2864 *Chem. Mater.* **2001,** *13,* 2864−2869

Soluble Dendron-Functionalized Carbon Nanotubes: Preparation, Characterization, and Properties[§,‖]

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Received January 26, 2001. Revised Manuscript Received June 20, 2001

Lipophilic and hydrophilic dendra which are terminated with long alkyl chains and oligomeric poly(ethylene glycol) moieties, respectively, were synthesized, and these dendron species were used to functionalize single-wall (SWNT) and multiple-wall (MWNT) carbon nanotubes via amidation and esterification reactions. The functionalized carbon nanotube samples are, depending on the functionalities, soluble in common organic solvents, such as hexane and chloroform, and water to form colored homogeneous solutions. Characterizations using NMR, electron microscopy, and optical spectroscopic techniques show that the homogeneous solutions contain carbon nanotubes. A preliminary understanding of the structural features and properties of these soluble dendron-functionalized SWNTs and MWNTs is discussed in terms of results from the characterizations, the defunctionalization reactions, and the trapping of metal nanoparticles by the functionalized nanotubes in solution.

Introduction

Since their discovery in 1991,[1] carbon nanotubes have attracted great scientific attention.[2,3] Significant progress has been made in the characterization of both single-wall (SWNT) and multiple-wall (MWNT) carbon nanotubes, mostly concerning the properties of individual nanotubes via applications of microscopy techniques. However, for a more complete understanding of carbon nanotubes and also for many of their potential applications, functionalization and solubilization of carbon nanotubes are required. Several research groups have recently experimented with different approaches.[4−10] For example, Margrave, Smalley, and co-workers reported the preparation of fluorinated SWNTs.[6] In various alcohol solvents, the functionalized SWNTs were solvated as individual tubes, making it possible to carry out solution chemistry. The successful solution-phase reactions of the fluorinated carbon nanotubes included the substitution with sodium methoxide and defluorination via the treatment with hydrazine.[6]

Haddon and co-workers pioneered the approach of functionalizing the carboxylic acid groups on shortened carbon nanotubes.[5] The solubilization was achieved by introducing long alkyl chains to the nanotube surface, where the carboxylic acids were first converted to acyl chloride, followed by the amidation reaction with octadecylamine or 4-tetradecylaniline.[5,8] NMR spectra of the soluble SWNTs exhibited broad aliphatic peaks due to the alkyl functionalities. The most convincing evidence for the presence of nanotubes in the soluble sample was from the Raman results, which showed no fundamental difference between the solubilized and pristine SWNTs.[5,8] The solubilized SWNTs were also studied by using IR and EPR techniques, and were subject to further chemical modifications.[5,8]

Similar amidation and esterification chemistry of functionalizing the nanotube-surface-bound carboxylic acid moieties has been used in our laboratory to attach SWNTs and MWNTs to highly soluble copolymers such as poly(propionylethylenimine-*co*-ethylenimine) and poly(vinyl acetate-*co*-vinyl alcohol).[11−13] The polymer-func-

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[§] This paper is dedicated to professor Fred Wudl on the occasion of his 60th birthday.

[‖] Presented at the 199th meeting of the Electrochemical Society, Washington, DC, March 2001 (*Symp. Proc.* 01−11, 223).

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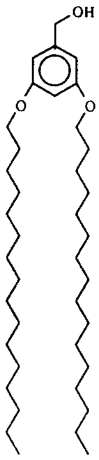
10.1021/cm010069l CCC: $20.00

tionalized carbon nanotubes were characterized by using a series of instrumental techniques, including the successful imaging of the soluble polymer-bound nanotubes at atomic resolution via scanning tunneling microscopy (STM).[11,13] The STM results show that the polymer is interacting with the length of the nanotube and, in some cases, following the macromolecular twist (or chirality) of the nanotube.[13] In addition, the polymer-bound SWNTs and MWNTs, which are soluble in both organic solvents and water, have already found applications in quantitative studies of the optical properties of carbon nanotubes.[11,12]

Here we report the functionalization of SWNTs and MWNTs by lipophilic and hydrophilic dendron species which are terminated with long alkyl chains and oligomeric poly(ethylene glycol) (PEG) moieties, respectively.[14] Results from characterizations using NMR, electron microscopy, and optical spectroscopic techniques are presented and discussed.



