

# Functionalizing Multiple-Walled Carbon Nanotubes with Aminopolymers

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Multiple-walled carbon nanotubes (MWNTs) produced using the chemical vapor deposition method were functionalized via attaching aminopolymer poly(propionylethylenimine-*co*-ethylenimine) to the nanotubes. Two different reaction conditions based on acylating the nanotube-bound carboxylic acids and on directly heating nanotubes in the polymer melt were used and compared. Both methods were effective in the nanotube functionalization, and the polymer-attached MWNTs were found to be soluble in many common organic solvents and in water. Results from the characterization of the functionalized nanotube samples using electron microscopy, optical spectroscopy, NMR, and thermal analysis techniques are presented and discussed.

## Introduction

The chemical modification and solubilization of carbon nanotubes have received much recent attention. Several successful functionalization reactions for both single-walled (SWNT) and multiple-walled (MWNT) carbon nanotubes have been reported.<sup>1–16</sup> For example, Margrave, Smalley, and co-workers reported the preparation of fluorinated SWNTs.<sup>1</sup> Haddon and co-workers first used the nanotube-bound carboxylic acid groups for attaching long alkyl chains to SWNTs via amide linkages<sup>2,3</sup> and via carboxylate–ammonium salt ionic interactions.<sup>4</sup> Sun and co-workers showed that the esterification of the carboxylic acid groups could also be used to functionalize and solubilize nanotubes of any lengths.<sup>5–7</sup> An advantage with the ester linkages is that they can be easily defunctionalized via acid- or base-catalyzed hydrolysis, allowing the recovery of carbon nanotubes from the soluble samples.<sup>7</sup> Both amidation and esterification reactions were employed in the functionalization of not only SWNTs but also MWNTs with lipophilic and hydrophilic dendron species, which were considered as being more effective than simple long-chain functionalities for the solubilization of nanotubes.<sup>6</sup> Recently, Wilson and co-workers reported that anilines could be used to functionalize and solubilize SWNTs.<sup>8</sup> Tour, Smalley, and co-workers derivatized small-diameter SWNTs via electrochemical reduction of aryl diazonium salts that contain various functional groups.<sup>9</sup>

Polymeric systems have also been employed for the solubilization or dispersion of carbon nanotubes.<sup>5,12–16</sup> In particular, polymer-bound amino or hydroxy moieties were used in the amidation and esterification reactions with the nanotube surface-bound carboxylic acid groups.<sup>5,14,15</sup> Here we report the functionalization and solubilization of MWNTs via attaching aminopolymers to the nanotubes. Two different reaction conditions based on acylating the carboxylic acids and on directly heating nanotubes in the polymer melt were used and compared. Results from characterizations using electron microscopy, optical

spectroscopy, NMR, and thermal analysis techniques are presented and discussed.

## Experimental Section

**Materials.** Poly(propionylethylenimine) (PPEI,  $M_w$  of 50,000 and 200,000), xylene, and ferrocene were purchased from Aldrich, and thionyl chloride was obtained from Acros. Solvent-grade THF was first dried and distilled over molecular sieves and then distilled over sodium before use. Other solvents were either of spectrophotometry/HPLC grade or purified via simple distillation. Carbon- and holey carbon-coated copper grids were obtained from Electron Microscopy Sciences. Dialysis membrane tubings were purchased from Spectrum Laboratories.

**Measurements.** Absorption spectra were recorded on a computer-controlled Shimadzu UV2101–PC spectrophotometer. Luminescence spectra were measured using 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. Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a 50 mW diode laser source for 780 nm excitation and a CCD detector.

NMR measurements were performed on Bruker AC-300 and JEOL Eclipse +500 NMR spectrometers. Tetramethylsilane (TMS) was used as an internal standard. Thermal gravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/SDTA851e system.

Scanning electron microscopy (SEM) images were obtained on a Hitachi 4700 field-emission SEM system equipped with an energy-dispersive X-ray analyzer. Transmission electron microscopy (TEM) analyses were conducted on Hitachi S7000 and Philips CM200/FEG TEM systems. The latter is equipped with a Gatan 794 Multi-Scan CCD camera for digital imaging.

