Functionalization of Carbon Nanotubes with Polystyrene

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Received June 3, 2002

ABSTRACT: Single-walled and multiple-walled carbon nanotubes were functionalized with a polystyrene copolymer, poly(styrene-*co-p*-(4-(4′-vinylphenyl)-3-oxabutanol)). The functionalization reaction conditions were designed for the esterification of the nanotube-bound carboxylic acids. The polymer-attached carbon nanotubes are soluble in common organic solvents, making it possible to characterize the samples using not only solid-state but also solution-based techniques. The solubility has also allowed an intimate mixing of the functionalized carbon nanotubes with polystyrene. Results from the characterization of the functionalized carbon nanotubes, including the chemical and thermal defunctionalizations of the soluble samples, and the fabrication of polystyrene−carbon nanotube composite thin films using a wet-casting method are presented and discussed.

Introduction

Polymer−carbon nanotube composite materials have attracted much recent attention for their many potential applications.[1−11] Both single-walled (SWNT) and multiple-walled (MWNT) carbon nanotubes have been used with various polymer matrices. For example, carbon nanotubes have been incorporated into matrices of conjugated polymers, such as poly(phenylenevinylene) and polythiophene, to prepare composites for optoelectronic applications.[1,3,4,6] Carbon nanotubes have also been used as fillers in epoxy resin to take advantage of the superior mechanical properties of the nanotubes.[2] However, several issues concerning the dispersion of carbon nanotubes in the polymer matrices and its effects on the properties of the resulting nanocomposite materials remain to be addressed.

Polystyrene is one of the most widely used commercial polymers. The dispersion of carbon nanotubes into polystyrene matrix for the fabrication of polystyrene−carbon nanocomposites has naturally stimulated significant interest among researchers.[8−11] For example, Qian et al. mixed MWNTs with polystyrene in a toluene solution via ultrasonication.[8] They reported that there are drastic increases in the elastic modulus and break stress in the polystyrene−MWNT nanocomposite of a nanotube content of only 1 wt % and that the mechanical properties of the nanocomposite compare favorably with those of the polypropylene−carbon fiber (10 wt %) composite.[8] These results are in general agreement with the prediction from a theoretical study of nonbonding polystyrene−carbon nanotube composite system.[10] Watts et al. used a similar ultrasonication method to prepare polystyrene composites with various carbon materials, including MWNTs and boron-doped MWNTs, and studied the conductivity in these composites.[11] They proposed that the conducting networks in the polystyrene−MWNT composites are built upon the nanotube−nanotube bundling and crossing, which are responsible for the relatively low resistance in the materials. However, the generally poor compatibility between polystyrene and MWNT bundles, which causes an inhomogeneous dispersion of MWNTs in the polystyrene matrix, is a problem with the nanocomposites. The nanotubes settle to the bottom side of a polystyrene−MWNT film, resulting in localized conductivity changes.[11] It is widely acknowledged that the quality of nanocomposites depends on the dispersion of carbon nanotubes in the polymer matrices.

The solubilization of carbon nanotubes via chemical functionalization is considered as an effective way to achieve a homogeneous dispersion of carbon nanotubes in polymer matrices for high-quality nanocomposites.[12,13] The defect sites on the surface of carbon nanotubes, which upon the treatment under oxidative conditions are transferred to carboxylic acid moieties,[14] allow covalent linkages of oligomers or polymers with the nanotubes.[15−21] For example, we have shown that the carbon nanotube-bound carboxylic acids can be used to attach aminopolymers via the formation of amide linkages.[20,21] The polymer-functionalized carbon nanotubes are particularly important to the preparation of polymeric carbon nanocomposites. In fact, an ideal approach is to functionalize carbon nanotubes with the matrix polymer of the composite. The implementation of such an approach requires investigations on functionalizing carbon nanotubes with various classes of polymers. In this paper, we report the functionalization of both SWNTs and MWNTs with a polystyrene copolymer. The polymer-attached carbon nanotubes are soluble in common organic solvents, making it possible to characterize the samples using not only solid-state but also solution-based techniques. The solubility has also allowed an intimate mixing of the functionalized carbon nanotubes with polystyrene. Results from the characterization of the polymer-attached SWNTs and MWNTs and the fabrication of polystyrene−carbon nanotube composite films using a wet-casting method are presented and discussed.