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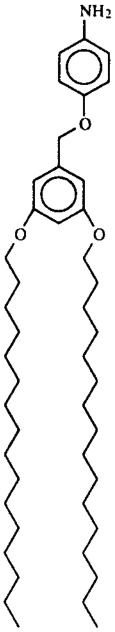
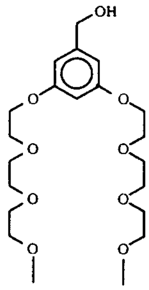
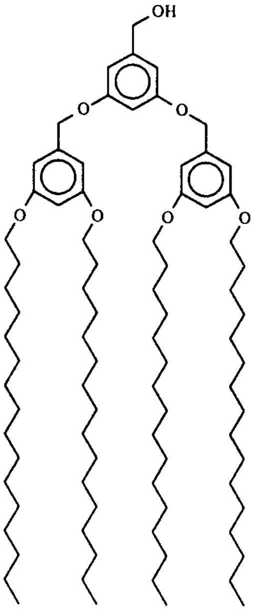


I$_N$



I$_{PEG}$



II

Experimental Section

Materials. Methyl 3,5-dihydroxybenzoate (98%) and 4-nitrophenol (97%) were purchased from Avocado Research Chemicals Ltd., 1-bromohexadecane (99%) and thionyl chloride (99.5+%) were purchased from Acros, triethylene glycol monomethyl ether (97%) was purchased from Fluka, diethyl azodicarboxylate was purchased from Aldrich, triphenylphosphine (99+%) and Pd/C catalyst were purchased from Alfa, and hydrazine was purchased from Fisher Scientific. Solvent grade THF was first dried and distilled over molecular sieves, and then distilled over sodium before use. Other solvents either were of spectrophotometry/HPLC grade or were purified via simple distillation. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories. Dialysis tubing (cutoff weight 12000) was purchased from Sigma.

SWNT and MWNT samples were either purchased from Tubes@Rice and MER Co., respectively, or produced by using an arc discharge apparatus at Rensselaer Polytechnic Institute (RPI), and were purified using procedures similar to those reported in the literature.[3,15,16] The experimental details on the purification and characterization are provided in the Supporting Information. Since the characterization has not allowed a realistic estimate of nanotube sizes and size distributions, the nanotube samples used in the functionalization reactions are best described as mixtures of nanotubes with different lengths and diameters.

Dendron **I** was synthesized as follows. Methyl 3,5-dihexadecoxybenzoate (8 g, 13 mmol), which was obtained from the etherification of methyl 3,5-dihydroxybenzoate and 1-bromohexadecane (97% yield), was dissolved in diethyl ether (250 mL), and to the solution was added $LiAlH_4$ (0.54 g, 14.3 mmol). The mixture was refluxed under nitrogen protection for 12 h. Upon the completion of the reduction reaction, water was added carefully to quench the unreacted $LiAlH_4$. Dendron **I** was extracted from the reaction mixture with diethyl ether and recovered as a colorless compound (96% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.6$ Hz, 6H), 1.26−1.55 (m, 52H), 1.71−1.79 (m, 4H), 3.93 (t, $J = 6.6$ Hz, 4H), 4.62 (d, $J = 3.0$ Hz, 2H), 6.38 (t, $J = 2.2$ Hz, 1H), 6.50 (d, $J = 2.2$ Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.34$, 22.92, 26.27, 29.48, 29.60, 29.91, 32.15, 65.71, 68.28, 100.76, 105.25, 143.40, 160.75 ppm. Dendra **I$_N$**, **I$_{PEG}$**, and **II** were similarly synthesized and characterized (see the Supporting Information for details).