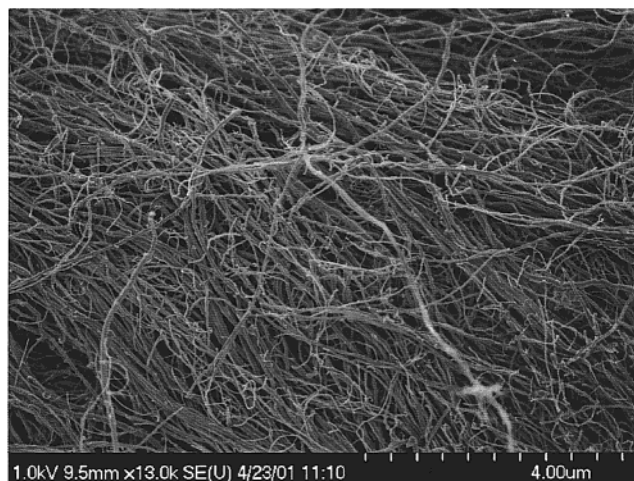
**Nanotubes.** MWNTs were produced via the chemical vapor deposition (CVD, or sometime called catalytic pyrolysis) method, as reported in the literature.<sup>17,18</sup> Xylene and ferrocene were used as precursor and catalyst, respectively.<sup>17</sup> The SEM analysis of the as-produced nanotube fraction showed that the sample contained predominantly MWNTs, with only a small

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**Figure 1.** An SEM image of purified MWNTs produced by the CVD method.

quantity of iron and iron oxide particles (from the catalyst). The result is consistent with the conclusion in the literature that nanotube samples produced via the CVD method are hardly contaminated with amorphous carbon and carbon nanoparticles.<sup>17,18</sup>

The nanotube sample was purified to remove the iron compounds. In a typical experiment, a MWNT sample (200 mg) was heated and refluxed in an aqueous  $\text{HNO}_3$  solution (2.6 M, 40 mL) for 48 h. The suspension was then vigorously centrifuged to recover MWNTs, followed by washing repeatedly with deionized water and then drying under vacuum. The purified MWNTs were either used for functionalization or further purified in a repeat of the same procedure. However, there was no evidence for any meaningful difference in the functionalization results of the nanotube samples that were subject to repeated purification procedures. Shown in Figure 1 is a typical SEM image of the purified MWNTs.

**PPEI–EI Copolymer.** Poly(propionylethylenimine-*co*-ethylenimine) (PPEI–EI) random copolymers were prepared via partially hydrolyzing PPEI polymers.<sup>19</sup> In a typical reaction, a PPEI sample ( $M_w \sim 200,000$ , 1 g) was dissolved in methanol (5 mL). After water (50 mL) was added, methanol was evaporated via heating, and the solution became opaque. To the solution was added aqueous HCl (1 M, 2 mL), followed by refluxing for 24 h. The reaction mixture was cooled to ambient and then was neutralized with aqueous NaOH to a pH of  $\sim 10$ . Upon the removal of water, the product was extracted with chloroform and then precipitated into hexane, followed by drying under vacuum to yield the PPEI–EI copolymer as a white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.6–3.2 ( $2\times\text{NCH}_2$ ), 2.9–2.6 ( $2\times\text{NHCH}_2$ ), 2.5–2.2 ( $\text{COCH}_2\text{CH}_3$ ), 2.1–1.8 ( $\text{NHCH}_2$ ), 1.2–1.0 ( $\text{COCH}_2\text{CH}_3$ ) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  174 ( $\text{C=O}$ ), 48.5 ( $2\times\text{NCH}_2$ ), 44 ( $2\times\text{NHCH}_2$ ), 26 ( $\text{COCH}_2\text{CH}_3$ ), 9.3 ( $\text{COCH}_2\text{CH}_3$ ) ppm. The EI mole fraction in the random copolymer  $x_{\text{NH}}$  was estimated in terms of the  $^1\text{H}$  NMR signal integrations<sup>19</sup>

$$x_{\text{NH}} = I_{2.8}/(I_{2.8} + I_{3.4}) \quad (1)$$

The mole fraction  $x_{\text{NH}}$  could be controlled via varying the hydrolysis reaction time. For the PPEI–EI copolymers used in this study, the  $x_{\text{NH}}$  value was generally  $\sim 20\%$ .

**Functionalization.** The nanotube surface-bound carboxylic acid groups were used in the functionalization of MWNTs with PPEI–EI under two different reaction conditions. One was the

use of thionyl chloride as an acylation agent for subsequent amidation, and the other was based on directly heating MWNTs in the polymer melt. Both reaction conditions resulted in functionalized nanotube samples that are readily soluble in many common organic solvents and in water.

