Design, Synthesis, and Characterization of Carbon Nanotube Solubilizers Carrying a Reactive Group

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We describe the design of new carbon nanotube (CNT) solubilizers based on a novel concept, that is, "reactive carbon nanotube solubilizers" that are compounds carrying a reactive moiety for the introduction of the desired functional groups.

Carbon nanotubes (CNTs) have high potentials for possible applications in many fields including energy, electronics, IT, and materials.[1–5] However, because of the insolubility of the nanotubes in solvents due to strong intertube van der Waals interactions, the chemical and biochemical approaches using nanotubes have been limited. Therefore, strategic approaches toward the solubilization of CNTs are important in wide fields including chemistry, physics, biochemistry, biology, and pharmaceutical and medical science.[6–9] Our interest focused on the fundamental and applications of soluble carbon nanotubes in aqueous and organic systems.[8,9] We[10–13] and others[14–16] have already described that compounds (including polymers) bearing a condensed polycyclic aromatic moiety such as pyrene, anthracene, porphyrin, or polyimide group dissolve CNTs in water or in organic compounds. Double-[17] and single-stranded[18,19] DNAs are also good CNT solubilizers in water.

We present here new CNT solubilizers based on a novel concept, that is, "reactive carbon nanotube solubilizers" that are compounds carrying a reactive moiety for the introduction of the desired functional groups. A schematic drawing showing this concept is presented in Figure 1. In this study, we designed and synthesized poly(styrene-*alt*-maleic anhydride)-based copolymers, Anth-P1 and Anth-P2 that carry the anthryl moiety (Figure 2). Interesting features of this study are one-pot synthesis of the "reactive carbon nanotube solubilizers" that dissolve single-walled carbon nanotubes (SWNTs) individually in many solvents, and the additional introduction of a functional group to the solubilizer. Dai et al. described noncovalent sidewall functionalization with 1-pyrenebutanoic acid succimidyl ester on SWNTs synthesized on meshed gold grids.[20] Prato et al. described the synthesis of amine-functionalized carbon nanotubes that can be derivatised with N-protected amino acids.[21]

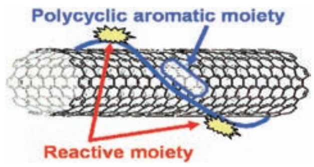
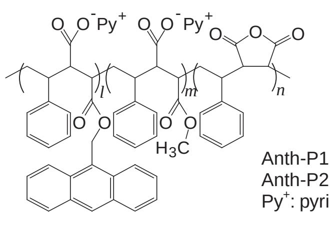


Figure 1. A concept of "reactive carbon nanotube solubilizers."



Anth-P1: (*l*, *m*, *n*) = (0.27, 0.24, 0.49)
Anth-P2: (*l*, *m*, *n*) = (0.20, 0.24, 0.56)
Py$^+$: pyridinium

Figure 2. Chemical structures of Anth-P1 and Anth-P2.

A typical procedure for the synthesis of Anth-P1 and Anth-P2 is as follows. Poly(styrene-*alt*-maleic anhydride) partial methyl ester (1.0 g, Aldrich, average MW 350,000) was reacted with 9-hydroxymethyl anthracene (3.0 g and 1 g for Anth-P1 and Anth-P2, respectively, Aldrich) in dry pyridine at 80 °C for ca. 40 h. The solutions were then twice reprecipitated from ethyl acetate to produce Anth-P1 and Anth-P2 (yield: Anth-P1, 1.2 g; Anth-P2, 1.2 g). The composition ratios of the copolymers were estimated by the curve fitting of the ^{1}H NMR spectra of the copolymers. SWNTs were purchased from Carbon Nanotechnologies, Inc., and were used as received. Typical SWNT solubilization procedures are as follows. A specific amount of the SWNTs were added to a DMF solution (spectral grade) containing Anth-P1, and then sonicated (ultrasonic cleaner, Branson 5510) for 2 h, followed by centrifugation at 10,000–50,000 *g* (SIGMA, 3K30C) for 1–5 h.

The copolymers Anth-P1 and Anth-P2 were found to be excellent SWNT solubilizers. For example, an Anth-P1 DMF solution (0.16 mg/1 mL) could dissolve/disperse ca. 0.20 mg of the SWNTs. It is noteworthy that the copolymer could solubilize/disperse the SWNTs highly effectively. As an example, a photograph of SWNTs dissolved/dispersed in DMF by the aid of Anth-P1 is shown in the Figure 3.

The visible–near-IR absorption spectra (JASCO, spectrophotometer, V-570) of a DMF solution of SWNTs/Anth-P1 is shown in Figure 4 (left panel), in which we see its characteristic structural spectral features, suggesting that the SWNTs are individually dissolved, while due to the strong absorption of the SWNTs near 350–400 nm, the spectral shift of the anthryl group was not evident. Other solvents such as methanol, ethanol, and THF were available to dissolve the SWNTs, while ethyl acetate and chloroform were not.