Functionalization of Nanotubes. In a typical experiment, a purified MWNT sample (30 mg) was treated in concentrated HCl solution to fully recover the carboxylic acid groups on the nanotube surface, followed by refluxing in thionyl chloride for 24 h to convert the carboxylic acids into acyl chlorides. After complete removal of residual thionyl chloride on a rotary evaporator with a vacuum pump (or by washing with anhydrous THF and then removing the solvent), the sample was well mixed with carefully dried dendron **I** (250 mg, 0.43 mmol) in a flask, heated to 75 °C, and vigorously stirred for 48 h under nitrogen protection. The reaction mixture was extracted with chloroform several times to obtain a dark red-brown solution. The chloroform solution was repeatedly precipitated into ethanol, yielding the functionalized MWNT sample **I**-MWNT. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.7$−1.5 (br), 3.5−3.9 (br), 4.0−4.2 (br), 6.0−6.5 (br) ppm. Similarly, MWNTs were functionalized with **I$_N$** and **II**, yielding **I$_N$**-MWNT [^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.7$−0.9 (br), 1.1−1.5 (br), 1.7−1.8 (br), 3.8−4.1 (br), 4.5−5.3 (br), 6.0−7.5 (br) ppm] and **II**-MWNT [^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.89$ (t, $J = 6.4$ Hz), 1.1−1.5 (br), 1.7−1.8 (br), 3.3−4.1 (br), 4.1−4.6 (br), 4.6−5.0 (br), 5.8−6.8 (br) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.2$, 22.7, 25.8−26.6, 29−30, 32, 66−69, 69−71, 72, 97−100, 100−102, 104−106, 106−109, 138−141, 142−145, 155−159, 159−161 ppm].[17]

The same experimental procedure was applied to the functionalization of SWNTs with the dendra, yielding **I**-SWNT [^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.5$ Hz), 1.1−1.5 (br), 1.6−1.8 (br), 3.5−3.9 (br), 4.0−4.2 (br), 6.0−6.5 (br) ppm] and **I$_N$**-SWNT [^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.87$ (t, $J = 6.5$ Hz), 1.1−1.5 (br), 1.7−1.8 (br), 3.2−4.0 (br), 4.6−5.3 (br), 6.0−7.2 (br) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.2$, 22.8, 26.2, 29.36, 29.46, 29.8, 32.0, 68.11, 71−72, 97−100, 103−106, 112−116, 135−137, 158−160 ppm].[17]

MWNTs were functionalized with **I$_{PEG}$** as follows. A solution of carefully dried **I$_{PEG}$** (240 mg, 0.56 mmol) in anhydrous THF

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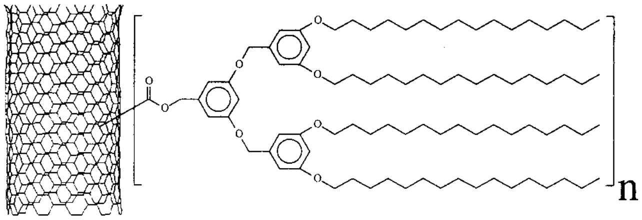
(17) Here, a range of chemical shifts is used to describe several overlapping broad and medium ^{13}C peaks in the range.

Chart 1



(2 mL) was prepared, and to the solution was added an excessive amount of NaH. After the solution was stirred at room temperature for 30 min, the thionyl chloride-treated MWNT sample (20 mg) was added. The reaction mixture was vigorously stirred for 24 h, followed by repeated extraction with chloroform. The dark-colored chloroform solution was briefly washed with water, followed by solvent removal on a rotary evaporator to yield $\mathbf{I}_{\mathrm{PEG}}$-MWNT as a red glassy solid. It was redissolved in deionized water for further purification via dialysis for 3 days. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.3$ (br), 3.4−4.2 (br), 4.5 (br), 6.2−6.7 (br) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 59.1$, 67.5, 67.7, 69.4, 69.6, 69.7, 70.2, 70.5, 70.6, 70.8, 71.9, 97−102, 103−109, 143−144, 159−160 ppm.[17]

In terms of the mass balance, the nanotube loadings in these soluble samples were estimated roughly to be on the order of a few weight percent.

Defunctionalization. For additional evidence on the ester linkages in the functionalization of carbon nanotubes, the **I**-MWNT sample was defunctionalized under base-catalyzed hydrolysis reaction conditions.[18] In a typical experiment, a purified sample of **I**-MWNT (~0.58 g) was dissolved in THF (20 mL) to form a brown-colored homogeneous solution. After NaH (0.5 g) was added,[18] the solution was refluxed under nitrogen protection for 2 h, resulting in the formation of dark-colored precipitates. The reaction was quenched by the addition of water, and the reaction mixture was centrifuged at a high speed (7000 rpm). The nearly black solids thus obtained were washed repeatedly with chloroform, water, and acetone, and then carefully dried for characterization.

Measurements. Absorption spectra were obtained using a computer-controlled Shimadzu UV2101-PC spectrophotometer. Emission spectra were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450 W xenon source, a Spex 340S dual-grating and dual-exit emission monochromator, and two detectors for visible and infrared wavelength regions. FT-IR measurements were performed on a Nicolet Magna-IR 550 FT-IR spectrometer. The samples for IR measurements were deposited on the surface of a KBr plate.

