

Dispersion and Noncovalent Modification of Multiwalled Carbon Nanotubes by Various Polystyrene-Based Polymers

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ABSTRACT: This article investigated the dispersion and modification of multiwalled carbon nanotubes (MWCNTs) through solution mixing based on the noncovalent interactions between polystyrene (PS) and MWCNTs. It was found that the interactions were robust enough to stabilize the debundled MWCNTs in solution after vigorous sonication. The PS attached, which altered the surface properties of MWCNTs and made them easily soluble in organic

solvents, can remain even after careful washing with solvents. Besides, many other PS-based polymers were proved to retain the ability to disperse MWCNTs to form stable solutions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3525–3532, 2008

Key words: multiwalled carbon nanotubes; polystyrene; preferential adsorption; modification

INTRODUCTION

It is well-known that carbon nanotubes (CNTs) have outstanding mechanical and electrical properties, which provide potential use in a wide spectrum of advanced applications in nanotechnology and electronic nanodevices.^{1,2} However, practical application of CNTs still faces the problem of good dispersion, as the substantial intertube van der Waals attraction makes them appear in bundles and affects their extraordinary properties. To overcome this disadvantage, both covalent and noncovalent functionalization methods have been adopted to modify the surface properties of CNTs.^{3–5} In chemical functionalization, functional groups are covalently linked to the surface of CNTs, making their mechanical and electrical properties change a lot, as compared with pristine tubes.⁶ On the contrary, noncovalent functionalization retains the structural integrity of CNTs and their properties are hence not disrupted, which is important for the following applications.

The noncovalent methods used to functionalize CNTs include using surfactants, aromatic solvents, DNA, starch, and polymers to “wrap” CNTs to enhance their solubility in both water and organic solvents.^{7–9} The underlying mechanism in each of these examples is believed to be the specific interac-

tions between a given substance and CNTs, among which π - π interaction is the most prevalent. Many small organic molecules with aromatic rings, such as porphyrin,¹⁰ aniline,¹¹ anthracene, and *p*-terphenyl,¹² are used to debundle CNTs to form stable dispersion, so are many polymers, including polyvinyl pyrrolidone (PVP), polystyrene sulfonate (PSS),⁵ and poly(*m*-phenylenevinylene-co-2,5-dioctoxyp-phenylenevinylene) (PmPV).¹³

Among numerous synthetic polymers, polystyrene (PS) is featured as a cheap and easily accessible material with an aromatic group in each monomer unit. Zhang et al. reported in their experiments that melt mixing of PS with multiwalled carbon nanotubes (MWCNTs) led to enhanced interactions between those two and increased the solubility of MWCNTs in some solvents, whereas simple solution mixing resulted in a colorless solution without any MWCNT after centrifugation.¹⁴ However, theoretical calculation and experimental observation both indicated that substantial interactions between PS and sidewalls of MWCNTs^{15,16} indeed exist. The results of our former work also demonstrated the ability of PS-based polymers to effectively disperse CNTs in organic solvents, based on the robust interactions between PS and CNTs.¹⁷ Here, in this work, we use simple solution mixing procedure to prepare effectively stable MWCNT dispersion, with the aid of various PS-based polymers, and present evidences for the noncovalent interactions between MWCNTs and these polymers, as well as an easy modification method for MWCNTs.

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EXPERIMENTAL

Materials

Multiwalled carbon nanotube (MWCNT) raw material was produced by catalytic pyrolysis of propylene¹⁸ and used after purification. Polystyrene [PS 666D with $M_w = 332,000$ measured by gel permeation chromatography (GPC)] was purchased from Yanshan Petrochemical, Beijing, China. The graft polymer, PS-*g*-(GMA-*co*-St), was prepared by free-radical melt-grafting of glycidyl methacrylate (GMA) onto PS using a styrene-assisted method.¹⁹ Styrene-butadiene-styrene triblock copolymer (SBS LG-501 with $M_w = 116,900$ measured by GPC) was purchased from LG Chem. Styrene-methyl methacrylate diblock copolymer (PS-PMMA with $M_w = 74,500$ measured by GPC) was synthesized via controlled living radical polymerization by ourselves.

