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In Situ Polymerization Initiated by Single-Walled Carbon Nanotube Salts

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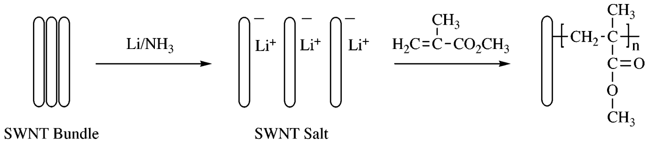
Nanotube salts serve as initiators for the in situ polymerization of methyl methacrylate onto the surface of the nanotubes. The poly(methyl methacrylate)-grafted single-walled carbon nanotubes (SWNTs) are soluble in chloroform, tetrahydrofuran, and acetone. Atomic force microscopy images and Raman spectroscopy show that the SWNT bundles were exfoliated during the reduction, leading mostly to individual tubes.

Introduction

Single-walled carbon nanotubes[1] (SWNTs) have been shown to exhibit the highest tensile modulus and tensile strength of any existing material,[2] properties that may lead to important applications of these materials in strong composites. The covalent attachment of polymers to the sidewalls of SWNTs is of interest in this regard, and functionalization of carbon nanotubes by various polymers through either amide or ester linkages has been reported.[3] Methods that lead to polymerization onto the surface of nanotubes have also been investigated.[4] These methods, however, require sonication, and this can be damaging and may not be practical for some applications. We have shown earlier that SWNT salts may be functionalized without sonication under conditions that lead to extensive debundling.[5] In this paper, we report the use of debundled nanotubes salt[5] as anionic initiators for the in situ polymerization of methyl methacrylate onto the surface of the SWNTs as illustrated in Scheme 1.

Scheme 1



Experimental Section

Materials. The SWNTs used during this study were produced by the HiPco[6] process and purified by heating in a water-rich atmosphere at 220 °C followed by extraction into HCl.[7] The iron content of the purified SWNTs was determined to be 2 wt % by thermogravimetric analysis (TGA) (Figure S1 in the Supporting Information). Methyl methacrylate (99%), poly(methyl methacrylate) (PMMA; average MW ∼15000 by gel permeation chromatography (GPC), powder), and lithium (granules, 99%) were purchased from Aldrich. Methyl methacrylate was washed twice with 5% NaOH and twice with water, dried over anhydrous MgSO$_4$, and vacuum distilled from CaH$_2$.

General Procedure for Polymerization. The polymerization experiments were carried out as follows: A sealed flame-dried 100 mL three-neck round-bottom flask containing purified single-walled carbon nanotubes (20 mg, 1.6 mmol of C) was evacuated and refilled with argon three times. Ammonia (∼60 mL) was then condensed into the flask followed by the addition of small pieces of lithium (∼10 mg) until a slightly blue color remained. Methyl methacrylate monomer (3.2 g, 32 mmol) was then added to the flask via a syringe. The ice bath was then removed and the reaction

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mixture allowed to stand overnight with the slow evaporation of NH_3. The reaction was worked up by quenching the reaction mixture with ethanol (10 mL) followed by the addition of water (20 mL). After acidification using 10% HCl, the nanotubes were filtered through a 0.2 μm PTFE membrane, washed extensively with ethanol and chloroform, and then dried in a vacuum oven (80 °C) overnight.

In a control experiment, ammonia (~60 mL) was then condensed into a flame-dried three-neck flask followed by the addition of small pieces of lithium (10 mg, 1.44 mmol). Methyl methacrylate monomer (3.2 g, 32 mmol) was then added via a syringe. The ice bath was removed, and the reaction was allowed to stand overnight as the NH_3 slowly evaporated. The reaction was worked up by first quenching the reaction mixture with ethanol (10 mL) followed by the addition of water (20 mL). The polymer was filtered, washed extensively with ethanol, dissolved in chloroform, and precipitated by the addition of ethanol. The precipitate was collected by filtration.