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-300 NMR spectrometer and a JEOL Eclipse +500 NMR spectrometer. Tetramethylsilane was used as an internal standard.

Powder X-ray diffraction measurements were carried out on a Scintag XDS-2000 powder diffraction system. Transmission electron microscopy (TEM) images were obtained on a Hitachi 600AB transmission electron microscope or a Hitachi 7000 transmission electron microscope. Scanning electron microscopy (SEM) analyses were performed on a Hitachi 4700 field emission scanning electron microscope.

Results and Discussion

The functionalization of SWNTs and MWNTs with the dendron species is likely via esterification (**I**, $\mathbf{I}_{\mathrm{PEG}}$, **II**) or amidation ($\mathbf{I}_{\mathrm{N}}$) of the nanotube-surface-bound carboxylic acid moieties (Chart 1).[5,8,11−13] The high temperature (typically 75 °C) was apparently a requirement for these reactions. For example, the reaction of a thionyl chloride-treated MWNT sample with **I** at a lower temperature of 45 °C resulted in a significantly less amount of functionalized nanotubes (on the basis of solution color or visible absorption; see below). As expected, these reactions were found to be sensitive to residual water in the reactants. **I**, $\mathbf{I}_{\mathrm{N}}$, and **II**, because of their near ambient melting points, were used as solvents in the functionalization reactions. Obviously, vigorous drying of the dendron samples was required for the best results. The same reactions were carried out with anhydrous THF as solvent, but similar results were obtained only when completely dry THF (freshly distilled over sodium) was used. For $\mathbf{I}_{\mathrm{PEG}}$, on the other hand, the mixing of reactants was better in the presence of solvent THF. However, it was somewhat difficult to obtain completely dry $\mathbf{I}_{\mathrm{PEG}}$ without risking sample damage. Thus, NaH was added to the reaction mixture, which apparently improved the functionalization results considerably.

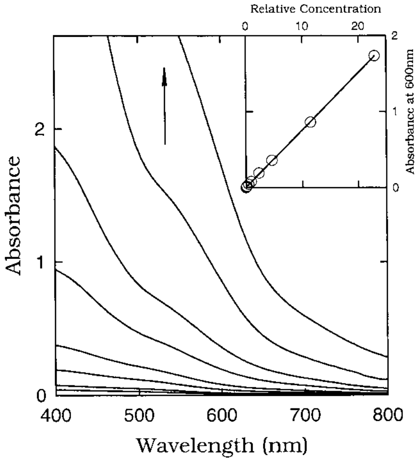


Figure 1. Absorption spectra of $\mathbf{I}_{\mathrm{N}}$-MWNT in room-temperature chloroform at different concentrations (increasing solution concentration in the direction of the arrow). Shown in the inset is the linear dependence of absorption on solution concentration.

SWNTs and MWNTs that are functionalized with lipophilic dendron moieties (**I**, $\mathbf{I}_{\mathrm{N}}$, or **II**) are soluble in a variety of nonpolar and weakly polar organic solvents, such as hexane and chloroform, but they are essentially insoluble in highly polar solvents such as ethanol and DMSO. However, the $\mathbf{I}_{\mathrm{PEG}}$-MWNT sample is soluble in both organic solvents, such as chloroform and DMSO, and water. Solutions of the functionalized SWNTs and MWNTs are colored, and the concentrated solutions are essentially black, but still homogeneous. UV−vis absorption spectra of the functionalized SWNT and MWNT samples are all similar. Shown in Figure 1 are the spectra of $\mathbf{I}_{\mathrm{N}}$-MWNT at different solution concentrations. The dependence of absorbance on solution concentration apparently obeys Beer's law (Figure 1), indicating no effects that are associated with aggregation or absorption of any bi- and multimolecular species. Since all of the dendron species are colorless, even after being subjected to the same reaction conditions in the absence of carbon nanotubes, the dark solution color for the functionalized nanotube samples in organic solvents and water may serve as a convenient indicator for the presence of SWNTs and MWNTs in these solutions.

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(18) The reaction with NaH is often classified as hydrogenolysis, though the effect in this work is the same as that of a classical hydrolysis reaction. See: Lamparth, I.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1727.