MWCNT dispersion

MWCNT dispersion was prepared with the aid of vigorous ultrasonication to break up the bundles of MWCNTs. At first, pristine MWCNTs were sonicated in chloroform at 70°C for 1 h, and then PS was added to prepare a 1.0 wt % solution, followed by sonication for another 3 h. The solution obtained was centrifuged at 4000 rpm to remove large aggregates, which were dried under vacuum before weighed, and the clear supernatant was reserved for the following experiments. The MWCNT concentration was determined by subtracting weight of undissolved aggregates from the original quantities. Seven different concentrations of MWCNT solutions (6, 10, 13.33, 20, 28, 36, 66 mg/L) with invariable PS concentration of 1.0 wt % were prepared for UV-vis spectra (Hitachi U-3010 spectrophotometer), using 1.0 wt % PS solution (in chloroform) as reference solution. Optical microscopy and transmission electron microscopy (TEM, JEOL, JEM-1200EX) were also used to characterize the morphology of MWCNT solutions with different concentrations. For optical microscopy observation, the solution was dropped or spin-coated onto a glass slide and then dried under vacuum. For TEM observation, the solution was dropped onto a copper grid and then dried under vacuum.

MWCNT-PS composite

The clear supernatant of MWCNT solution with the highest concentration (66 mg/L) was passed through a 0.45- μm polyvinylidene fluoride filter, and the filtration residues were washed with chloroform three times to remove any free polymer. The solid product was dried at 80°C in vacuum to remove residual chloroform, and the final composite

was named MWCNT-PS. The thermal stability of MWCNT-PS was measured by thermogravimetry and differential thermal analysis (Shimadzu DTG-60/60H) with a heating rate of 15°C/min in a continuous nitrogen flow. High-resolution TEM (JEOL JEM-200CX), FTIR spectrum (Nicolet 560-IR spectrometer), Raman spectra, and ¹H NMR spectrum were also used to characterize MWCNT-PS. For HR-TEM observation, MWCNT-PS was redissolved in chloroform and the dispersion was dropped onto a copper grid and then dried under vacuum. Raman spectra were collected by the confocal microscope attachment of a Nicolet Omega dispersive Raman spectrometer with a 514-nm excitation source. ¹H NMR spectrum was obtained on a JOEL JNM-ECA600 NMR spectrometer with CDCl₃ as the solvent. The sample was prepared by redispersing MWCNT-PS (after removing solvents) in CDCl₃ using mild sonication. In addition, The UV-vis spectra of PS, pristine MWCNT, and MWCNT-PS in CHCl₃ were recorded. To prepare a sample for atomic force microscopy (AFM, Shimadzu SPM-9500J3) observation, the dry powders of MWNT-PS were redispersed into chloroform by mild sonication, and then a drop of the solution obtained was dropped on two freshly cleaved mica substrates which were subsequently dried in contact with air for 12 h. The experimental procedure of sample preparation and characterization is illustrated in Figure 1.

RESULTS AND DISCUSSION

Characterization of MWCNT dispersion

Many researchers have theoretically reported that PS main chain could preferentially attach to the sidewalls of exfoliated CNTs through noncovalent electrostatic and van der Waals attraction,^{15,20} and resulted in stable dispersions. In our experiment, photos of seven supernatant dispersions with different MWCNT concentrations which have been kept static for over 4 weeks are shown in Figure 2. It can be seen that, these supernatant solutions were transparent and macroscopically homogeneous, with an incremental black color, indicating that PS can be used to disperse MWCNTs effectively. In addition, the longtime stability proves that the interactions between the PS main chain and sidewalls of MWCNTs are robust and persistent enough to surpass the substantial van der Waals attraction existing between MWCNTs, and prevent the dispersed MWCNTs from forming bundles and precipitating again when sonication stopped.

UV-vis absorption spectra were used to determine solubility of MWCNTs. The absorption spectra of these samples were recorded using a 1.0 wt % PS

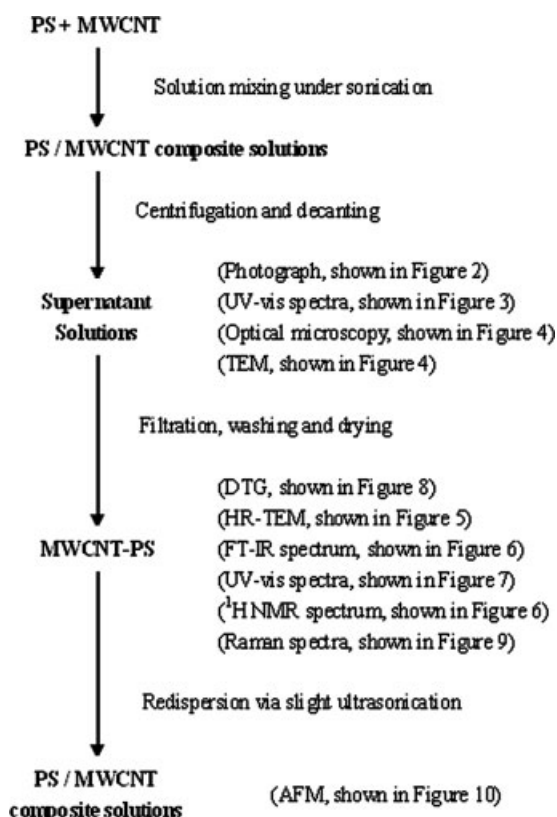


Figure 1 Experimental procedures for sample preparation and characterization.