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10.1021/ma020855r CCC: $22.00

Experimental Section

Materials. *p*-Chloromethylstyrene (90%), sodium hydride (NaH, 60% dispersed in mineral oil), and ethylene glycol (99+%) were purchased from Acros, styrene was from Baker, 2,2′-azobis(isobutyronitrile) (AIBN, 98%) was from Aldrich, and thionyl chloride and polystyrene ($M_w \sim 100\,000$) were from Alfa Aesar. THF was distilled over sodium before use. Deuterated chloroform for NMR measurements (containing tetramethylsilane as internal standard) was obtained from Cambridge Isotope Laboratories.

SWNT and MWNT samples were produced using the arc-discharge method and the chemical vapor deposition (CVD) method, respectively. The as-produced samples were purified by following procedures already reported in the literature.[19a,21,22] Briefly, a pristine SWNT or MWNT sample (500 mg) was suspended in an aqueous HNO_3 solution (2.6 M, 100 mL) and then refluxed for 48 h. Upon centrifuging the suspension (3300 rpm) and discarding the supernatant, the remaining solids were washed repeatedly with deionized water and dried under vacuum.

Measurements. NMR measurements were performed on a JEOL Eclipse +500 NMR spectrometer. UV/vis absorption spectra were recorded on a Shimadzu UV2101-PC spectrophotometer. 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. Transmission electron microscopy (TEM) analyses were conducted on a Hitachi H-7000 TEM system and a Hitachi HF-2000 TEM system equipped with a Gatan Multi-Scan CCD camera for digital imaging.

4-(4′-Vinylphenyl)-3-oxabutanol (VPOB). A slurry of NaH (4.8 g, 0.2 mol) in THF (50 mL) was added dropwise to ethylene glycol (620 g, 10 mol) with stirring over 2 h. To the slurry was added slowly a solution of *p*-chloromethylstyrene (7.6 g, 0.05 mol) in THF (20 mL). The mixture was stirred at 60 °C for 24 h, followed by the addition of water (300 mL) to quench the reaction. The reaction mixture was extracted with chloroform. The resulting chloroform solution was concentrated for separation by column chromatography. The product was obtained as a colorless oil (8.9 g, 0.05 mol, ~100% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, 2H), 7.28 (d, 2H), 6.70 (q, 1H), 5.74 (d, 1H), 5.23 (d, 1H), 4.51 (s, 2H), 3.72 (t, 2H), 3.58 (t, 2H), 2.45 ppm (br, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.61, 137.24, 136.57, 128.17, 126.40, 114.06, 73.06, 71.56, 61.82 ppm.

Poly(styrene-*co*-*p*-(4-(4′-vinylphenyl)-3-oxabutanol)) (PSV). A THF (100 mL) solution of VPOB (1 g, 5.6 mmol) and styrene (5.3 g, 51 mmol) was mixed with a THF (10 mL) solution of AIBN (200 mg, 1.2 mmol). The mixture was stirred at 70 °C overnight under nitrogen protection, followed by being concentrated and precipitated into cold methanol. Upon the filtration and then washing with methanol, the copolymer was obtained as a white solid (3.45 g, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4−6.3 (69H), 4.6−4.3 (2H), 3.8−3.7 (2H), 3.6−3.4 (2H), 2.3−0.8 ppm (broad). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.5 (broad), 128.1, 127.8, 127.5, 125.9, 125.6, 73.3, 71.4, 62.0, 43.8 (broad), 40.5, 34.8, 34.6 ppm.

According to the ^{1}H NMR peak integrations, the VPOB mole fraction in the copolymer is ~7%. Gel permeation chromatography with polystyrene standards: $M_w \sim 5500$ and polydispersity ~ 1.6.