**Acylation–Amidation.** In a typical reaction, a purified MWNT sample (20 mg) was refluxed with  $\text{SOCl}_2$  (5 mL) for 24 h to convert the carboxylic acids into acyl chlorides. Upon evaporating the unreacted  $\text{SOCl}_2$  under vacuum, PPEI–EI ( $M_w \sim 200,000$ , 200 mg) was added to the acylated nanotube sample. The mixture was heated to 160–180  $^\circ\text{C}$  and kept in that temperature range under nitrogen protection for 12 h. After the reaction mixture was allowed to return to the ambient temperature, it was repeatedly extracted with chloroform. The functionalized nanotubes in the dark chloroform solution were precipitated into hexane. The sample was redissolved in deionized water for dialysis (dialysis tubing cutoff molecular weight  $\sim 100,000$ ) against freshwater for 3 days. Further purification included the precipitation from chloroform solution into hexane, followed by the solvent removal and drying under vacuum. The PPEI–EI polymer-functionalized MWNTs were obtained as dark solids.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.3–3.1, 2.9–2.7, 2.6–1.9, 1.4–0.8 ppm.

**Direct Heating.** In a typical reaction, a MWNT sample (20 mg) was heated with PPEI–EI ( $M_w \sim 200,000$ , 200 mg) at 160–180  $^\circ\text{C}$  under nitrogen protection for 12 h. The extraction and purification procedures were the same as those described above. The PPEI–EI polymer-functionalized MWNTs thus obtained were also dark solids.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.5–2.9, 2.9–2.7, 2.7–1.9, 1.5–0.4 ppm.

## Results and Discussion

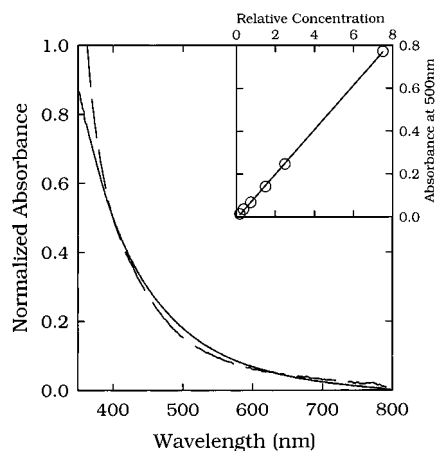
The CVD method is known to produce MWNT samples that are generally free from amorphous carbons and carbon nanoparticles.<sup>17,18</sup> These relatively pure nanotube samples are particularly valuable to the study of functionalization reactions to eliminate any ambiguities on whether the functionalization is indeed with the nanotubes. Thus, the characterization of the soluble PPEI–EI–MWNT samples was focused on the detection of MWNTs in solution and on the properties of the nanotube solution.

The PPEI–EI–MWNT samples from both acylation–amidation (“ $\text{SOCl}_2$  method”) and direct heating (“heating method”) are soluble in many common organic solvents such as chloroform and DMSO and also in water, forming dark-colored solutions. Since PPEI–EI is colorless, the dark solution color is a simple visual indication for the solutions to contain nanotubes. Shown in Figure 2 are observed UV/vis absorption spectra of the samples from the two functionalization methods in room-temperature (22  $^\circ\text{C}$ ) chloroform. These are essentially featureless curves, similar to the spectra of other solubilized carbon nanotubes with different functionalities.<sup>5–7,15</sup> The observed absorption spectra are dependent on the solution concentrations in a linear fashion (Figure 2 inset), following the Lambert–Beer’s law.

