

Solubilization of Single-Wall Carbon Nanotubes by Supramolecular Encapsulation of Helical Amylose

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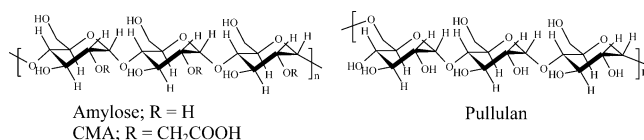
Single-wall carbon nanotubes (SWNTs, abbreviated as NTs) have been intensively investigated over the last several years due to growing interests in the exploitation of their unique chemical and physical properties for molecular electronics¹ and chemical/biological sensors.² However, the major disadvantage is the insolubility and a strong tendency to “rope up” in solutions that hamper molecular level studies and device applications. One solution for this problem is the use of polymers as solubilizing agents, and, so far, a few polymers³ are known to effectively solubilize NTs. Polymers have, however, a strong tendency to randomly wrap around NT bundles,^{3c} unless they have a specific binding interaction and an encapsulation process with NTs.

We were interested in the molecularly controlled encapsulation of NTs using helical amylose. During our investigation, a similar approach was reported.^{3e} We were prompted to disclose our method because it is distinctly different in the molecular notion of the complexation and in the process. The reported method^{3e} requires amylose to be in a prearranged helical state produced by complexing with iodine. We believe that the helical complexation of amylose takes place more favorably via a cooperative binding of NTs by amylose in a loosely elongated helical state. This process resembles the folding process of an optically active foldamer, oligo(*m*-phenylene ethynylene), toward a guest molecule.⁴

It has been known^{5,6} that a supramolecular inclusion of amylose with organic molecules commonly requires water (30–50%) in a DMSO mixture, which gives amylose an interrupted helical state, as opposed to the helical conformation^{6a} in pure DMSO. This suggests that the helical complexation takes place through hydrophobic binding interactions and concomitant size recognition. We thought that amylose solubilization of NTs needs to meet two important criteria for efficient encapsulation and colloidal stability: NTs must be effectively separated and dispersed from their bundles and there must be subsequent, strong binding interactions with amylose. The former can be done by means of a powerful sonication, but the latter requires an optimal solvent condition for amylose complexation. We have envisioned the possibility of a helical encapsulation of NTs by amylose, due to the fact that amylose helix is somewhat flexible, to extend the number of glucose residues per turn from six to seven or even higher units⁷ where a guest molecule is sterically demanding.

We have also investigated the encapsulation behavior of two amylose homologues, pullulan and carboxymethyl amylose (CMA) as shown below, to elucidate the sensitivity of the backbone structure and the functionality of the polymers to the host/guest interactions and encapsulations. Pullulan has a partial kink due to an α -1,6-linkage in every three glucose residues as the repeat unit, while amylose is a fully linear chain polymer. CMA is also a linear chain (α -1,4-linkage) polymer like amylose except for the charged group ($-\text{COOH}$), which makes the supramolecular complexation relatively less efficient.⁸

In this communication, we disclose a unique process that is simple, fast, and efficient to produce a stable colloidal solution of amylose-NT complexes. We also compare the solubilization behavior of amylose with that of the homologues. Further, we show the surface morphology of amylose encapsulated NTs by scanning electron micrograph (SEM) and atomic force micrograph (AFM).



For solubilization, a small piece of HiPco NT mat was presonicated (Sonix Model, VCX 750, 20 kHz) in water for 20 min (at a pulse cycle; 0.2 s on, 0.5 s off and 250 W), and the resulting fine suspension of NTs was mixed with amylose dissolved in DMSO and subsequently sonicated for a few minutes, during which the suspended NTs were completely dissolved.^{9a} The resulting colloidal solution is stable and exhibited no precipitation over several weeks. For purification, the solution of amylose/NT complex in a DMSO/H₂O mixture was briefly filtered to eliminate a few suspended particles, and then subjected to ultracentrifugation for ≥ 30 min to separate the encapsulated NTs. After the supernatant, which was rich in the excess free amylose, was removed, the precipitate was washed with sufficient water and centrifuged again. This washing/centrifuging cycle was repeated several times to obtain amylose-encapsulated NTs.^{9b}

It was found that the solubilization of NTs in water by pullulan and CMA was significant, ca. 60 and 70% of the level of amylose, respectively. Such a high degree of solubilization is thought to be associated with their high solubility in water, particularly for CMA because the solubilization by CMA in DMSO mixtures was markedly lowered. This means that the good solubility of polymers is an important parameter as long as the solvent condition does not interfere with their binding interactions. The relatively low solubilization power of pullulan can be therefore ascribed to the kink in the chain structure that hinders a long-range encapsulation.

