# Preparing a Styrenic Polymer Composite Containing Well-Dispersed Carbon Nanotubes: Anionic Polymerization of a Nanotube-Bound *p*-Methylstyrene

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ABSTRACT: Multiple-walled carbon nanotubes (MWNTs) were chemically modified by a ligand-exchange reaction of ferrocene (Cp-Fe-Cp). The modified MWNTs (Cp-Fe-MWNTs) were next monolithiated by *tert*-butyllithium and terminated by *p*-chloromethylstyrene (*p*MS). The *p*MS-terminated species (*p*MS-Cp-Fe-MWNTs) were then functionalized with living polystyryllithium anions via anionic polymerization. The resulting polystyrene-functionalized MWNTs exhibited as polymeric nanocomposites and were soluble in common organic solvents showing distinct colors from a neat polystyrene solution. Syntheses results and the characterization data of the functionalized MWNTs, collected from GC-MS, NMR, electron microscopy, and optical spectroscopy, are presented and discussed.

## Introduction

Nanocomposites have recently gained considerable interest in both the academic and industrial fields due to their unique mechanical, thermal, and electronic properties. Nanoscaled particulates such as carbon nanotubes have been studied as fillers in a variety of polymeric matrices to produce enhanced properties. However, carbon nanotubes tend to aggregate, and their nonuniform dispersion in the polymer matrix often results in deleterious effects. Therefore, making a homogeneous nanocomposite often resorts to special mixing methods. Qian et al. mixed 1 wt % of carbon nanotubes with polystyrene in toluene via ultrasonication.[1] Watts et al. used a similar ultrasonication method to mix polystyrene with either carbon nanotubes or boron-doped carbon nanotubes.[2] Liu et al. found an improved dispersion and thermal and mechanical properties of the nanocomposites in the presence of nonionic surfactant.[3] Star and Stoddart synthesized a hyperbranched dendrimer to efficiently break the carbon nanotube bundles by fitting the nanotubes inside the pockets of the dendrimer and also found the wrapping of the bundles with conducting polymer-solubilized carbon nanotubes in organic solvents.[4] Tang and Xu prepared via in-situ polymerization of phenylacetylene polymer-wrapped carbon nanotubes that were soluble in common solvents.[5] Nevertheless, the insolubility of the carbon nanotubes and the inherently poor compatibility between the carbon nanotubes and the polymer make the uniform dispersion of carbon nanotubes in the polymer matrix very difficult, and the resulting inhomogeneous nanocomposites often have unsatisfying properties. Consequently, various methods have been proposed for functionalizing the carbon nanotubes (i.e., anchoring the matrix polymer on the carbon nanotubes) before using them as the fillers in the matrix. Among those methods, most of the reported functionalization methods comprise oxidatively generating carboxylic acid groups on the surface of the carbon nanotubes and covalently linking oligomers or polymers with these carboxylic acid groups.[6−14] Tour et al. prepared polystyrene composites with functionalized carbon nanotubes by the in-situ generation of diazonium compounds.[6] Sun et al. functionalized the carbon nanotubes with poly(vinyl alcohol) and made the functionalized carbon nanotubes soluble in highly polar solvents.[7] Haddon and co-workers used the carboxylic acid groups for attaching long alkyl chains to carbon nanotubes via amide linkages or via carboxylate−ammonium salt ionic interactions.[8] Sun et al. successfully anchored aminopolymers or polystyrene copolymers on the carbon nanotubes via the formation of amide linkages or ester linkages, respectively.[14]

In this paper an alternative method for anchoring polymer molecules on the carbon nanotubes is presented—the unsaturated double bonds were first appended to the carbon nanotubes and then reacted anionically with the living polymer molecules. These unsaturated double bonds were, in turn, generated through successive reactions—ligand exchange of ferrocene, monolithiation on cyclopentadienyl, and termination by *p*-chloromethylstyrene. The polymer-attached carbon nanotubes are soluble in common organic solvents, and the samples were characterized using NMR, electron microscopy, and optical spectroscopic techniques.