Functionalization of Carbon Nanotubes with PSV. A purified SWNT sample (75.2 mg) was refluxed in thionyl chloride (25 mL) for 24 h, followed by the removal of excess thionyl chloride under vacuum. Separately, PSV (500 mg) in a minimal amount of THF was added through a syringe to a slurry of NaH (800 mg) in THF (125 mL) with stirring. After refluxing for 2 h, the slurry was mixed with the SWNT sample. The mixture was stirred in a sealed container under inert atmosphere at room temperature for 48 h, resulting in a dark suspension. Solid materials in the suspension were removed by centrifuging at 7500 rpm, and the clear solution thus obtained was evaporated to remove the solvent THF. The crude reaction product was dissolved in chloroform and precipitated into cold hexane. Upon washing with deionized water and drying under vacuum, the PSV-functionalized SWNT sample was obtained as a dark glassy solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6−6.0, 4.7−4.0, 4.0−3.2, 2.5−0.7 ppm.

The identical procedure was applied to the functionalization of MWNTs with PSV, yielding the soluble sample as a grayish powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6−6.0, 4.6−4.2, 3.8−3.3, 2.4−0.7 ppm.

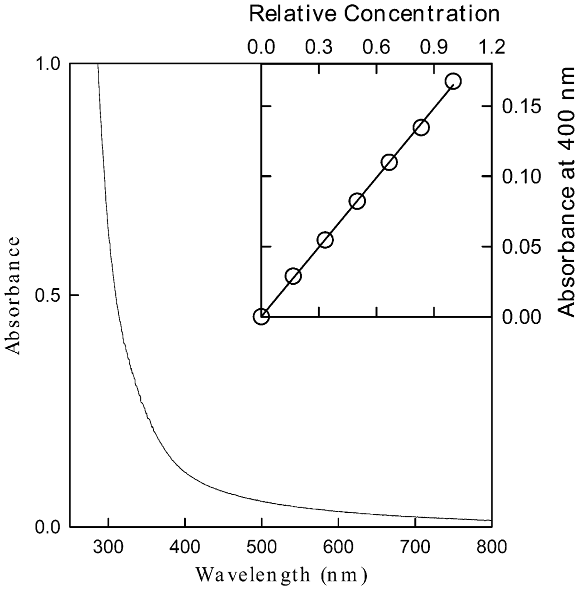


Figure 1. UV/vis absorption spectrum of PSV-functionalized MWNTs in room temperature THF solution. Shown in the inset is a Lambert−Beer's law plot at 400 nm.

Results and Discussion

The PSV-functionalized carbon nanotube samples are soluble in toluene, THF, chloroform, and other common organic solvents that are compatible with polystyrene. The resulting solutions are colored (from dark yellow to essentially black depending on the concentration), different from the colorless PSV solutions. The UV/vis absorption spectrum of the PSV-functionalized MWNT sample in room temperature (22 °C) THF is shown in Figure 1. It is primarily a featureless curve with the absorbance decreasing gradually from UV to near-IR, similar to the absorption spectra of other solubilized carbon nanotubes of different functionalities.[15,19−21] The absorption spectra are linearly dependent on the solution concentrations, following Lambert−Beer's law (Figure 1, inset). In a dilute solution, the characteristic absorption band of polystyrene at ~260 nm can be observed.

The solution color typically serves as a visual indicator for the presence of carbon nanotubes in the soluble samples obtained from the functionalization reactions. However, for more direct evidence the PSV-functionalized carbon nanotubes were analyzed via TEM imaging. The specimens for the measurements were prepared by applying a few drops of the sample solution (nanotube concentration 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. Shown in Figure 2a are TEM images of PSV-functionalized MWNTs of different lengths (up to a few microns) and diameters (up to 80 nm). The results suggest that the functionalized nanotubes are well-dispersed in solution. At higher magnification, the TEM image shows that the surface