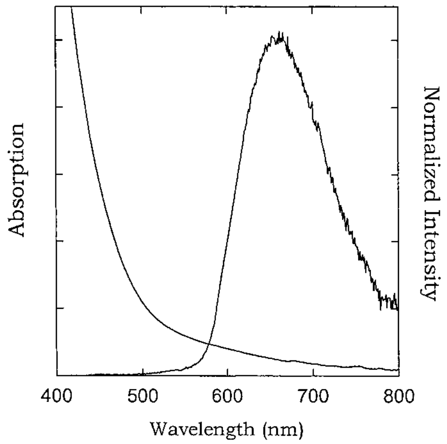

Figure 2. Absorption and luminescence (600 nm excitation) spectra of **I**$_{PEG}$-MWNT in room-temperature chloroform.

The functionalized SWNTs and MWNTs are luminescent.[11,19] For example, shown in Figure 2 is a luminescence spectrum of **I**$_{PEG}$-MWNT in chloroform, and the spectrum in water is similar when excited at the same wavelength. In fact, the luminescence was so intense that it prevented the detection of Raman scattering under a variety of experimental conditions. Despite repeated efforts, no meaningful Raman results were obtained with excitation laser wavelengths of 514.5, 647.1, and 780 nm due to overwhelming interference of luminescence. On the other hand, the FT-IR spectra of the functionalized carbon nanotube samples (in comparison with those of the dendron species) all exhibit a small peak in the 1680−1740 cm^{-1} region, which might be assigned to the nanotube-bound carbonyl groups.[5,8]

^{1}H NMR spectra of the soluble nanotube samples in room-temperature $CDCl_3$ are broad. Here, the proton signals are due entirely to the nanotube-bound dendron moieties. Shown in Figure 3 is a comparison of ^{1}H NMR spectra of dendron **II** before and after functionalizing with MWNTs. The considerable signal broadening for the dendron species upon functionalizing with carbon nanotubes could in principle be explained in terms of two different mechanisms: the attachment of the monomeric dendron to a "polymer-like" nanotube vs the effect of possible paramagnetic impurities in the solution. The latter is obviously relevant to these nanotube-containing samples because of the possibility of residual metal catalysts. Thus, NMR relaxation times are considered for differentiating the two mechanistic possibilities.

With paramagnetic relaxation, the nuclei spin−lattice (T_1) and spin−spin (T_2) relaxation times should be approximately equal, $T_1 \approx T_2$.[20a] Experimentally, T_2 values can be roughly estimated from the line width of proton signals using the simple relationship $\Delta\nu_{1/2} = 1/(\pi T_2)$, where $\Delta\nu_{1/2}$ is the line width at half-height. For the **II**-MWNT sample as an example, $\Delta\nu_{1/2}$ values for the proton signals are in the 100−300 Hz range, except for the narrower signal at 0.88 ppm, Thus, T_1 values for the broad proton signals should be on the order of a few milliseconds. On the other hand, for dipole−dipole relaxation, there is a different relationship between T_1 and T_2, with $T_1 \gg T_2$ for diamagnetic compounds of high molecular weight and low molecular mobility.[20b] Obviously, solid-state NMR represents the extreme in this regard. According to the T_1 measurements for representative proton signals of the **II**-MWNT sample in $CDCl_3$ solution at 20 °C (6.4 ppm, 1.35 s; 3.8 ppm, 0.43 s; 1.25 ppm, 0.87 s; 0.88 ppm, 2.15 s), the T_1 relaxation is apparently slow, from hundreds of milliseconds to seconds, and $T_1 \gg T_2$. Thus, It may be concluded that the observed broad proton signals are associated with diamagnetic species of high molecular weight and low mobility.[20b] Here, the only possible polymeric species in the solution are functionalized carbon nanotubes.

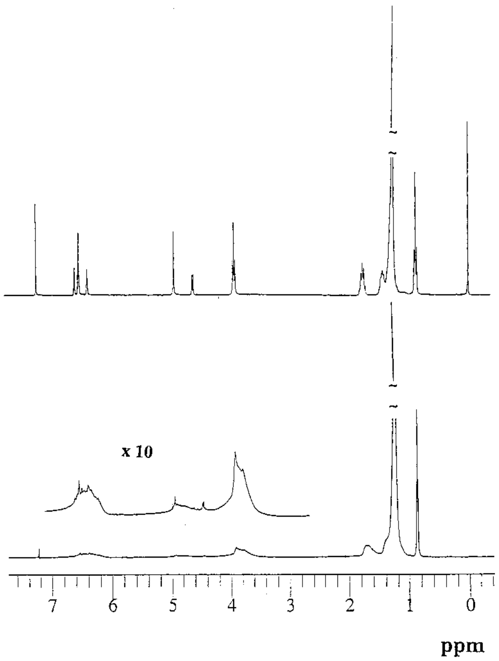

Figure 3. ^{1}H NMR spectra of dendron **II** (top) and **II**-MWNT (bottom) in $CDCl_3$.