In the following, we describe two examples to demonstrate

Figure 3. A photograph of SWNTs dissolved by Anth-P1.

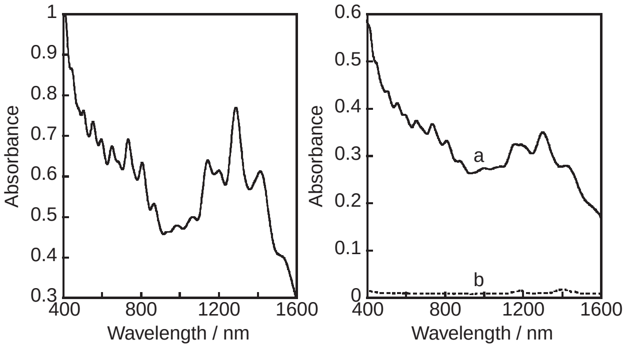


Figure 4. Visible–near-IR absorption spectra of the SWNTs/Anth-P1 in DMF (left panel) and of the SWNTs/Anth-P2-C12 (a) and the SWNTs/Anth-P2 (b) in ethyl acetate (right panel). Optical cell length, 1 cm.

the concept of a "reactive nanotube solubilizer." The synthesized copolymers possess the maleic anhydride moiety that is a highly reactive functional group for many bases, such as amines and alcohols. Anth-P2 (50 mg) was reacted with 1-dodecylamine (65 mg) in dry pyridine (15 mL) at 80 °C for 6 h, and then the solution was reprecipitated from water to give Anth-P2-C12 (67 mg). Anth-P2 was not soluble in ethyl acetate, therefore, the SWNT solubilization did not occur in this solvent. On the contrary, Anth-P2-C12 was soluble in ethyl acetate, and the SWNTs were solubilized in this solution (Figure 4, right panel). This result indicates that the introduction of an additional group to the solubilizer to change its property is easy. To demonstrate the concept of a "reactive nanotube solubilizer" in a solubilized nanotube solution, we have conducted the following experiment. The SWNTs were dissolved in a THF solution of Anth-P1 and the then 1-hexylamine was added to the solution, which was stirred at room temperature for 30 min. After the reaction, the FT-IR spectrum of a cast film from the solution on a CaF_2 substrate was measured and it was found that an amide stretching band via the reaction of 1-hexylamine and the maleic anhydride moiety on Anth-P1 appeared at $1670\,cm^{-1}$. The obtained preliminary result indicates that the SWNTs/Anth-P1 solution acts as the reactive carbon nanotubes.

To obtain a direct image of the individually dissolved SWNTs, we measured atomic force microscopic (AFM) images (Veeco, NanoScope® IIIa). A mica substrate was dipped in a SWNTs/Anth-P1 DMF solution for a few seconds, followed by rinsing with DMF and then dried under vacuum. A typical AFM image is demonstrated in Figure 5 (left). From the height distribution histogram of the AFM image, the diameters of ca. 80% nanotubes are in the range of 0.8–1.8 nm. Figure 5 (right) shows the surface plot of the AFM image, which suggests individually dissolved SWNTs that were wrapped with the solubilizer.

In conclusion, we described a novel concept called "reactive carbon nanotube solubilizers," which were synthesized by a one-pot synthesis from *alt*-copolymers of styrene and maleic anhydride. These new compounds are able to dissolve SWNTs individually. We demonstrated that the additional introduction of functional groups to the maleic anhydride group on the solubilizer was possible. The presented concept should be applicable to the construction of individually dissolved SWNTs with a variety of chemical, physical and biochemical and medical functions.

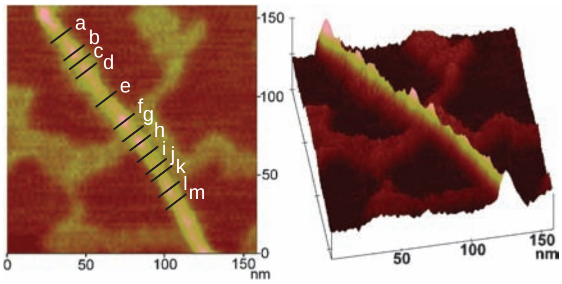


Figure 5. Typical AFM images (left: top view, right: its surface plot) of the SWNTs/Anth-P1 on mica. The heights of the tube are: (a) 1.42, (b) 1.93, (c) 1.29, (d) 1.71, (e) 1.05, (f) 1.82, (g) 0.92, (h) 1.49, (i) 1.10, (j) 1.45, (k) 1.03, (l) 1.68, and (m) 1.17 nm.

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