solution in chloroform as reference solution, and the one with MWCNT concentration of 6 mg/L was shown as an example (Fig. 3). The MWCNT concentrations were determined by subtracting weight of undissolved aggregates from the original quantities. This concentration (in mg/L) in conjunction with the absorbance at 500 nm allowed to gain a plot shown in the inset of Figure 3, as Bahr et al.⁸ performed experiments of SWCNT samples. The sample with the highest concentration was not included in the

plot, as the baseline of its UV-vis spectra was full of disturbances and the absorbance at 500 nm became meaningless. Values of the plot were used to figure out the concentrations of other samples, which were also determined by the same measuring procedure as indicated earlier, and the results were found to be consistent within 15%. Besides, optical microscopy and TEM images in Figure 4 reveal that MWCNTs in PS solutions were well dispersed, which further confirm the effectiveness of PS.

Direct structural characterization of an individual MWCNT in solution was realized by high-resolution TEM imaging, and a typical image is presented in Figure 5(a). Figure 5(b) is the magnification of the area specified by a dashed square in Figure 5(a). From the image, a uniform amorphous layer along the tube length can be clearly seen, indicating a favorable wrapping of PS on MWCNTs.

Characterization of MWCNT-PS composite

More attention was focused on the state of individual MWCNT-PS in the solution. As indicated earlier, PS chains were theoretically proved to have the ability to attach to sidewalls of MWCNTs in solution, due to both electrostatic and van der Waals attraction, and the adsorption should be robust even after careful washing with solvent. It means that MWCNT-PS would have some PS remains on the tube wall, which was indeed detected using ¹H NMR and FTIR spectra (Fig. 6), in consistent with the earlier HR-TEM results. Since MWCNT-PS was washed carefully to remove free polymer, the evident signals that belong to hydrogen atoms (¹H NMR) and C—H bending vibration (FTIR spectrum) in benzene ring can only be attributed to the remained adsorptive PS. Combining the HR-TEM images, ¹H NMR, and FTIR spectra, it was observed that PS macromolecular chain preferentially attached to sidewalls of MWCNTs in the dissolved state, and



Figure 2 Photos of the supernatant solutions obtained by sonication and centrifugation of MWCNT/PS mixtures with increasing MWCNT concentrations: (from left to right) 6, 10, 13.33, 20, 28, 36, 66 mg L⁻¹, all the samples have been kept static for over 4 weeks.

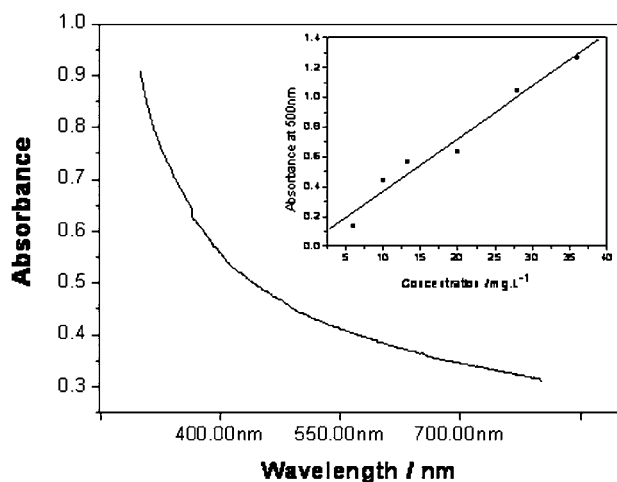


Figure 3 Absorption spectrum of the MWCNT material in the supernatant solution (a 1.0 wt % PS solution with MWCNT concentration of 6 mg L^{-1} , using 1.0 wt % PS solution as reference solution). Inset: optical density of the MWCNT material at 500 nm in 1.0 wt % PS solutions of different concentrations. The straight line is a linear-least-squares fit to the data, slope = 0.0353.

the interaction was robust enough to provide steric repulsion to stabilize the debundled MWCNTs in solution.

Moreover, the results of UV-vis spectra further supported the above point. As shown in Figure 7, the absorption curve of MWCNT-PS has an additional band at about 270 nm, as compared with the curve of pristine MWCNTs. It is well-known that phenyl groups have typical absorption bands at about 230 and 260 nm, so the above 270 nm band should be assigned to the adsorptive PS. Furthermore, the band at 270 nm slightly broadened and hypsochromic shifted as compared with PS, presumably as a result of π - π interaction between MWCNTs

and phenyl groups of PS, which is an important part of noncovalent interactions.