## Experimental Section

**Materials.** MWNTs were purchased from Nanotech Port Co. (Taiwan). These MWNTs were produced via the chemical vapor deposition (CVD, or sometimes called catalytic pyrolysis) method. The TEM analysis of the these MWNTs showed that besides a small quantity of iron and iron oxide particles (catalyst residues) the MWNTs contained little amorphous carbon or carbon nanoparticles, which is consistent with the previous findings about the CVD method.[15] The purchased MWNTs were then purified to remove the iron compounds. In a typical experiment, a MWNT sample (200 mg) was heated and refluxed in an aqueous $HNO_3$ solution (2.6 M, 40 mL) for 48 h. The suspension was then vigorously centrifuged to recover MWNTs, followed by a repeated washing with deionized water and a drying under vacuum. The purified MWNTs were later used for functionalization. Typical TEM images of the purified MWNTs have been taken at different magnifications. As shown in Figure 1, these MWNTs have lengths up to a few microns and diameters between 60 and 100 nm.

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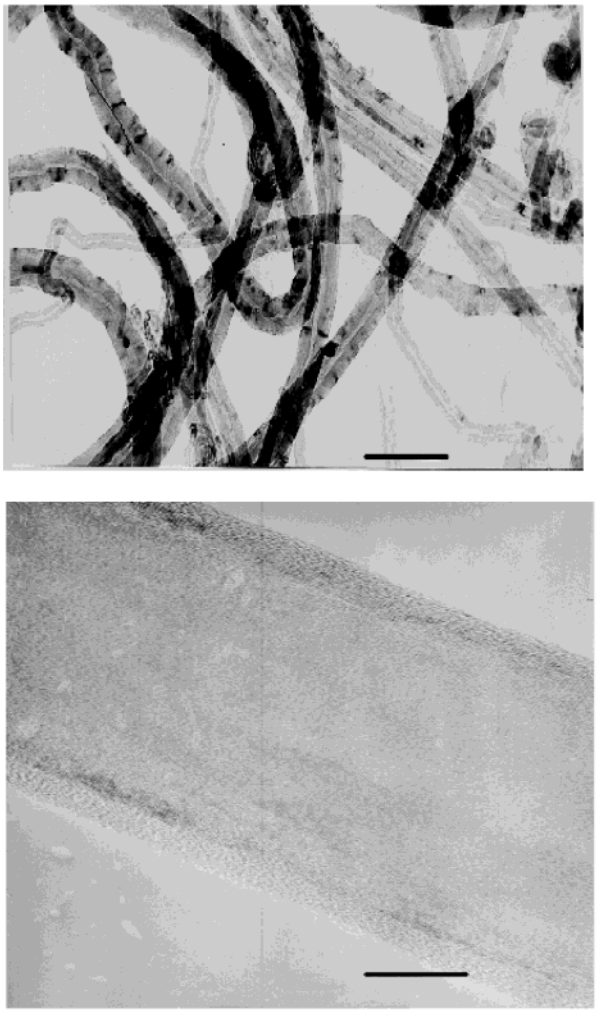
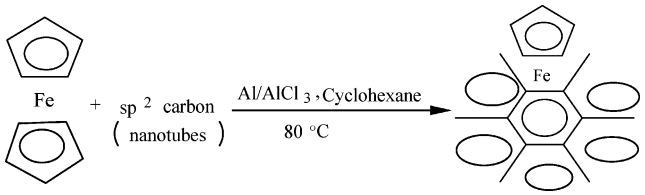


