

Solubilization of Carbon Nanotubes with a Pyrene-carrying Polymer in Water

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A pyrene-bearing vinyl monomer **1** and compound **2**, which is a copolymer of **1** and acrylamide, were synthesized. Transmission electron and atomic force microscopic investigation revealed that both **1** and **2** dissolved/dispersed single-walled carbon nanotubes in water by direct sonication with an ultrasonic cleaner. The dissolution/dispersion of SWNTs by **1** and **2** in water would be due to the physical adsorption of the pyrene group onto the sidewall of the nanotubes. Upon heating up to 49-50 °C, an aqueous solution of SWNTs-**1** produced a precipitate, which was readily separated from the solution/dispersion by filtration as a solid nanocomposite of SWNTs-**1**.

Keywords: carbon nanotubes, solubilization, pyrene-bearing monomer, pyrene-bearing copolymer, atomic force microscopy

1. INTRODUCTION

Since the first finding¹, carbon nanotubes have been in the forefront of nanoscience and nanotechnology because of variety of their unique properties and specific functions². The preparation of soluble carbon nanotubes in aqueous and organic system are of interests since they may open the door of a novel nanotube chemistry^{3,4}. Our approach is the use of cyclic aromatic compounds to obtain soluble nanotubes⁴. Carbon nanotubes have been reported to be soluble in the aqueous micellar solutions of detergents such as sodium dodecyl sulfate and Triton-X⁵. Some polymers such as poly(vinylpyrrolidone) dissolve carbon nanotubes in water after a pretreatment using a surfactant⁶. Stoddart et al. reported that nanotubes are insoluble in an aqueous solution of starch but soluble in an aqueous solution of a starch-iodine complex⁷. Taton et al. described the preparation of nanotube solution by polymer-micelle encapsulation followed by cross-linking of the polymer⁸. The development of a polymer that dissolves carbon nanotubes directly in water would be important and useful. We have already reported that a pyrene-bearing ammonium compound

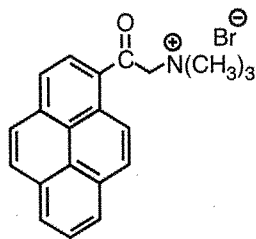


Figure 1. Chemical structure of a pyrene-bearing amphiphile.

dissolves/disperses single-walled carbon nanotubes (SWNTs) in water (Figure 1). In this report, we describe the synthesis of a pyrene-carrying vinyl monomer **1** and a polymer **2** (Scheme 1), which is a copolymer of **1** and acrylamide. Solubilization behavior for SWNTs using these compounds was examined by means of transmission electron microscope (TEM), atomic force microscope (AFM) and UV-visible-near IR spectral measurements.

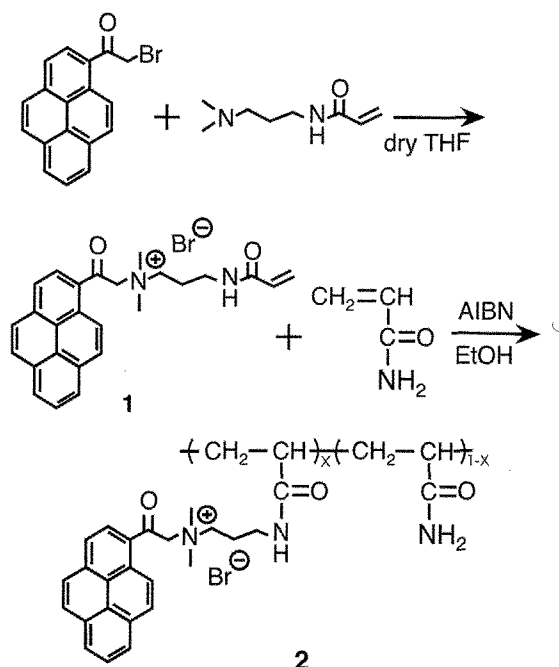
2. EXPERIMENTAL

A pyrene-carrying vinyl monomer **1** was synthesized by the reaction of 1-(bromoacetyl)pyrene and *N,N*-dimethylaminopropylacrylamide in dry THF. A copolymer **2** was synthesized with the copolymerization of **1** and acrylamide in ethanol (see Scheme 1) using azobisisobutyronitrile as a polymerization initiator. The identification of these products was conducted with FT-IR, ¹H NMR, and elemental analysis.