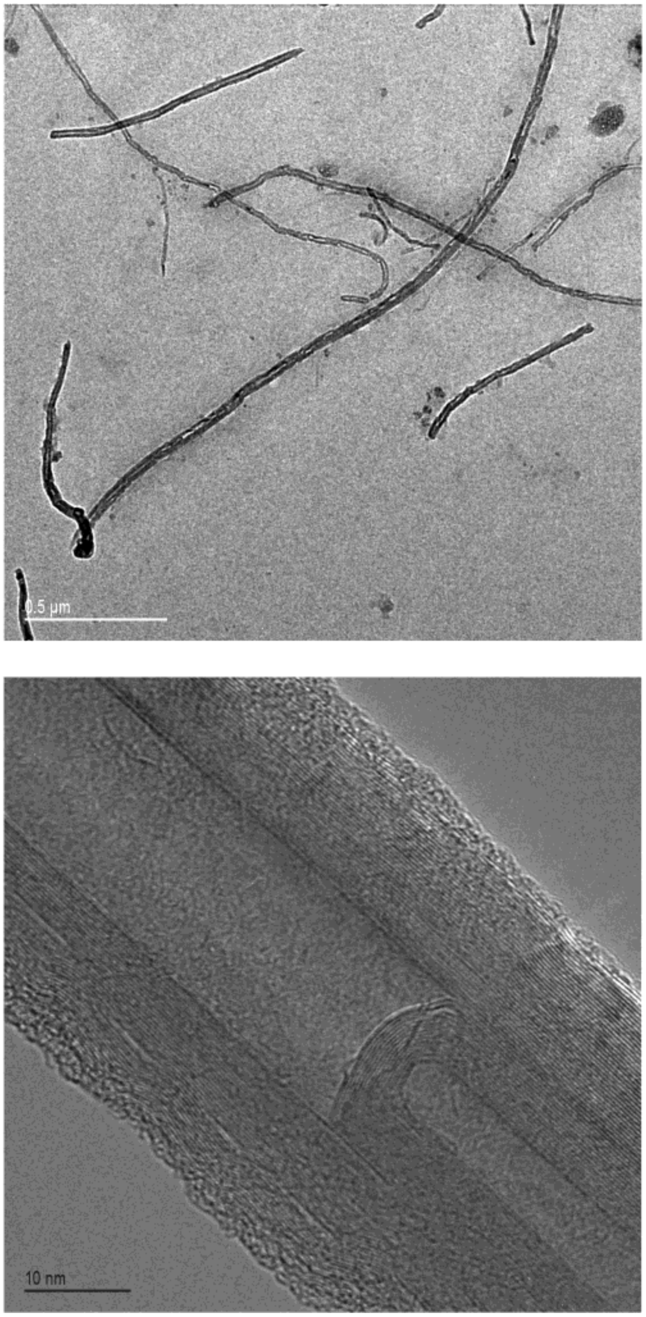


Figure 2. TEM images of PSV-functionalized MWNTs: (a, top) scale bar = 500 nm and (b, bottom) scale bar = 10 nm.

of a MWNT is covered by amorphous materials, which might be attributed to the attached PSV polymers.

The TEM imaging of functionalized SWNTs is more difficult because of the relatively small object sizes and the masking interference by a large amount of PSV polymers on the nanotube surface. Thus, a specifically designed $LaCrO_3$-coated holey stainless steel grid was used to allow thermal treatment of the PSV-functionalized SWNT sample on the grid. The purpose of the thermal treatment (450 °C for 30 min in a continuous nitrogen flow) was to remove some of the PSV polymers from the nanotube surface prior to TEM imaging. A typical TEM image thus obtained for the PSV-functionalized SWNTs is shown in Figure 3. Again, the TEM results confirm that the soluble sample from the functionalization reaction with PSV polymers does contain SWNTs.

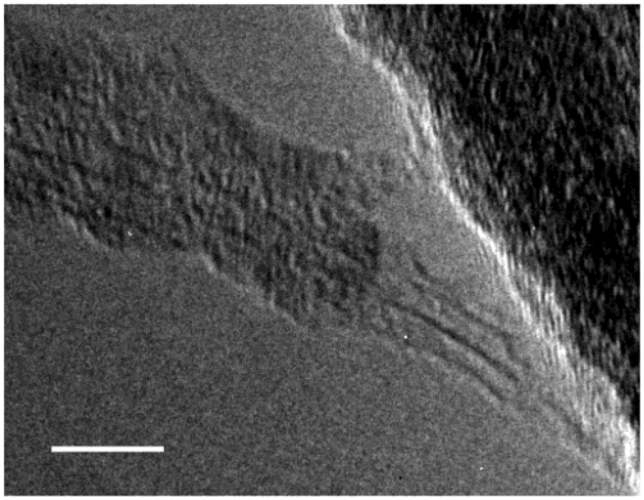


Figure 3. A picture from the high-resolution TEM imaging of PSV-functionalized SWNTs on a $LaCrO_3$-coated stainless steel grid after the thermal treatment (450 °C for 30 min in a continuous nitrogen flow). Scale bar = 5 nm.