**Figure 1.** TEM image of the purified MWNTs: (a, top) scale bar = 200 nm and (b, bottom) scale bar = 10 nm.

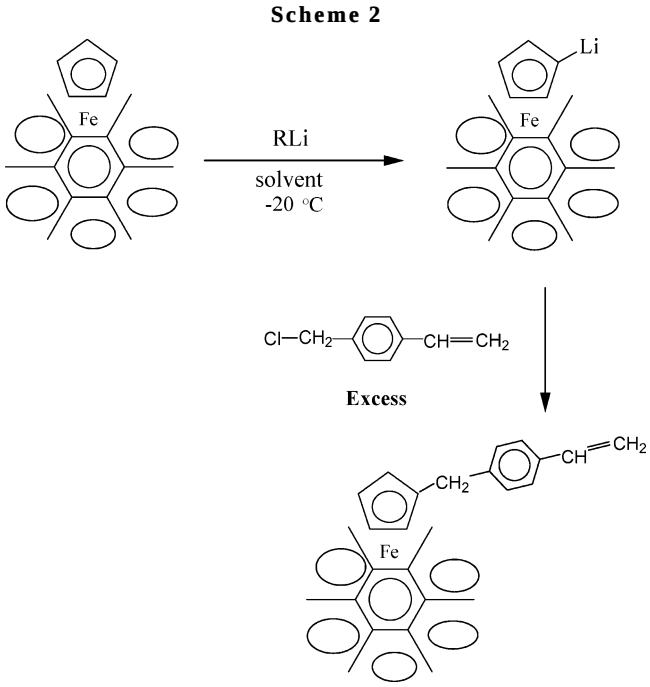
Styrene was obtained from Taiwan Synthetic Rubber Corp. (TSRC) and pretreated with activated alumina (Alcoa Co.) prior to their use. *p*-Chloromethylstyrene (*p*MS) was purchased from Merck and purified by distillation before use. *tert*-Butyllithium (*t*-BuLi) was purchased from Merck as a 1.5 M solution in hexane. Ferrocene (98%), and anhydrous aluminum chloride (99%) were purchased from Fluka. Aluminum powder (90%) was purchased from Riedel-de Haën. Tetrahydrofuran (THF) was purchased form BDH. All solvents were first dried over molecular sieves and then distilled over sodium before use.

**Measurements.** Scanning electron microscopy (SEM) images were obtained from a JEOL JSM-5200 SEM system. Transmission electron microscopy (TEM) analyses were conducted by a JEOL JEM-2010 TEM system. GC-MS spectra were recorded from a Shimadzu GCMS-QP5000 system. NMR measurements were performed by a Varian-Unity INOVA-500 NMR spectrometer. UV/vis absorption spectra were recorded from a Shimadzu UV2101-PC spectrophotometer, and the attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were measured by a Bomem instrument (model DA 8.3) with the internal reflection element being a KRS-5 prism with a face angle of 45 °C. The thermal gravimetric analysis (TGA) was carried out on a TA Instruments TGA/2050 system. The molecular weight distribution of synthesized polymers was determined by the Waters gel permeation chromatograph (GPC) equipped with the Waters M-486 absorbance (UV) and the Waters 410 differential refractive index (RI) detectors. The GPC was operated using four Waters Styragel HR columns (HR0.5, HR3, HR4, HR5E) at a nominal flow rate of 1 mL/min with a sample concentration of 0.1% in THF solvent.

**Scheme 1**




**Scheme 2**

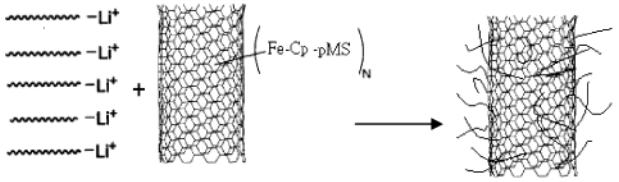



**Preparation of Cp-Fe-MWNTs via a Ligand Exchange of Ferrocene with MWNTs.** Typical ligand-exchange procedures for synthesizing Cp-Fe-MWNTs are depicted in Scheme 1. 7.44 g (40.0 mmol) of ferrocene, 13.33 g (100 mmol) of $AlCl_3$, 0.68 g (25 mmol) of Al powder, 400.0 mL of cyclohexane, and 0.5 g of MWNTs were added to a flask and agitated at 80 °C. The reaction mixture was then heated under reflux, with rapid stirring, in a nitrogen atmosphere for 12 h. Afterward, methanol was added to the mixture at 0 °C, and the solid material was collected by a centrifuge. The collected material was then washed with methanol, acetone, and ether under ultrasonication for 2 h and dried at 60 °C under vacuum for 5 h.