Characterization. The PMMA-grafted SWNTs were characterized by Raman spectroscopy, TGA−FTIR, atomic force microscopy (AFM), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM). Raman spectra were collected from solid samples, using a Renishaw 1000 micro-Raman system with a 780 nm laser source. The thermal degradation studies were carried out using an SDT 2960 simultaneous differential scanning calorimeter−thermogravimetric analyzer from TA Instruments. The gaseous species released from the sample during pyrolysis were fed into the FTIR spectrometer, and the concentration of the thermally detached radicals was monitored with time and temperature. AFM was performed using a Digital Instruments Nanoscope IIIa in tapping mode using a 3045 JVW piezo tube scanner. A scan frequency of 1.0 Hz was used. The surfaces of PMMA-grafted SWNTs were sputter coated with gold and then examined with an FEI XL-30 environmental scanning electron microscope (FEI Co., Hillsboro, OR). TEM images were obtained with a JEOL 2010F microscope operating at 100 kV. Molecular weight distributions of the polymers from the control experiments were determined by GPC on a PL-GPC-220 high-temperature chromatograph equipped with a refractive index (RI) detector using a PL gel column (PL gel is a highly cross-linked porous polystyrene/divinylbenzene matrix, analytical particle size 5 μm, individual pore size packing 10^5 Å) from Polymer Laboratories. The GPC instrument was operated using THF as eluent with a normal flow rate of 1.0 mL/min at 40 °C. Polystyrene standards in the range 1800000−500 g/mol were used for calibration.

Results and Discussion

Raman Spectroscopy. Raman spectra provide direct evidence for covalent sidewall functionalization. The Raman spectrum of the starting purified SWNTs displays a small disorder mode (D-band) at 1290 cm^{-1} (Figure 1A). The much larger disorder mode exhibited by the polymer-grafted nanotubes relative to the large tangential mode (G-band) provides confirmation of covalent functionalization (Figure 1B). The Raman resonance enhancement seen in Figure 1A is also suppressed after functionalization, consistent with covalent attachment.[8]

Certain radial breathing modes (RBMs) in the Raman spectra of the nanotubes reflect the extent of bundling in a sample. It has been shown that decreasing the bundle size causes a relative decrease in the 266 cm^{-1} (10, 2) RBM and an increase in the 236 cm^{-1} (12, 1) RBM at 785 nm excitation.[9] The sample of purified SWNTs (Figure 1A) shows a large peak at 266 cm^{-1} and a much smaller peak near 236 cm^{-1}. The polymer-grafted SWNTs show a greatly diminished peak at 266 cm^{-1} and a substantially larger peak near 236 cm^{-1} (Figure 1B). This emphasizes the extensive debundling that occurs by intercalation of the lithium into the SWNT bundles as the SWNT salts are formed.

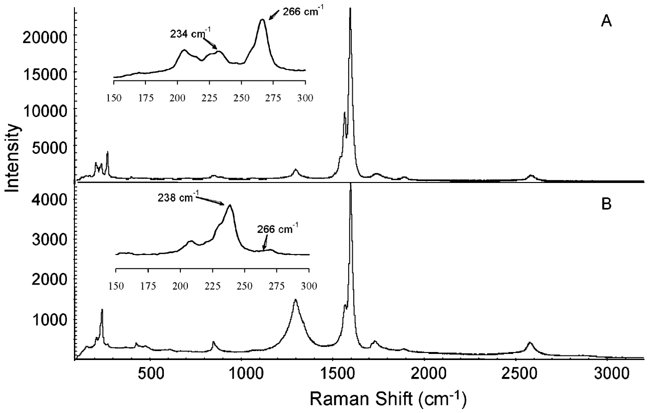

Figure 1. Raman spectra (780 nm excitation) of pristine SWNTs (A) and PMMA-grafted SWNTs (B).

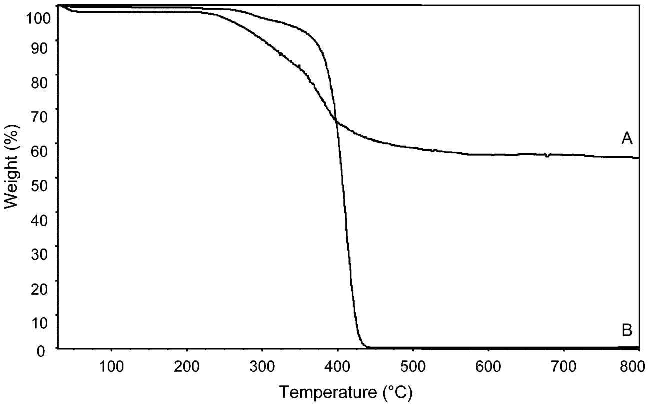

Figure 2. Correlation of the TGA weight percentage during pyrolysis in an atmosphere of argon: (A) PMMA-grafted SWNTs, (B) PMMA (typical MW 15000).