The purification procedure of SWNTs (HiPco™, Carbon Nanotechnologies) was described elsewhere⁴. Briefly, SWNTs were heated at 225 °C in humid air, and then sonicated with an ultrasonic cleaner (Branson 5510) in HCl. The nanotubes were then collected by a porous filter, and then washed with sodium hydrogencarbonate. SWNTs were collected by a porous filter, and then dried at 50 °C to obtain the purified SWNTs (p-SWNTs), which were used in this experiment. Fe_{2p3/2} did not appear in the region of 706 – 714 eV in the XPS diagram of the nanotubes, indicating that the Fe was almost removed by this purification procedure.

A typical solubilization procedure is as follows. About 0.5 mg of p-SWNTs was sonicated with the bath-type ultrasonifier in water (or D₂O) containing 0.1 mM (1 M = 1 mol dm⁻³) of **1** (or **2**) for 1 h, and then

Scheme 1



centrifugation (Hitachi CF-15R, 1000 g) of the suspension was carried out for 1 h to remove insoluble nanotubes.

A carbon-coated grid (Ouken-Shoji, 200-A mesh) was immersed in a SWNTs-1 (or **2**) solution for a few seconds, and then dried under vacuum. Transmission electron microscope (TEM) images were measured on a JEOL JEM-100S electron microscope. A freshly cleaved mica substrate was immersed in the aqueous solution of SWNTs-1 (or **2**) dispersion/solutions for a second, and then was dried under vacuum. Atomic force microscope (AFM) images were recorded on a SPI3800N (Seiko Instruments Inc.) with a Si_3N_4 cantilever (SN-AF01).

UV-visible-near IR (NIR) spectra were measured at 20 °C on a spectrophotometer (JASCO, V-570).

3. RESULTS AND DISCUSSION

We have already described the dissolution of SWNTs with the pyrene-carrying amphiphile (see Figure 1) in water. Both pyrene-carrying vinyl monomer **1** and the copolymer **2** were found to give similar result, that is, after sonication of SWNTs in aqueous solutions of **1** and of **2** with a bath-type ultrasonic cleaner, followed by centrifugation, we could obtain transparent yellowish black-colored transparent solutions. This suggests that both **1** and **2** can disperse/dissolve SWNTs in water. No precipitation was appeared in the obtained solutions even after several months upon storage at room temperature. On the contrary, thermal stability of the aqueous solutions of SWNTs-1 and SWNTs-2 at higher temperatures above 50 °C was different. As shown in Figure 2, the aqueous solution of SWNTs-1 produced a precipitate upon heating up to 50 ± 1 °C. It is evident that the SWNTs-1 solution

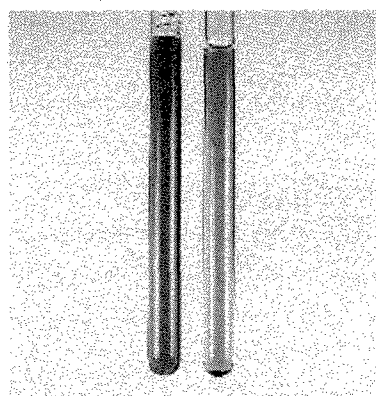


Figure 2. A photo for aqueous solutions of a SWNTs-1 taken at 25 °C (left) and 50 °C (right).