**Synthesis of *p*MS-Terminated Cp-Fe-MWNTs (*p*MS-Cp-Fe-MWNTs).** The *p*MS-terminated Cp-Fe-MWNTs (*p*MS-Cp-Fe-MWNTs) was prepared as depicted in Scheme 2. 0.5 g of Cp-Fe-MWNTs was stirred in a 400.0 mL mixed solvent comprised of hexane and THF at a 1/1 volume ratio under nitrogen at 25 °C. After a 30 min agitation the system was cooled to −20 °C. 30 mL (45 mmol) of *t*-BuLi was added dropwisely at a rate of approximately 3 mmol/min, and the reaction mixture was continuously stirred for 1 h. Afterward, 7 mL (50 mmol) of *p*MS was added, and the reaction mixture was stirred for an additional hour. After a methanol quenching, the solid material was collected by a centrifuge and washed with THF and methanol under ultrasonication for 2 h. Finally the material was dried at 60 °C under a vacuum for 5 h.

**Functionalization of *p*MS-Cp-Fe-MWNTs with Polystyrene.** To a 1 L pressure vessel under a slight nitrogen overpressure were added 500 mL of cyclohexane and 0.1 mL of THF (200 ppm, for accelerating the rate of polymerization). Styrene (39.5 mL) was then polymerized at 40 °C for 1 h in this vessel using *t*-BuLi (3.0 mL) as the initiator. The color turned to reddish-orange, indicating the formation of living polystyryllithium anions. A small quantity of the solution was sampled, and the weight-average molecular weight ($M_w$) as

**Scheme 3**




determined by GPC was 10 000 with a polydispersity ($M_w/M_n$) <1.03. This determined molecular weight agreed with the expected value based on the normal 80% initiation efficiency of *t*-BuLi and the 100% anionic polymerization efficiency. The polystyrene-functionalized MWNTs were made as depicted in Scheme 3 by adding the living polystyryllithium solution into a degassed solution of *p*MS-Cp-Fe-MWNTs (0.3 g) in cyclohexane to continue the anionic polymerization. The anionic polymerization was continued under an inert atmosphere at room temperature for 12 h, resulting in a dark suspension. Solid residues in the suspension (containing unfunctionalized MWNTs and MWNTs functionalized with insufficient amount of polystyrene to impart solubility) were removed by a centrifuge, and the clear solution thus obtained was put under vacuum to evaporate the solvent. The solid product, comprised of the polystyrene-functionalized MWNTs and the unbound polystyrene, was then redissolved in chloroform and precipitated into cold hexane to leave the unbound polystyrene in the solvent. Upon washing with deionized water and drying under vacuum, the polystyrene-functionalized MWNTs appeared as a dark glassy solid.

## Results and Discussion

Ferrocene (Cp-Fe-Cp) consists of a metal species sandwiched with two cyclopentadienyl ligands. Hendrickson et al. found that when ferrocene underwent a ligand-exchange reaction, only one of the ligands took part in the reaction.[16] Moreover, Miyake and co-workers successfully exchanged one of the ligands on ferrocene with carbon black and a highly oriented pyrolytic graphite.[17] In our work, we have extended this line of research and conducted a ligand-exchange reaction of ferrocene with MWNTs. The Cp-Fe-MWNTs obtained from the ligand-exchange reaction of ferrocene with MWNTs were analyzed using SEM/EDS. A new peak pertaining to Fe appears in the EDS figure for Cp-Fe-MWNTs but not in the EDS figure for the original MWNTs. The Fe peak remained even after a 20 min wash of Cp-Fe-MWNTs in 1 M HCl aqueous solution, thus strongly indicating that ferrocene was chemically bound to MWNTs rather than physically adsorbed on MWNTs. Moreover, because no polymer trace would be detected by GPC from a sample obtained when ferrocene, $AlCl_3$, and Al powder were reacted in cyclohexane in the absence of MWNTs, the possibility of the formation of polyferrocene was excluded. The Cp-Fe-MWNTs were further analyzed by GC-MS to verify the ligand-exchange reaction of ferrocene. A parent ion peak was observed in the mass spectrum for the main peak of GC chromatogram at $m/z = 121$ ($C_5H_5Fe$), which corresponds to the molar mass of Cp-Fe- species (because MWNTs cannot be volatilized in GC). Although the molecular peak of ferrocene ($m/z = 186$, $C_5H_5FeC_5H_5$) was also detected, its intensity was only about half of that for the Cp-Fe- peak. Moreover, the peak corresponding to the atomic weight of Fe atom was also observed at $m/z = 56$. As a comparison, the physical mixture of MWNTs and ferrocene at the same molar ratio gave a distinct mass spectrum with the molecular ion of ferrocene having the largest peak. These GC-MS results have thus corroborated the formation of Cp-Fe-MWNTs. TGA thermogram (as shown in Figure 7) for Cp-Fe-MWNTs indicated that the content of the chemically bound ferrocene was approximate 21 wt %.