The functionalized carbon nanotubes were also characterized by ^{13}C NMR, but no signals due to carbons on the nanotubes themselves or the nanotube-bound carbonyl carbons were detected. This is likely due to the fact that the carbon nanotube concentrations in these solutions are too low even when saturated and that the relaxation times of the nanotube carbons are expected to be very long.[21]

The functionalized MWNT samples were analyzed by TEM. For the analysis, a small droplet of the sample solution was deposited on a carbon-coated copper grid, followed by the evaporation of the solvent. Shown in Figure 4 is a typical TEM image for the functionalized MWNTs, which provides the most direct evidence that the soluble samples contain carbon nanotubes.

The nearly black solids obtained from the defunctionalization of **I**-MWNT were analyzed by SEM. At both low and high resolutions, SEM images of the sample show composite-like materials (Figure 5), which contain

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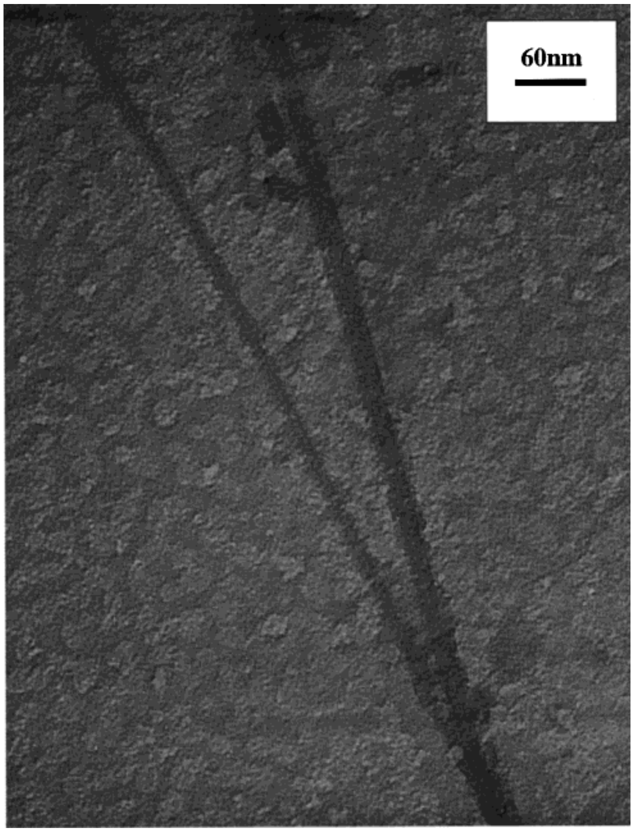

Figure 4. TEM image of the soluble sample $\mathbf{I}_N$-MWNT deposited on a carbon-coated copper grid.

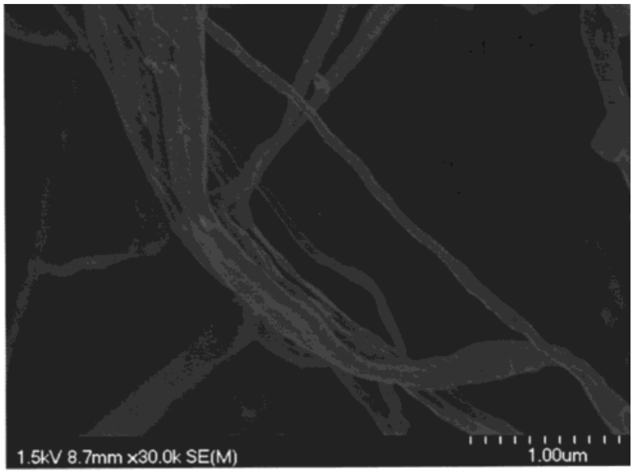

Figure 5. SEM image for the precipitates obtained from the defunctionalization reaction of **I**-MWNT.

nanotubes and likely residual functional groups. Because of the specific hydrolysis reaction conditions in the defunctionalization, the results provide strong evidence for the ester linkages between the nanotubes and the dendron functionalities.