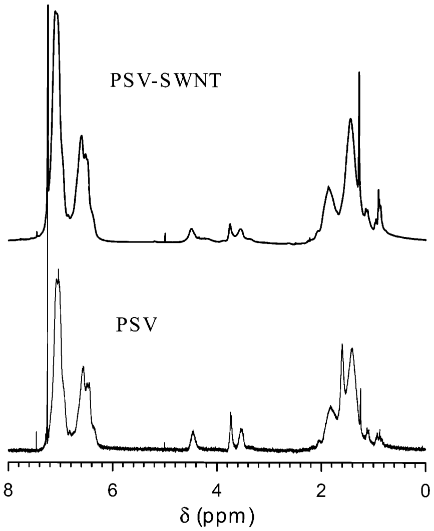
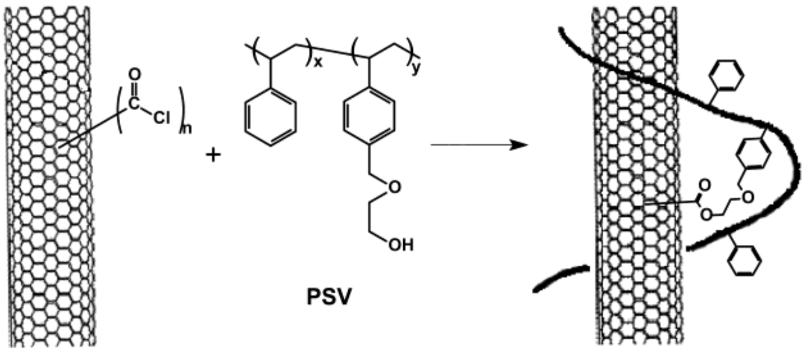


Figure 4. ^1H NMR spectrum of PSV-functionalized SWNTs is compared with that of the parent PSV polymers in deuterated chloroform.

The solubility of the PSV-functionalized carbon nanotubes in common organic solvents makes it possible to carry out NMR characterization in solution. The ^1H NMR spectrum of the PSV-functionalized SWNTs in deuterated chloroform solution is compared with that of the parent PSV in Figure 4. While the spectra are generally similar, both due to protons in PSV, the signals are somewhat broader in the spectrum of the PSV-nanotube sample. For example, the peak broadening in the 3−5 ppm region corresponding to the pendent ethylene protons may be attributed to interactions of the polymers with carbon nanotubes. Similar NMR peak broadening has been reported for other functionalized carbon nanotubes in solution.[15,19−21] However, since no specific effort was made to ensure a complete removal of unbound PSV, the NMR results are only qualitative. Several strategies are being pursued for eliminating residual PSV from the functionalized carbon nanotube samples.

The functionalization reaction conditions were designed to attach PSV polymers to carbon nanotubes via the esterification of the nanotube-bound carboxylic acids

Scheme 1



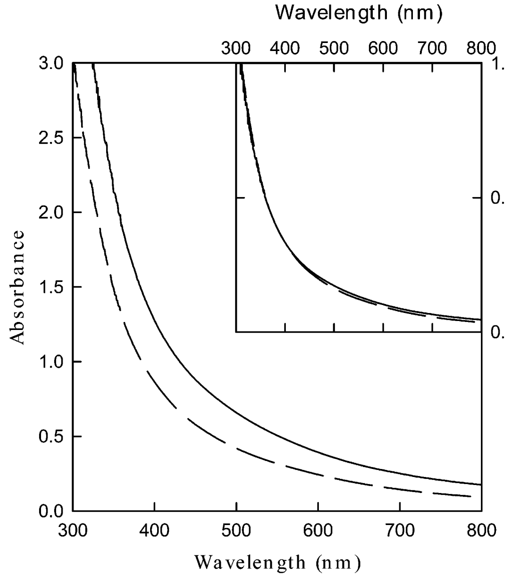


Figure 5. UV/vis absorption spectra of the PSV-functionalized SWNT sample before (—) and after (- - -) chemical defunctionalization. Shown in the inset are the normalized spectra.