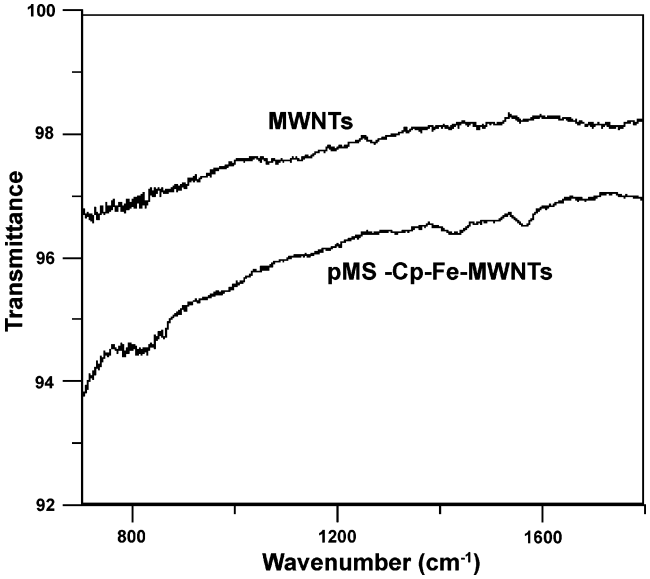



**Figure 2.** FTIR spectrum of *p*MS-Cp-Fe-MWNTs is compared with that of the purified MWNTs.

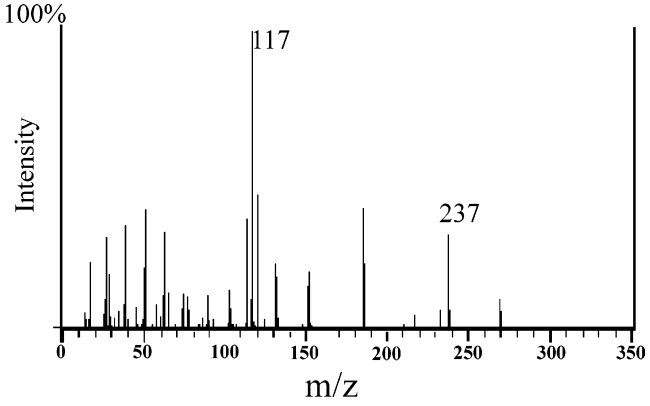



**Figure 3.** GC-MS spectrum of *p*MS-Cp-Fe-MWNTs.

The purified Cp-Fe-MWNTs were then lithiated by *tert*-butyllithium. According to a prior study by Kagan and Guillaneux[18] on the direct lithiation of ferrocene, the lithiation procedures would result in a monolithiation of ferrocene giving predominantly monosubstituted products. The lithiated Cp-Fe-MWNTs were then terminated with *p*-chloromethylstyrene, forming *p*MS-Cp-Fe-MWNTs. The FTIR spectrum (in ATR mode) of the *p*MS-Cp-Fe-MWNTs in Figure 2 exhibits weak signals in the region 1400−1600 $cm^{-1}$, indicating the presence of the aromatic C═C stretch. The change of the broad band between 750 and 900 $cm^{-1}$ was attributed to the aromatic or vinyl C−H (out-of-plane bend). The GC-MS spectrum of *p*MS-Cp-Fe-MWNTs is shown in Figure 3. The molecular ion peak was observed at $m/z = 237$ ($C_2H_3C_6H_4CH_2$ $FeC_5H_4$), which corresponded to the sum of the mass of Cp-Fe (minus the atomic weight of H atom) and the mass of *p*MS (minus the atomic weight of Cl atom). Other species shown at low $m/z$ were the fragment ions of the parent ion. These results strongly corroborated that Cp-Fe-MWNTs had been monolithiated by *t*-BuLi and then terminated with *p*MS, forming *p*MS-Cp-Fe-MWNTs. Since *p*MS started decomposing near 600 °C, the extent of *p*MS grafted onto *p*MS-Cp-Fe-MWNTs was determined approximately as 6.3 wt %