The possibility of encapsulating nanoscale silver inside the functionalized carbon nanotubes was explored.[15a,22,23] While no silver-filled nanotubes were found, the experiments did produce some interesting results concerning the trapping of silver nanoparticles by the nanotube-bound dendron moieties in solution. In a typical experiment, a solution of $\mathbf{I}_N$-MWNT in anhydrous THF was prepared, and to the solution was added $AgNO_3$ until saturation. After the solution was briefly sonicated, the solvent THF was removed on a rotary evaporator. The remaining solid sample was repeatedly washed with water to remove $AgNO_3$, and then was redissolved in anhydrous THF to form a clear solution. To the solution was added hydrazine, which apparently resulted in the chemical reduction of residual silver cations, and the clear solution turned into more of a suspension. A small aliquot of the suspension was diluted and deposited on a carbon-coated copper grid for TEM measurements, and the remaining suspension was evaporated to obtain a solid sample for X-ray powder diffraction analysis. The X-ray diffraction pattern of the sample exhibited broad peaks centered at 2θ of approximately 38.1°, 44.3°, 64.4°, 77.5°, and 81.5°, characteristic of nanocrystalline silver particles.[24,25]

The TEM images of the sample are rather interesting, showing that the nanocrystalline silver particles are aligned next to certain sections of a nanotube (Figure 6). The results from the control experiments with purified raw nanotubes are rather different, showing instead separate aggregates of nanotubes and silver particles. According to the experimental procedure detailed above, the solid sample containing $\mathbf{I}_N$-MWNT and $AgNO_3$ was repeatedly washed with water before chemical reduction in hydrazine solution. Thus, there is likely something special with those sections of the nanotube, which allows the trapping of either silver cations before chemical reduction or silver nanoparticles. A logical explanation seems to be that these special sections of the nanotube contain the sites linking the dendron functionalities, or in other words, it is the nanotube-bound dendron moieties that facilitate the trapping of nanoparticles. In this regard, the aligned nanocrystalline silver particles may actually be considered as high electron density markers for indicating the branching points or regions on the dendron-functionalized carbon nanotubes.

Summary and Conclusion

SWNTs and MWNTs were functionalized by lipophilic and hydrophilic dendron species under classical amidation and esterification reaction conditions. The experimental results suggest no significant differences between amidation and esterification reactions and between reactions with SWNTs and MWNTs. The functionalization is probably with the nanotube-bound carboxylic acid groups, as supported by some preliminary evidence from FT-IR measurements[5,8] and by the results from the defunctionalization reactions. However, an unambiguous confirmation for the proposed amide and ester linkages is still needed in further investigations.

The lipophilic dendron-functionalized carbon nanotubes are soluble in hydrocarbon and weakly polar organic solvents, while the nanotubes functionalized with oligomeric PEG moieties are soluble in both organic