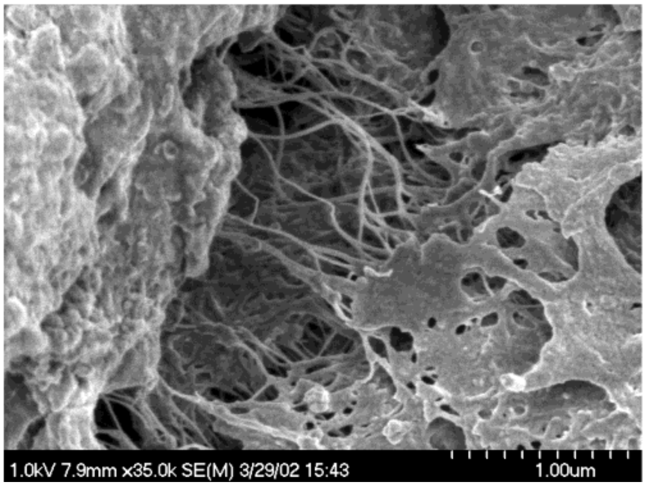


Figure 6. An SEM image of the solid precipitate obtained from the chemical defunctionalization of PSV-functionalized SWNTs. The sample was coated with platinum via sputtering for 30 s.

(Scheme 1).[15,19] Evidence for the presence of ester linkages in the functionalized carbon nanotube samples includes results from the chemical defunctionalization of the functionalized carbon nanotubes. The defunctionalization was based on base-catalyzed hydrolysis of ester linkages[23] to detach PSV polymers, resulting in the precipitation of some carbon nanotubes.[19] In a typical defunctionalization experiment, a PSV-functionalized SWNT sample (21.5 mg) was dissolved in THF (3 mL) to form a dark-colored homogeneous solution. After NaH (15 mg) was added, the solution was refluxed for 12 h under nitrogen protection. Water (1 mL) was then added carefully to quench the excess NaH, followed by refluxing for 1 h. The reaction mixture was centrifuged at a high speed (7800 rpm) to obtain a dark-colored precipitate. The UV/vis absorption spectra of the sample solution before and after the hydrolysis are compared quantitatively in Figure 5, where the decrease in absorbance is a result of the chemical defunctionalization that has removed some of the carbon nanotubes from the solution.[19]

The dark-colored precipitate obtained under the base-catalyzed hydrolysis conditions was washed repeatedly with water and then carefully dried for electron microscopy analyses. Shown in Figure 6 is an SEM image of the solid precipitate from the chemical defunctionalization of PSV-functionalized SWNTs. It is obvious that the sample contains a substantial amount of SWNTs. The results from the defunctionalization via base-catalyzed hydrolysis and the subsequent SEM analysis serve as strong evidence for the conclusion that ester linkages are at least in part responsible for the covalent attachment of PSV polymers to SWNTs. The SEM image also suggests that there is a significant amount of polymers in the solid precipitate. In fact, the presence of the polymers as organic species caused strong surface charging effects in the SEM analysis, which had to be suppressed by coating the specimen with a thin layer of platinum. The defunctionalization via base-catalyzed hydrolysis apparently removes only a portion of the PSV polymers from the functionalized SWNTs, leading to the precipitation of nanotubes that are still attached with some PSV polymers. Once precipitated, further hydrolysis to remove the remaining PSV polymers from the defunctionalized SWNTs is inefficient under the heterogeneous reaction conditions. Thus, the solid precipitate recovered from the chemical defunctionalization reaction is best described as a composite of SWNTs with some attached PSV polymers.[19]

In addition to the chemical method, the defunctionalization of functionalized carbon nanotubes may be achieved thermally in processes such as TGA scans.[21] The decomposition temperature of the parent PSV polymer sample is much lower than that of the carbon nanotubes, as demonstrated by the TGA traces in Figure 7. Thus, the PSV polymers in the functionalized MWNT sample may be selectively removed in a relatively slow TGA scan (10 °C/min), leaving behind the thermally defunctionalized MWNTs at temperatures