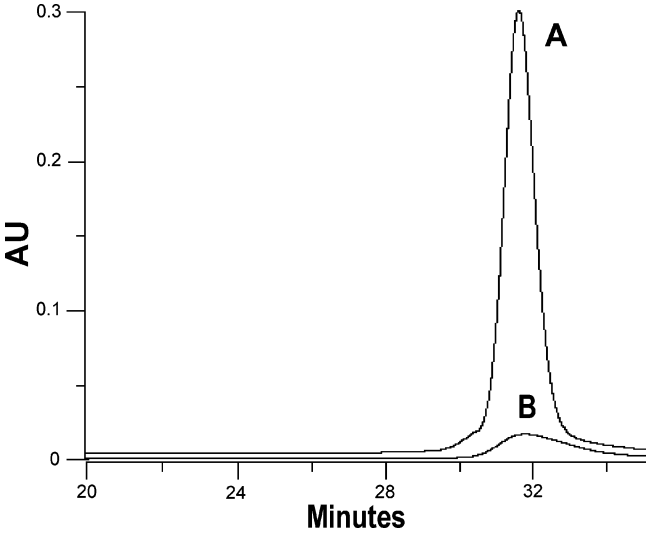



**Figure 4.** GPC chromatograms of (A) the parent polystyrene under identical analytical conditions and (B) the filtrate (passing a product sample solution through a 0.1 $\mu$m filter).

(as shown in Figure 7) by comparing the TGA thermograms of *p*MS-Cp-Fe-MWNTs and Cp-Fe-MWNTs.

The goal of functionalizing MWNT was achieved when the unsaturated double bond in *p*MS was anionically attacked by the living polystyryllithium anions that were prepared beforehand. To examine the amount of unbound polystyrene entrained in the final product, a sample was dissolved in THF and passed through a 0.1 $\mu$m filter. The GPC chromatogram of the filtrate was then compared to that of the parent polystyrene under identical analytical conditions. The magnitudes of the areas underneath the two peaks in Figure 4 indicated that the amount of unbound polystyrene was minimal. Although not tried in our work, other experimental conditions such as a different composition of the solvent system, a different molecular weight of polystyrene, and a few more times of precipitation might improve the "cleanness" of the sample. The polystyrene-functionalized carbon nanotubes were soluble in cyclohexane, toluene, THF, and other good solvents for polystyrene. The resulting solutions had distinct colors (from dark yellow to essentially black depending on the concentration) from the colorless polystyrene solutions. The UV/vis absorption spectra of the polystyrene-functionalized MWNTs in cyclohexane solution at room temperature were studied. The UV/vis absorption spectra at different concentrations of the polystyrene-functionalized MWNTs showed that absorption phenomena were linearly dependent on the solution concentrations, thus indicating an absence of any optical behaviors typically caused by aggregation or absorption of any bi- and multimolecular species.[12−14]

The $^1$H NMR spectrum of the polystyrene-functionalized MWNTs in deuterated chloroform solution is compared with that of the neat polystyrene. While the spectra were generally similar, the signals were broader in the spectrum of the polystyrene-functionalized MWNTs, probably due to the interactions of the polymers with carbon nanotubes.[13,14] It was noteworthy that the peak broadening might well be caused by other heterogeneous impurities, and these spectra therefore served only as an indirect evidence.

Shown in Figure 5a is an SEM image of the solid polystyrene-functionalized MWNTs. It is obvious that the sample contained a substantial amount of MWNTs.

