PEG/α-CD are typical examples.[15−18]

To conclude, we are reporting the proliferation of the PEG/α-CD inclusion complex with crystal structure of hexagonal unit cells to 3-dimensional hexagonal crystalline structure on a micrometer scale. The inclusion complex formation was confirmed by XRD, FTIR, CP/MAS, and DSC. The threading followed by recrystallizing methodology might be a simple route to prepare a well-defined polymer structure on a micrometer scale. This finding might be important for the material science that needs a long-range three-dimensional crystalline structure.

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Supporting Information Available: Scanning electron microscopic image of IC-2 recrystallized in deionized water and electron diffraction image of an inclusion complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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