The influence of solvent composition on the NT solubilization by amylose was assessed by UV/vis absorption at 500 nm (Figure 1), a region of relatively featureless absorptions. This has been reported previously.^{10a-c} The inset shows the trend of the solubilization as a function of DMSO volume fraction, which is represented by the absorption at 500 nm.^{10d} While the solubilization is negligibly low at a higher DMSO > 50%, it increases sharply between 30 and 50% DMSO, reaching a maximum around 10–20%. Such a strong dependence of the NT solubilization on the solvent composition is indicative of a special binding interaction^{5a} present between NTs and helical amylose. It seems that once binding occurs, encapsulation/folding proceeds very quickly because

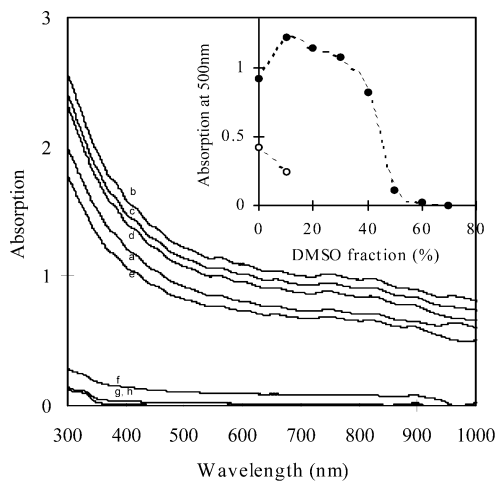


Figure 1. Absorption spectra of amylose-encapsulated SWNT prepared in various DMSO–H₂O mixtures: 0 (a), 10 (b), 20 (c), 30 (d), 40 (e), 50 (f), 60 (g), and 70 (h) vol % DMSO. The inset shows the NTs solubilization with (●) or without (○) presonication.

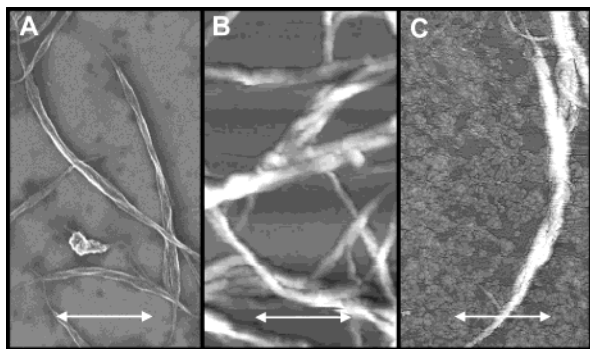


Figure 2. SEM (A) and AFM (B and C) images of amylose-encapsulated NTs. The markers are (A) 600 nm, (B) 500 nm, and (C) 250 nm.

the presonicated NT suspension dissolved almost immediately upon addition of amylose solution, followed by a brief sonication.

On the other hand, the NT solubilization in 100% water by amylose is somewhat lower than that in 10–30% DMSO. This is partly due to the poor solubility of amylose in water. This situation is in contrast to the case of CMA (vide supra). Regardless of the solvent conditions, a marked decrease in the NT solubilization occurs when NTs in suspension are sonicated together with amylose as a one-pot process without the presonication (see Figure 1). This implies that amylose (or any chain polymers) tends to aggregate onto NT bundles by sonication such that the separation of NT bundles is hampered and subsequent molecular-level binding interactions are hindered. In this regard, the presonication is an important process for NT solubilization.

As shown in Figure 2, the SEM image (A) gives loosely twisted NTs with a diameter¹¹ of approximately 30 nm. The AFM gives an enhanced image of the helical twist (C), which reveals also a locally intertwined multiple twist (B) but no clumps of free amylose on the NT capsules. This twisted structure discloses a totally new feature that amylose can encapsulate a large diameter (>1 nm) guest molecule, which is driven by hydrophobic interactions, the crucial role being still played by the chirality and the linear chain structure. Raman spectra (not shown) of amylose-encapsulated NTs indicated a small shift (3–5 cm⁻¹) relative to the pristine NTs in the radial

breathing mode frequency. This structure is similar to that described previously for polymer-wrapped NTs.¹²

In conclusion, we have developed a simple, efficient process for the solubilization of NTs with amylose in aqueous DMSO as well as in pure water. This process requires two important conditions, presonication of NTs in water and subsequent treatment of the fine NT dispersion with amylose in a specified DMSO–H₂O mixture, followed by a postsonication. The former step disaggregates the NT bundles, and the latter step maximizes cooperative interactions between NTs and amylose, leading to the immediate and complete solubilization. The best solvent condition for this is around 10–20% DMSO, in which amylose assumes an interrupted loose helix. This indicates that the helical state of amylose is not a prerequisite for amylose encapsulation of NTs. Two amylose homologues, pullulan and CMA, show a significant but lesser solubilization relative to that of amylose. The SEM and AFM display images of twisted ribbons in the encapsulation of NTs by amylose.

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Supporting Information Available: A photo demonstrating the differences in the solubilization of NTs by amylose and its homologues, and electronic absorption spectrum (600–1600 nm) associated with the NT size in the solubilization (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) (a) In a typical experiment, 0.2 mg of SWNT (HiPco) was sonicated in 5 mL of water for 20 min and subsequently treated with a solution of 15–20 mg of amylose in DMSO by 4 min of sonication for complete solubilization. (b) From the low yield of the pure final product obtained after repeated washing/centrifugation cycles, it was estimated that about 50% of the product remains in the washing solutions along with free amylose. The supernatants containing smaller bundles and free NTs encapsulated were recovered for later characterizations.
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- (11) Although the amylose coating would be significantly bulky, it is assumed that many NTs exist as small bundles in the solution as prepared, which was used for the micrographs after a brief filtration without any size fractionation.
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