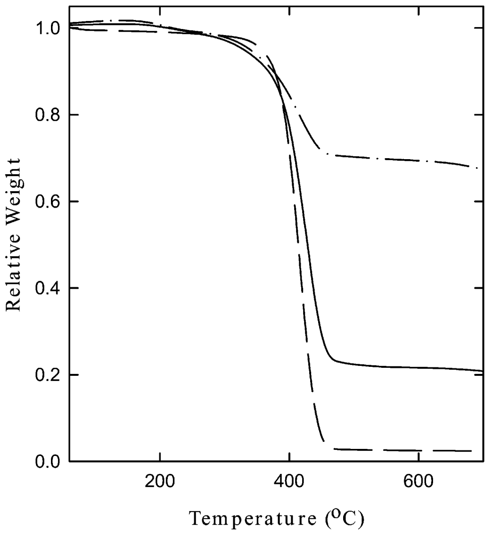


Figure 7. TGA traces (heating rate 10 °C/min in continuous nitrogen flow) of the PSV-functionalized MWNT sample (—), the solid residue recovered from the functionalization reaction mixture (- • -), and the parent PSV polymer sample (- - -).

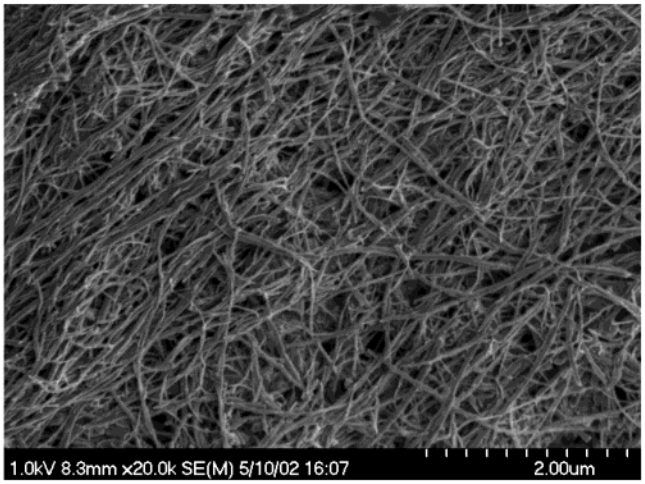


Figure 8. An SEM image of the thermally defunctionalized (in a TGA scan to 900 °C in continues nitrogen flow) PSV–MWNT sample.

above 460 °C (Figure 7). Upon the thermal treatment in a TGA scan to 900 °C in an inert atmosphere (nitrogen gas), the defunctionalized sample was analyzed by SEM. The SEM image shows abundance of MWNTs with negligible surface charging effects (Figure 8), suggesting a nearly complete removal of the polymers from the nanotube surface. According to the TGA traces, the carbon nanotube contents in the PSV-functionalized SWNT and MWNT samples are approximately 12% and 18%, respectively.[25]

In the functionalization of SWNTs and MWNTs with PSV polymers, the insoluble residues of the reaction mixtures also contain some polymers that are likely associated with partially functionalized nanotubes (insufficient to introduce solubility) and perhaps cross-linked materials. This is confirmed by the results from TGA analyses of the insoluble residues. For the residue obtained from the functionalization of MWNTs with PSV polymers, the TGA trace shows that the polymers account for ~30% of the residual sample (Figure 7). Since the residue was repeatedly extracted in the postfunctionalization treatment to remove all soluble materials, the presence of a significant amount of PSV polymers in the residue according to TGA also suggests that the nanotube–PSV relationships are specific (covalent functionalization), fundamentally different from those in the surfactant-assisted dispersion of carbon nanotubes.