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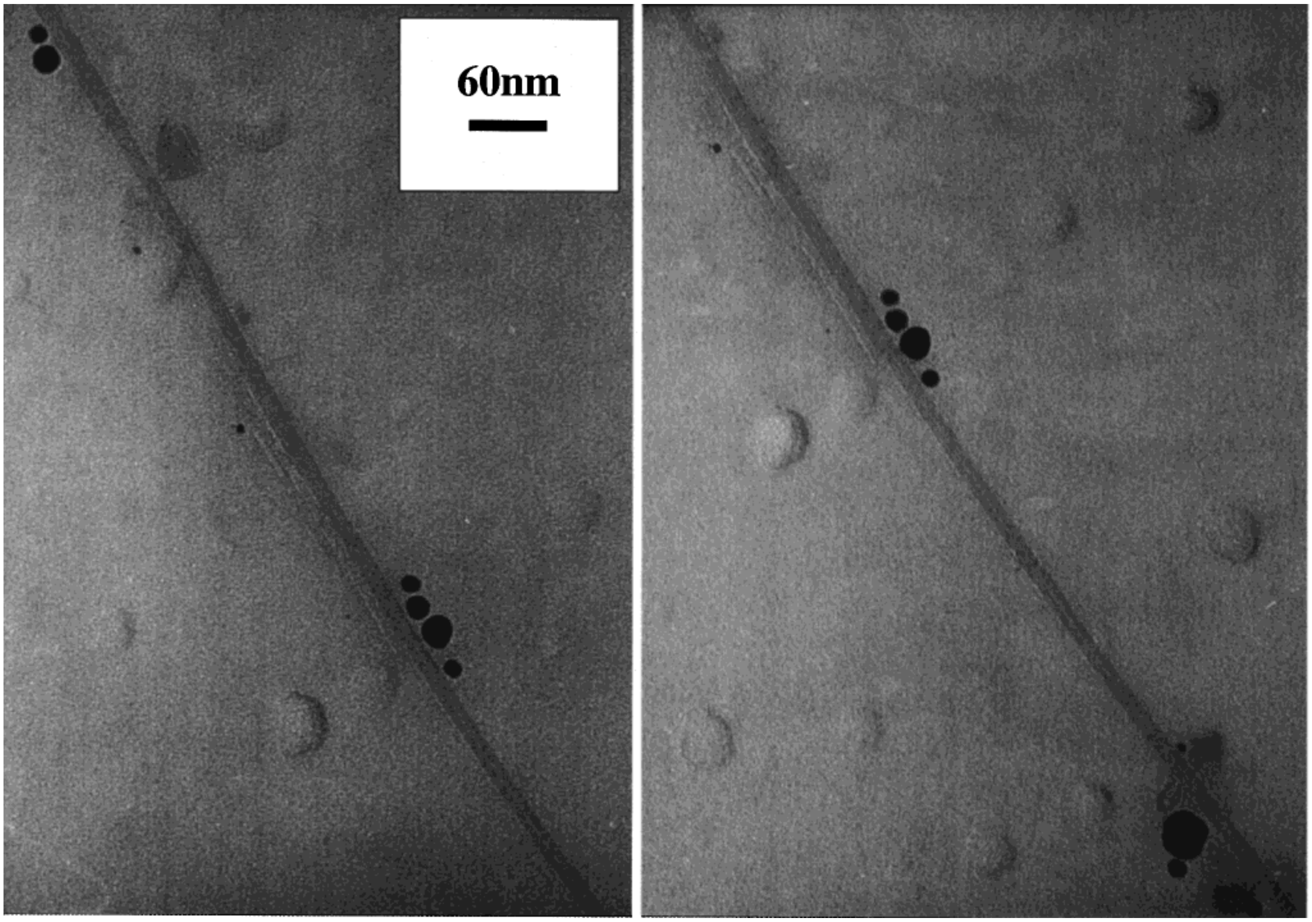

Figure 6. TEM images showing the trapping of nanocrystalline silver particles by $\mathbf{I}_{\mathrm{N}}$-MWNT. The two images are for two different sections of the same nanotube (see the four particles in the middle of both images).

solvents and water. The color of these homogeneous solutions serves as a visual indicator for the presence of carbon nanotubes in the soluble samples because the reactants of the functionalization reactions, except for carbon nanotubes, are colorless. This is particularly reliable with the $\mathbf{I}_{\mathrm{PEG}}$-MWNT sample, for which the dialysis effectively removes all possible nonpolymeric byproducts of the functionalization reaction. The NMR results provide complementary evidence for the soluble samples being functionalized carbon nanotubes. Despite the lack of clear NMR signals from the nanotubes themselves, there is no doubt that the dendra are attached to polymeric species, for which nanotubes are the only candidates in these solutions. For the functionalized MWNTs the most direct evidence is of course the TEM images (Figures 4 and 6). The same direct observation of SWNTs in the soluble samples by use of high-resolution TEM is needed in further investigations.

Acknowledgment. We thank J. Riggs, Z. Guo, F. Lin, J. Roberts, K. Henbest, and R. Czerw for experimental assistance. Financial support from the NSF (Grant CHE-9727506 and, in part, Grant EPS-9977797), NASA, the South Carolina Space Grant Consortium, and the Center for Advanced Engineering Fibers and Films (NSF-ERC at Clemson University) is gratefully acknowledged. L.A.R. and Y.J.Y. were participants of the Summer Undergraduate Research Program sponsored jointly by NSF, DOE, and Clemson University. The support of the NSF (Grant CHE-9700278) for the acquisition of the 500 MHz NMR instrument is also acknowledged.

Supporting Information Available: Experimental details and SEM images of the SWNTs and MWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

CM010069L