Thermogravimetric Analysis. The PMMA-grafted SWNTs were pyrolyzed under an atmosphere of argon. After 10 min at 800 °C, the weight percentage curve leveled at ~55% (Figure 2A). The weight loss was determined to be ~45%. In a control experiment, all of the bulk PMMA (typical MW 15000) was lost below 450 °C (Figure 2B), suggesting that the entire PMMA component of the PMMA-grafted SWNT sample was lost during the TGA analysis.

Chemigram profiles of the PMMA-grafted SWNTs were obtained by pyrolysis in the furnace of a TGA apparatus that was coupled to an FTIR spectrometer. The samples were held at 100 °C for 20 min, ramped at 10 °C min^{-1} to 800 °C, and then held for 10 min at 800 °C. The gaseous species released from the sample were fed into the FTIR spectrometer and monitored versus time and/or temperature (Figure 3). The time derivative percentage weight loss curve shows two main weight loss steps. According to the heating profile,

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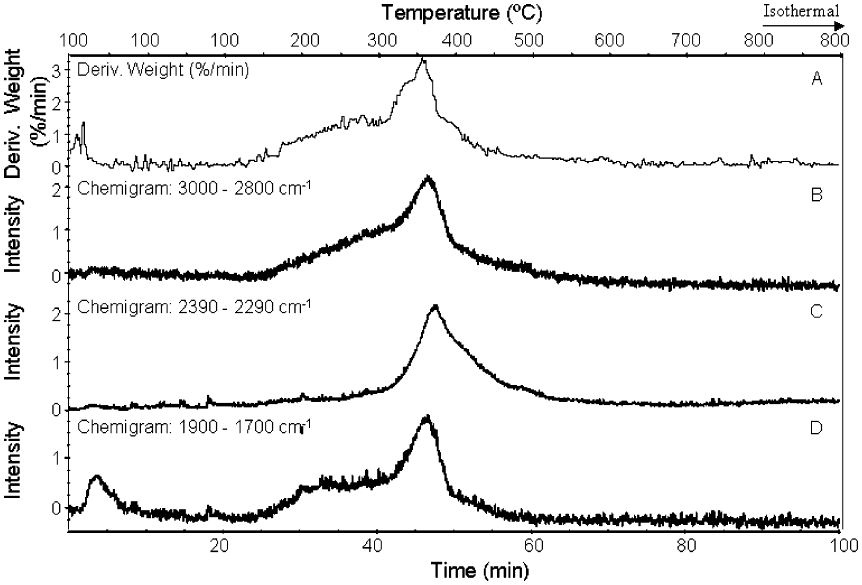

Figure 3. Correlation of the TGA derivative weight percentage (%/min) curve (A) and chemigrams of the gaseous species released from the PMMA-grafted SWNTs during pyrolysis in an argon atmosphere (B−D).