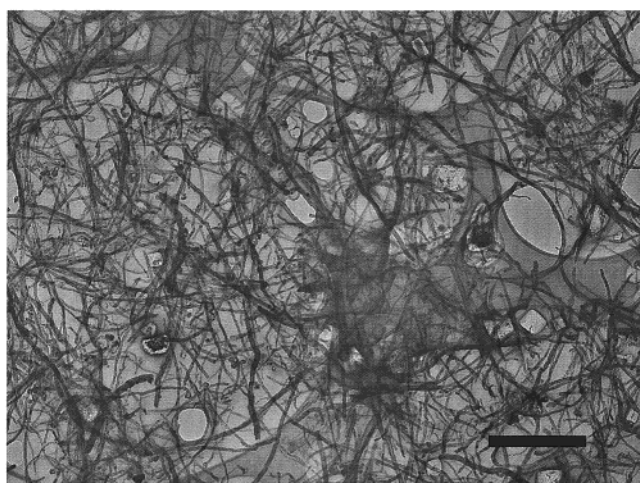
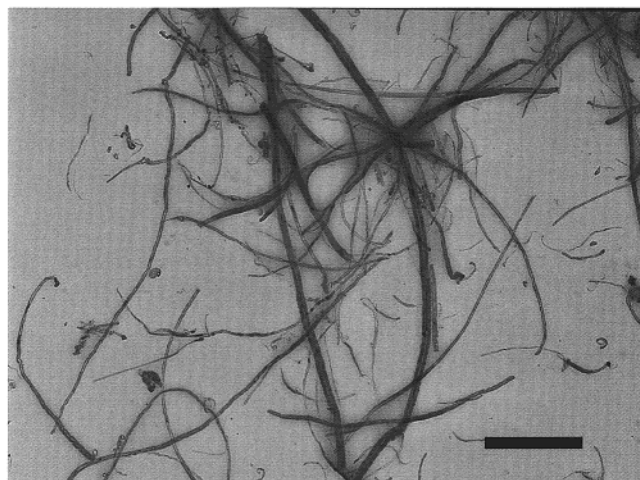
The Raman spectral measurements were subject to strong interference of luminescence even with near-infrared excitation (780 nm). The interference was overwhelming for the functionalized MWNTs in solution. However, the Raman spectra of the solid-state samples exhibit the characteristic tangential-mode peaks<sup>20</sup> at 1312, 1584, and 1611  $\text{cm}^{-1}$  over a strong luminescence background.

More direct evidence for the presence of MWNTs in dark-colored solution was due to the TEM analysis. In the preparation



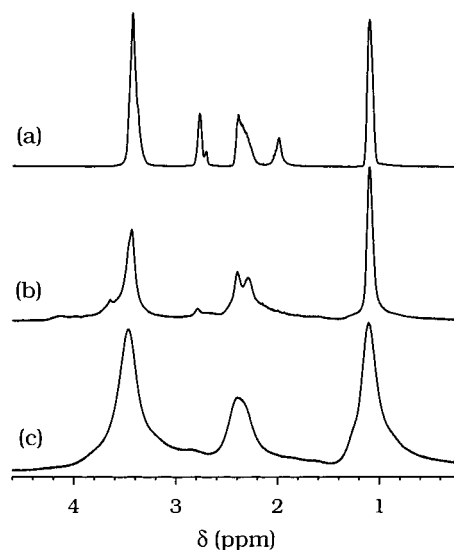


**Figure 2.** UV/vis absorption spectra of the PPEI-EI-MWNT samples from the  $\text{SOCl}_2$  method (—) and the heating method (---) in room-temperature chloroform solutions. Shown in the inset is a Lambert-Beer's plot for the sample from the  $\text{SOCl}_2$  method.

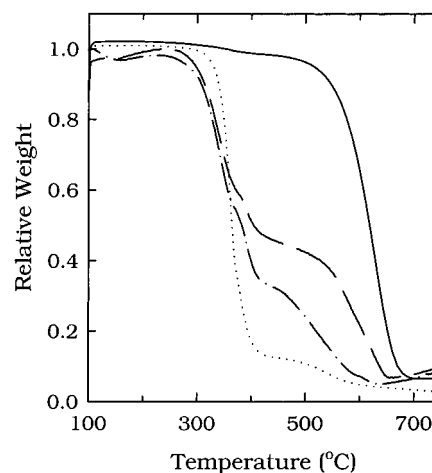


**Figure 3.** TEM images of the PPEI-EI-MWNT samples from the  $\text{SOCl}_2$  method (top) and the heating method (bottom). The scale bars in both images represent 1  $\mu\text{m}$ .

of a sample for TEM imaging, a drop of the chloroform solution of PPEI-EI-MWNT was placed onto a carbon- or holey carbon-coated copper grid, followed by the evaporation of the solvent. Shown in Figure 3 are typical TEM images of functionalized MWNT samples from the two methods. Both images exhibit well-dispersed MWNTs of different lengths (up to 5  $\mu\text{m}$ ) and diameters (up to 150 nm). The dense population



**Figure 4.**  $^1\text{H}$  NMR spectra of (a) PPEI-EI, (b) PPEI-EI-MWNT from the  $\text{SOCl}_2$  method, and (c) PPEI-EI-MWNT from the heating method in  $\text{CDCl}_3$ .