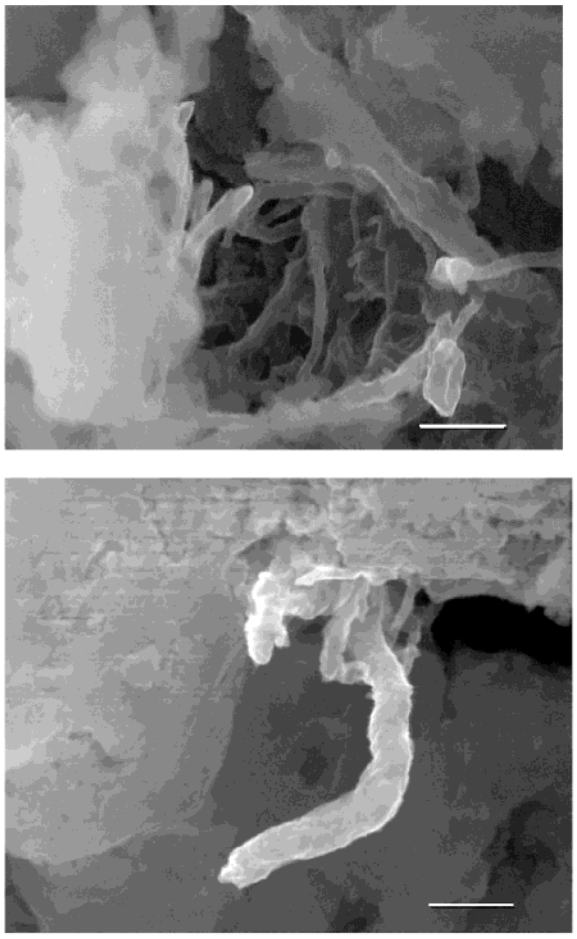


**Figure 5.** SEM image of the solid precipitate obtained from the polystyrene-functionalized MWNTs: (a, top) scale bar = 500 nm and (b, bottom) scale bar = 100 nm.

At a higher magnification (Figure 5b), it can be seen that the MWNTs were covered by polystyrene. The polystyrene at the surface of MWNTs has imparted strong surface charging effects to the MWNTs, therefore causing the vagueness of the image. These SEM images thus provided strong evidence for the conclusion that living polystyryllithiums were covalently bound to *p*MS-Cp-Fe-MWNTs.

More evidence for the polystyrene-functionalized MWNTs has been collected from the TEM imaging. The specimens for the measurements were prepared by applying a few drops of the sample solution (with the concentration of MWNTs on the order of 0.1−0.5 mg/mL) onto a carbon-coated or holey carbon-coated copper grid and then evaporating off the solvent. The TEM image in Figure 6a shows well-dispersed MWNTs with little aggregation, thus strongly suggesting the MWNTs have been functionalized. Another TEM image at a higher magnification (Figure 6b) clearly shows that the surface of a MWNTs was covered with polystyrene.

The weight fraction of MWNTs in the polystyrene-functionalized MWNTs was determined from a TGA scan by thermally decomposing the polystyrene. As shown in Figure 7, the weight of the polystyrene-functionalized MWNTs decreased rapidly near 400 °C due to the decomposition of polystyrene, leaving behind the barren MWNTs at temperatures above 600 °C. This observation has been fortified by the fact that neat MWNTs decomposed minimally at 600 °C, if not insignificant (also shown in Figure 7). The small beginning