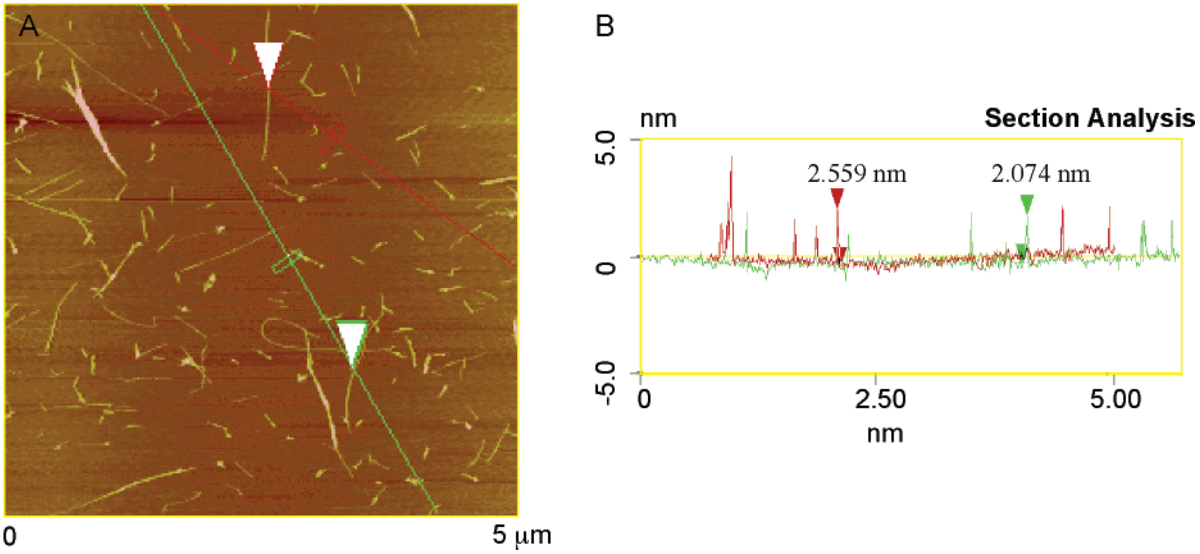

Figure 4. Tapping mode AFM image of PMMA-grafted SWNTs spin-coated from chloroform onto mica: (A) AFM height profile of individual tubes, (B) section analysis.

the first weight loss occurred at ∼200−300 °C and the second at ∼300−400 °C. Cleavage of the polymer chain from the sidewall of the carbon nanotubes would account for this observation. The chemigram profiles exhibited in Figure 3 show that thermolysis yields CO_2 (2390−2290 cm^{-1}, trace C) and other gaseous species that exhibit aliphatic C−H stretching bands at 3000−2800 cm^{-1} (trace B) and C═O stretching bands (1900−1700 cm^{-1}, trace D).

Since it is not possible to determine the molecular weight of the polymer chains grafted onto the SWNTs, a control polymerization of methyl methacrylate initiated by Li/NH_3 has been carried out. GPC analysis of the PMMA sample showed that polymerization occurs under these conditions (Figure S2 in the Supporting Information). Furthermore, combining the weight loss data with the Raman spectrum provides evidence of a polymerization rather than a simple functionalization or short oligomerization. With a weight loss of ∼45%, if only dimers or trimers were present, there would be between ∼20 and ∼30 carbon atoms per attached group. Such a high presence of sp^3-hybridized carbon on the sidewall of the SWNTs would likely cause the Raman spectrum to show a D-band/G-band ratio of 1/1 as it does for dodecylated SWNTs with ∼25 carbon atoms per attached group prepared using the same lithium/ammonia conditions.[5a] The Raman spectrum of PMMA-grafted SWNTs, however, shows a more modest presence of sp^3-hybridized carbons on the nanotubes as indicated by a D/G ratio of ∼1/3.

Atomic Force Microscopy. The diameters of the PMMA-grafted SWNTs were determined by tapping mode AFM microscopy. A typical AFM image of PMMA-grafted SWNTs spin coated from chloroform onto mica is presented in Figure 4. It is clear that most of the PMMA-grafted SWNTs are dispersed as individuals. The average height, and thus diameter, from 30 measurements of different tubes and at different places of the same tube range from 2 to 3 nm with an average diameter of 2.6 nm. The diameters of

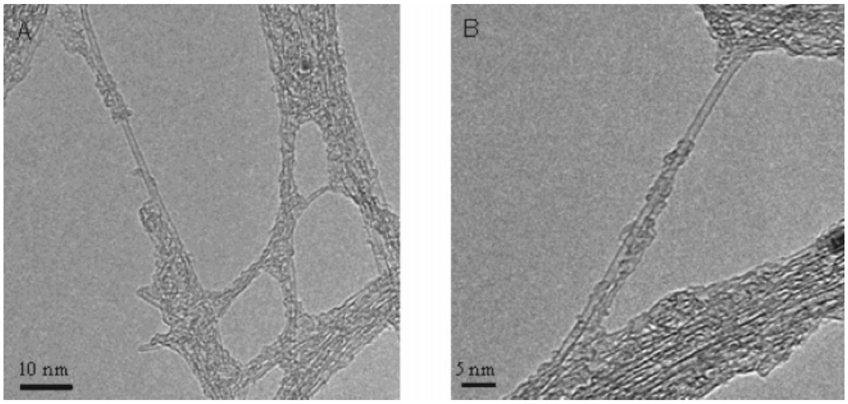

Figure 5. HRTEM images of PMMA-grafted SWNTs.