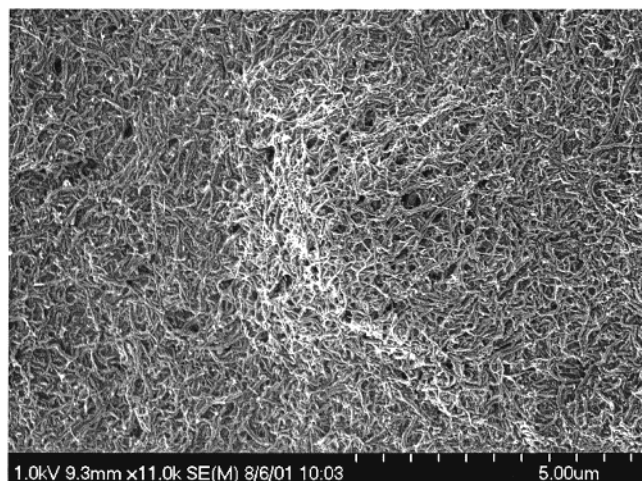
**Figure 5.** TGA results of the PPEI-EI polymer sample (.....), purified MWNT sample (—), PPEI-EI-MWNT sample from the  $\text{SOCl}_2$  method (— · —), and PPEI-EI-MWNT sample from the heating method (— — —).

of MWNTs in one of the images indicates that the predeposited solution contained a high concentration of functionalized nanotubes.

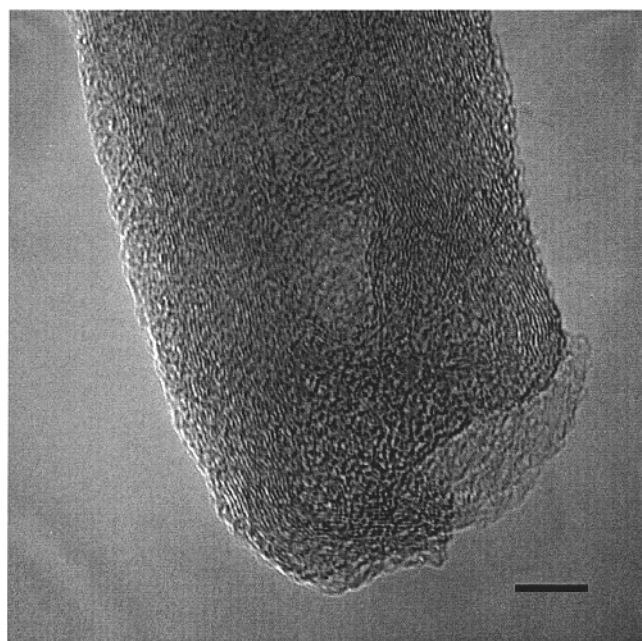
The  $^1\text{H}$  NMR spectra of the PPEI-EI polymer-functionalized MWNTs in deuterated chloroform are compared with that of the parent PPEI-EI in Figure 4. The broad proton signals in the parent PPEI-EI are further broadened upon the attachment of the polymer to nanotubes.

The broadening effect might be attributed to the fact that the nanotubes are even larger "polymeric" species of significantly lower mobility. Another significant change is that the proton signals at  $\sim 2.8$  and  $\sim 2$  ppm due to the ethylenimine (EI) units in the spectrum of PPEI-EI are absent in the spectra of the functionalized MWNT samples (Figure 4). The results are consistent with the notion that the amino moieties are responsible for the functionalization reactions with the nanotube surface-bound carboxylic acids.<sup>2-6,15</sup> However, an identification of the linkages from such reactions is hindered by the broadness of the signals in the spectra of the PPEI-EI polymer-functionalized MWNTs.

The nanotube contents in the functionalized MWNT samples could not be estimated gravimetrically because the weight of



**Figure 6.** SEM image of a PPEI-EI-MWNT sample after being subject to the TGA analysis to 500 °C.



**Figure 7.** High-resolution TEM image of a PPEI-EI polymer-functionalized MWNT. The scale bar represents 15 nm.

the residual nanotubes from the functionalization reaction was typically higher than that of the starting nanotube sample. A possible scenario was that some MWNTs were functionalized by PPEI-EI only to the extent that was insufficient for the solubilization; namely, those attached PPEI-EI species contributed to the weight of the residual nanotube sample.