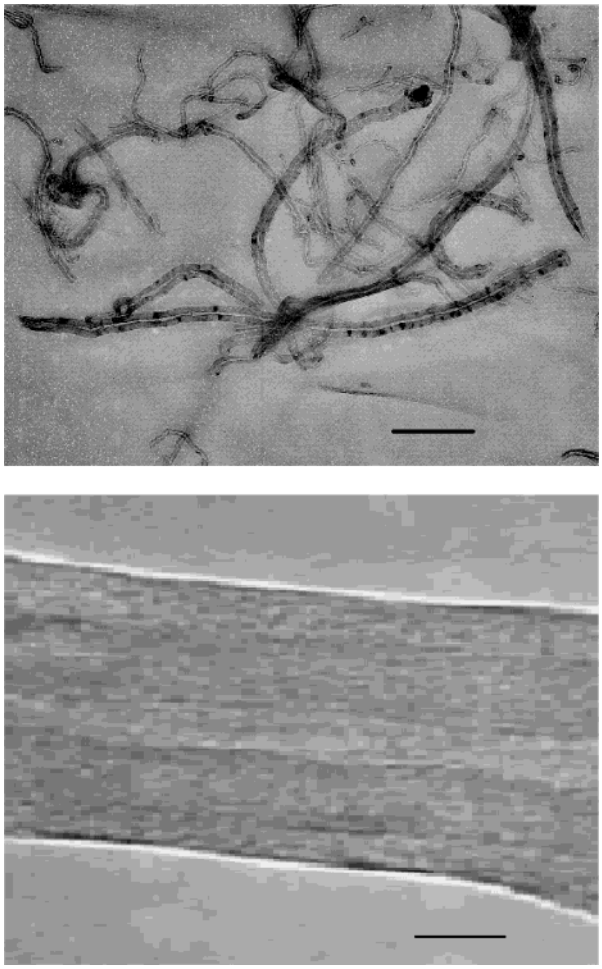


**Figure 6.** TEM images of polystyrene-functionalized MWNTs: (a, top) scale bar = 500 nm and (b, bottom) scale bar = 10 nm.

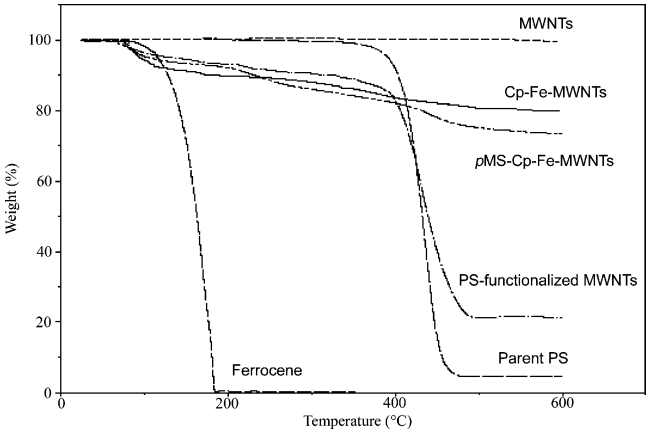



**Figure 7.** TGA traces (heating rate 10 °C/min in continuous nitrogen flow) of the purified MWNTs, ferrocene, Cp-Fe-MWNTs, *p*MS-Cp-Fe-MWNTs, the polystyrene-functionalized MWNTs sample, and the parent polystyrene sample.

weight loss which occurred from the start to 200 °C was attributed to the decomposition of Cp-Fe. According to these TGA traces, the MWNTs content in the polystyrene-functionalized MWNTs was approximately 20%.

## Conclusion

In summary, MWNTs were chemical modified by a ligand exchange reaction of ferrocene. The modified MWNTs underwent a direct monolithiation via the ferrocene moieties by *tert*-butyllithium and was terminated with *p*-chloromethylstyrene. The *p*-chloromethylstyrene-terminated species were then functionalized with living polystyryllithiums via anionic polymerization. The final products—the polystyene-functionalized MWNTs—dissolved in common organic solvents and showed distinct color and absorption spectra. The formations of Cp-Fe-MWNTs and *p*MS-Cp-Fe-MWNTs intermediates were confirmed by GC-MS, and the formation of the polystyrene-functionalized MWNTs was evidenced by SEM and TEM images. These images showed that the MWNTs were well-dispersed and had polystyrene attached to the surface.

**Supporting Information Available:** (1) SEM/EDS spectra of purified MWNTsand Cp-Fe-MWNTs (after in 1 M HCl aqueous solution); (2) gas chromatogram of Cp-Fe-MWNTs, the mass spectrum of its main peak, and the mass spectrum of the physical mixture of MWNTs and ferrocene; (3) UV/vis absorption spectrum of polystyrene-functionalized MWNTs in room temperature cyclohexane solution and a Lambert−Beer's law plot at 300 nm; (4) $^1$H NMR spectra of polystyrene-functionalized MWNTs and the parent polystyrene in deuterated chloroform. This material is available free of charge via the Internet at http://pubs.acs.org.

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