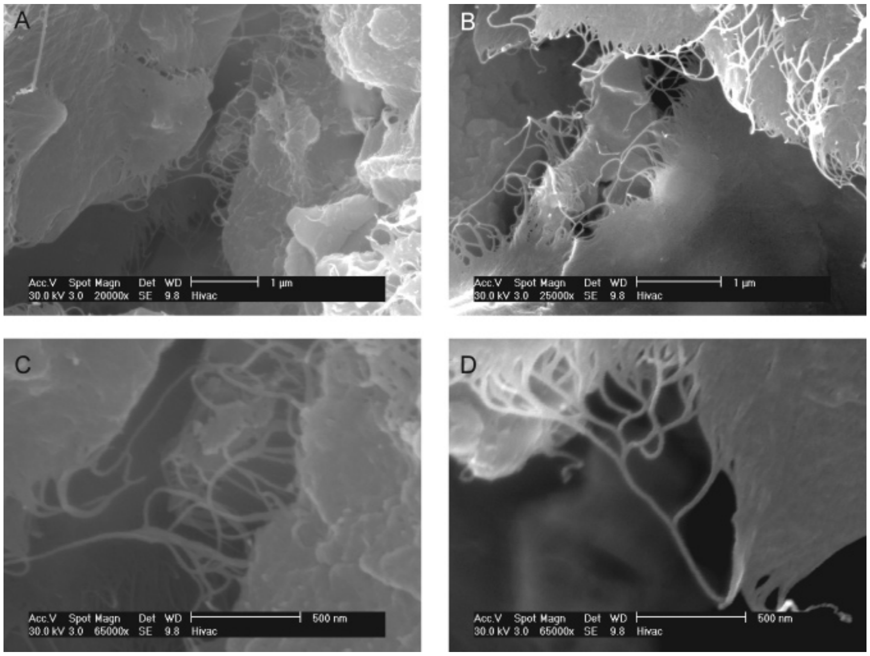

Figure 6. SEM images of PMMA-grafted SWNTs: (A) magnification 20000×, scale bar 1 μm; (B) magnification 25000×, scale bar 1 μm; (C) magnification 65000×, scale bar 500 nm; (D) magnification 65000×, scale bar 500 nm.

individual pristine HiPco SWNTs range from 0.6 to 1.3 nm.[10] These diameter changes may be attributed to surface modification.

Transmission Electron Microscopy. HRTEM images provide confirmation for the unbundling of the PMMA-grafted SWNTs (Figure 5). The nanotubes exhibit a morphology that can be attributed to polymer that is grafted onto the nanotubes. Similar features have been observed by others.[3g,3h]

Scanning Electron Microscopy. SEM images of PMMA-grafted SWNTs are illustrated in Figure 6. These images demonstrate a high SWNT content for these materials.

Finally, several experiments in which the lithium/methyl methacrylate ratio was varied demonstrated that the degree of polymerization is proportional to the amount of monomer that is used. In situ polymerization experiments using acrylonitrile and *tert*-butyl acrylate by carbon nanotube salts have also been carried out. Good dispersibility of these samples in chloroform, THF, and acetone was achieved.

Conclusion

In conclusion, SWNT salts can be used to initiate the polymerization of methyl methacrylate in a simple, scalable process that results in SWNT bundle exfoliation and covalent attachment to the polymer in a single step and without the use of sonication. In principle, this in situ polymerization is feasible for a wide range of vinyl monomers. Further work on the properties of these polymers is currently in progress.

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Supporting Information Available: TGA of purified SWNTs carried out in an atmosphere of air and GPC chromatograms of poly(methyl methacrylate) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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