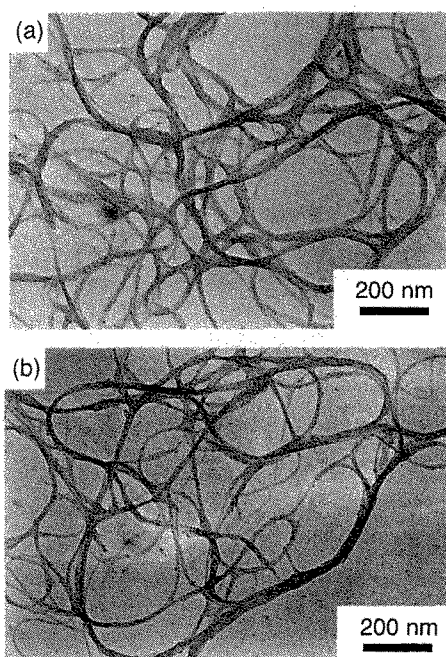


Figure 3. TEM images for aqueous solutions of SWNTs-1 (a) and (b).

possesses the critical temperature for the phase separation. The produced precipitate was insoluble when the temperature was cycled back to room temperature, and hence, the precipitate could be readily separated from the solution with a porous filter (pore size, 0.2 μm) as a nanocomposite of SWNTs and **1**, which would be a pyrene-containing polymer-wrapped solid carbon nanotubes. On the contrary, no such precipitation appeared in the SWNTs-2 aqueous solution upon heating up to 95 °C. The generation of the precipitate at the SWNTs-1 solution would be resulted from the desorption of certain amounts of monomer **1** from the sidewall of the SWNTs. The desorption would be due to the lower binding constant of SWNTs and **1** compared to those of SWNTs and **2**.

Typical TEM images of aqueous solutions of SWNTs-1 and of SWNTs-2 are shown in Figure 3. Dispersed bundled SWNTs with flexible network structures are

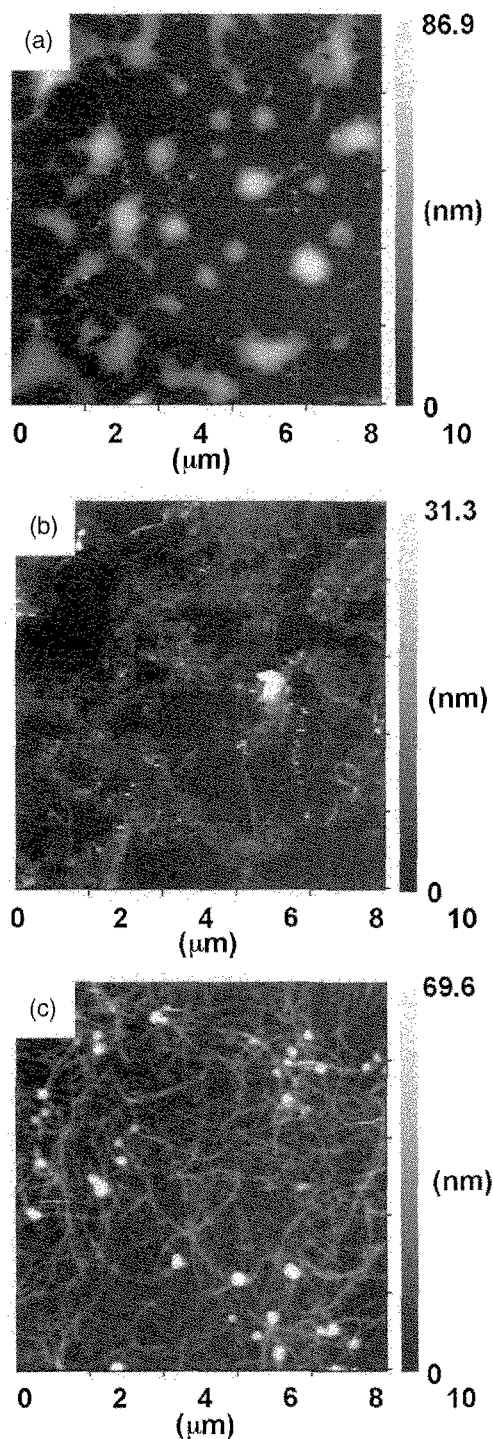


Figure 4. AFM images of aqueous solutions of SWNTs-1 (a) and SWNTs-2 (b and c). apparently seen in both solutions. Figure 4 shows typical AFM images of aqueous solutions of SWNTs-1 and SWNTs-2. Although the nanotubes of SWNTs-2 on mica that SWNTs were dispersed in water with bundle structures, some nanotubes were dissolved individually. In contrast, the AFM image of SWNTs-1 gave an aggregated structure (Figure 4a), which is quite different from the TEM image shown in Figure 3. Such aggregates might be formed at the sample preparation