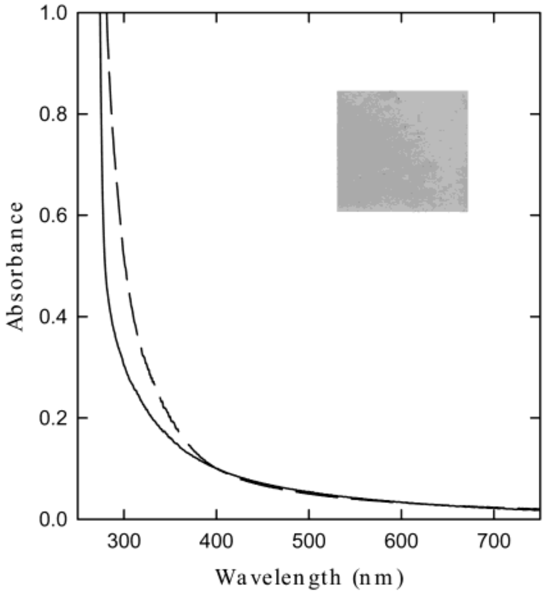


Figure 9. UV/vis absorption spectra of PSV-functionalized SWNTs in polystyrene matrix (nanocomposite thin film, —) and in room temperature solution (- - -). Shown in the inset is a picture of the thin film obtained by scanning the film directly on a flat-bed scanner.

The compatibility of the PSV-functionalized carbon nanotubes with polystyrene and the dispersion of the nanotubes in polystyrene matrix were evaluated via the fabrication of nanocomposite thin films. In a typical experiment, a PSV-functionalized SWNT sample (75 mg, SWNT content 12% according to TGA) was dissolved in room temperature chlorobenzene (0.5 mL) to form a visually transparent solution of a dark-brown color. The solution was centrifuged at a high speed (7500 rpm) to remove any residual insoluble species.[26] Polystyrene (75 mg, $M_w \sim 100\,000$) was added to the solution, followed by stirring for 6 h. The resulting solution was allowed to settle overnight and then vigorously centrifuged again to remove any residual insoluble species,[26] followed by being concentrated to attain the desired viscosity. The viscous but transparent solution was used for the casting of a thin film. In the wet-casting, the solution was poured onto a glass slide, followed by slow removal of the solvent in a dust-free environment. The polystyrene–SWNT composite thin film thus obtained has a thickness of ~50 μm, with the carbon nanotube volume fraction on the order of 5%. It is transparent with a high optical quality (appearing as a small piece of commercially available colored transparency, Figure 9). The UV/vis absorption spectrum of the PSV-functionalized SWMTs in the nanocomposite film is similar to that in room temperature solution, as compared in Figure 9.

The successful fabrication of optically high-quality nanocomposite thin films reflects the excellent compatibility of the PSV-functionalized carbon nanotubes with polystyrene. It also serves as initial evidence for the notion that functionalized carbon nanotubes can be dispersed homogeneously into polymeric matrices. More characterizations of the nanocomposite thin films toward an understanding of their material properties will be pursued in further investigations.

In summary, SWNTs and MWNTs were functionalized with a polystyrene copolymer containing hydroxyl moieties. The solubility of the resulting samples in common organic solvents, as reflected in the solution color and absorption spectra, provided visual indication for the functionalization of the carbon nanotubes. Strong evidence for the functionalization was from the results of chemical and thermal defunctionalization experiments. The TEM images were supportive of the conclusion that there were carbon nanotubes in the soluble samples. Finally, the homogeneous dispersion of the functionalized carbon nanotubes in the polystyrene matrix offers an initial example for the widely held hope that the nanotube solubilization will enable the preparation of desirable polymeric carbon nanocomposite materials.

Acknowledgment. We thank B. Zhou, K. McGuire, B. Sadanadan, and M. Trznadel for experimental assistance. Y.-P.S. acknowledges financial support from NSF (CHE-9727506 and, in part, EPS-9977797), NASA (NCC1-01036, NGT1-52238, and NAT1-01036), the South Carolina Space Grant Consortium, and the Center for Advanced Engineering Fibers and Films (NSF-ERC at Clemson University). A.M.R. acknowledges financial support from the NASA Ames Research Center (NCC2-5421). We also acknowledge the sponsorship by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the Department of Energy (DE-AC05-00OR22725).

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(25) According to these results, the estimated degree of functionalization is on the order of 10−15 PSV chains per 1000 nanotube carbons for both SWNTs and MWNTs.

(26) The solid species recovered from centrifuging were partially soluble in chlorobenzene. The solution thus obtained was added to the parent solution.

MA020855R