The thermal defunctionalization of the PPEI-EI polymer-functionalized MWNTs was investigated by TGA, followed by SEM analyses. For the parent PPEI-EI ( $M_w \sim 50\,000$  and  $x_{NH} \sim 19\%$ ), the TGA experiment was conducted with a heating rate of  $10\text{ °C/min}$  in the presence of air. As shown in Figure 5, the onset of the weight loss is at  $\sim 340\text{ °C}$ , with bulk of the weight loss occurring before  $\sim 400\text{ °C}$ . Similarly, for the purified MWNT sample, the significant weight loss starts at  $\sim 550\text{ °C}$  and ends at  $\sim 680\text{ °C}$  (Figure 5). The TGA patterns of the PPEI-EI polymer-functionalized MWNT samples are apparently intermediate between those of the parent PPEI-EI and the purified MWNTs, as compared in Figure 5. There are essentially two temperature regions in each of the TGA patterns. The rapid weight reduction in the first region ( $300\text{--}400\text{ °C}$ ) may readily be attributed to the loss of PPEI-EI polymer. The slower but

still significant weight reduction in the second region ( $400\text{--}650\text{ °C}$ ) is likely due to the loss of MWNTs and perhaps some associated PPEI-EI polymer. However, if no loss of PPEI-EI polymer in this region is assumed, the amount of weight reduction,  $\sim 30\%$  for the sample from the  $\text{SOCl}_2$  method and  $\sim 40\%$  for the sample from the heating method, serves as a first approximation in the estimate of the MWNT contents in the functionalized nanotube samples. These nanotube content values probably represent the upper limits because the weight reduction in this temperature region is likely due in part to the loss of attached PPEI-EI polymers, namely, that the nanotube-attached polymers may have different TGA behavior from that of the neat PPEI-EI.

The notion that polymers are thermally removed in this temperature region is also supported by results from the SEM analysis. For example, shown in Figure 6 is an SEM image of the PPEI-EI polymer-functionalized nanotube sample after being subject to the TGA analysis to  $500\text{ °C}$ . It exhibits a high-density of MWNTs, similar to those in the SEM image of the starting purified MWNT sample (Figure 1).

The functionalization of MWNTs with PPEI-EI is probably through the nanotube surface-bound carboxylic acid moieties. These acid groups are likely associated with the surface defects on the tips and throughout the side-wall, which are oxidized during the production and the subsequent oxidative purification under strongly acidic conditions. In fact, the MWNT sample produced by the CVD method seems more readily functionalized and solubilized than the sample obtained from the arc discharge method (based on a comparison of the resulting nanotube solutions),<sup>5,14,15</sup> consistent with the understanding<sup>17,18</sup> that the CVD-produced MWNTs contain more defects. Shown in Figure 7 is a TEM image of a PPEI-EI-functionalized MWNT on a holey carbon-coated copper grid at a higher resolution. According to the image, there are definitely defects on the nanotube tip that are dislocated from the graphite fringes.

Mechanistically, the functionalization using the  $\text{SOCl}_2$  method likely results in the formation of amide linkages,<sup>2,6</sup> and the heating method may cause amidation (thermally induced condensation) as well, in addition to the ionic interactions suggested by Haddon and co-workers.<sup>4</sup> While both methods are obviously applicable to the functionalization and solubilization of MWNTs, the  $\text{SOCl}_2$  method seems somewhat more effective in the nanotube dispersion because the corresponding solution of the functionalized nanotubes exhibits less scattering in the UV/vis absorption measurements. On the other hand, the heating method seems to produce functionalized MWNT sample of a higher nanotube content, consistent with the observation of Haddon and co-workers in the functionalization of SWNTs.<sup>4</sup>

In summary, MWNTs can be functionalized and solubilized via attaching aminopolymers to the nanotubes. Both the acylation-amidation method and the direct heating method are effective for the functionalization and solubilization. The aqueous solubility of these functionalized nanotube samples as a result of the hydrophilicity of the aminopolymers may find applications in introducing carbon nanotubes into biologically significant systems.

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