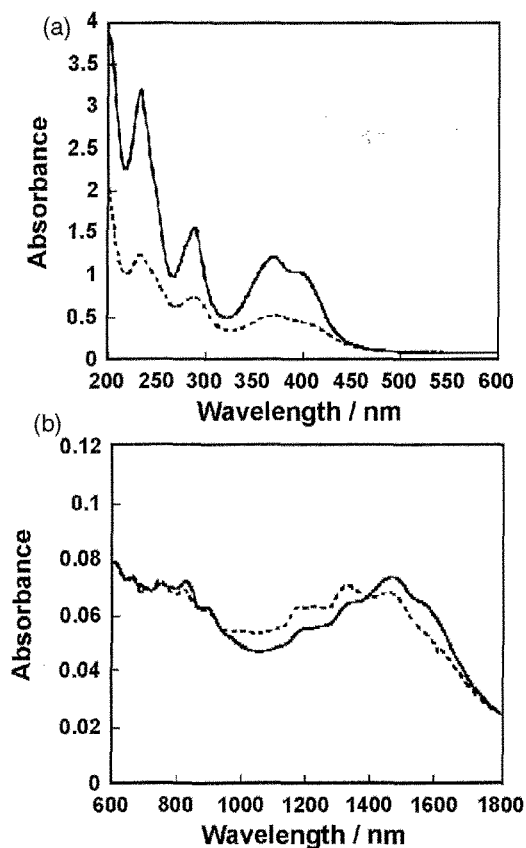


Figure 5. UV-visible (a) and Visible-near IR (b) spectra of aqueous solutions of SWNTs-1 (solid lines) and SWNTs-2 (dotted lines).

process for AFM measurements.

Both aqueous dispersions/solutions of SWNTs-1 and of SWNTs-2 showed characteristic absorption bands in the NIR region due to the interband transition between the mirror image spikes in the density of states (DOS) of SWNTs⁹ (Figure 5), which are similar with those of the reported HiPco SWNTs¹⁰. The absorption maxima for the dispersions/solutions of SWNTs-1 and of SWNTs-2 in the UV-visible region corresponding to the pyrene moieties appeared at 232, 288, and 369 nm for SWNTs-1 and 232, 288, and 371 nm for SWNTs-2, which were almost identical with those of aqueous solutions of **1** and of **2**. This result suggests that i) the spectra are governed by **1** and **2** in the bulk solutions and/or ii) adsorbed **1** and **2** does not cause any spectral shift.

4. CONCLUSION

We prepared in this study pyrene-bearing vinyl monomer (**1**) and copolymer (**2**)-wrapped carbon nanotubes in water by direct sonication with an ultrasonic cleaner. In a SWNTs-2 solutions/dispersions, we could observe bundled SWNTs (major structure) and individually dissolved SWNTs (minor structure) in water. The

dissolution/dispersion of SWNTs would be resulted from the physical adsorption of the pyrene moieties onto the sidewall of the nanotubes. The solid SWNTs-1 nanocomposite was readily phase-separated from the solution/dispersion by simple heating at 50 °C. This kind of carbon nanotube-based nanocomposites would be of interest from a viewpoint of the formation of functional carbon nanotubes in a solid phase.

5. ACKNOWLEDGEMENTS

This work was in part performed under the management of Nano Carbon Technology project supported by NEDO and by the support of the Grant-in-Aids from the Ministry of Education, Science, Sports, and Culture, Japan.

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(Received October 15, 2003; Accepted October 20, 2003)