To determine the amount of PS remained, MWCNT-PS was also analyzed using thermogravimetry and differential thermal analysis, with a comparison to pristine MWCNTs, and the results are shown in Figure 8. Since the weight loss of MWCNTs began at about 600°C , as indicated in the line that belongs to MWCNTs, the weight loss at the temperature below 600°C would only be attributed to other components, probably PS in the sample of MWCNT-PS. In the line of MWCNT-PS, the first weight loss that began at about 350°C and end at around 420°C was in consistent with a typical DTG curve of PS, and the content of PS in the sample was estimated to be 8.0 wt %. The DTG result again confirmed that PS remained on the tube walls of MWCNTs even after washing with solvent.

It is well-known that through chemical modification the outstanding electrical and mechanical properties of CNTs could be impaired, and the drastic sonication could also damage the tube walls of CNTs, and result in defects and change their properties. These changes would be reflected in the Raman spectra at some typical band ranges, by comparing the starting materials with the final processing products. Figure 9 shows Raman spectra of pristine MWCNTs and MWCNT-PS, which had been processed by ultrasonication and vacuum filtration. In the spectra, the curves of MWCNT-PS and pristine MWCNTs are identical in shape, whereas the D-band (in the region of 1300 – 1370 cm^{-1}) and G-band (in the region of 1580 – 1600 cm^{-1}) of the former are slightly broader than the latter and shift toward the low wave number side. This result indicates that in the MWCNT-PS products the main component MWCNTs maintained their extraordinary merits. Actually, MWCNT-PS composite benefited from the

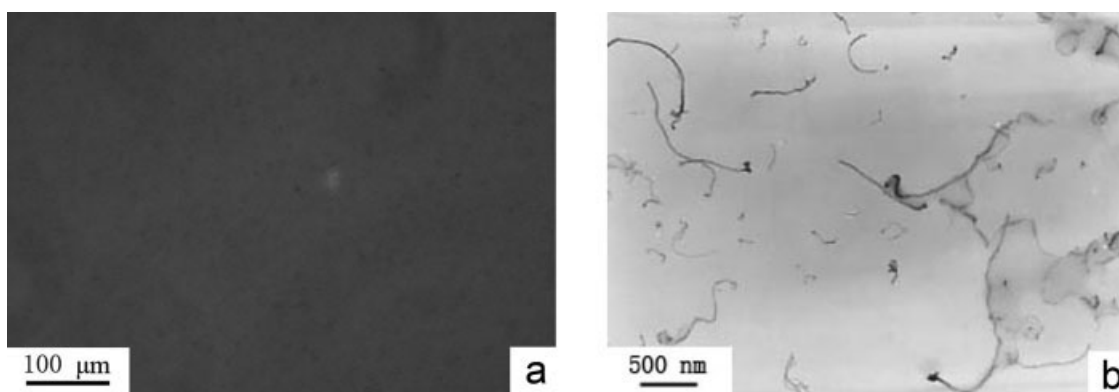


Figure 4 (a) Optical microscopy and (b) TEM images of MWCNTs dispersed in 1.0 wt % PS solution (in chloroform). For optical microscopy observation, the solution was dropped onto a glass slide and then dried under vacuum. For TEM observation, the solution was dropped onto a copper grid and then dried under vacuum.

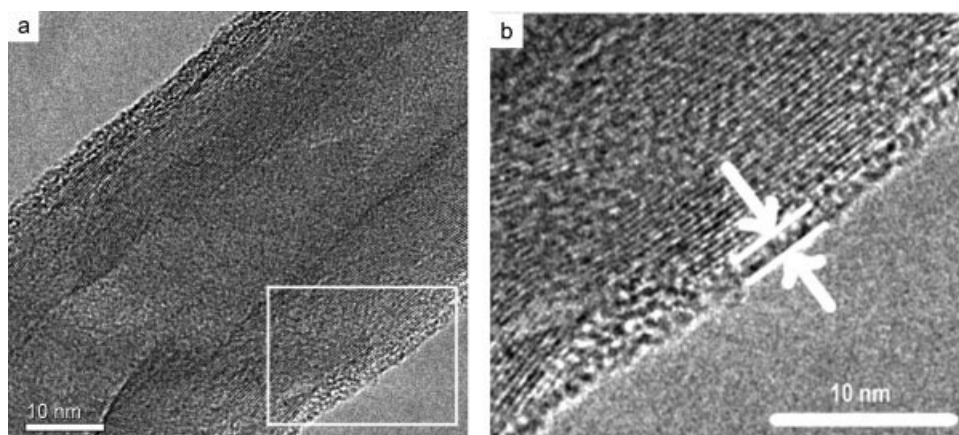


Figure 5 (a) High-resolution TEM image of an individual MWCNT-PS. (b) Magnification of the area specified by the dashed square in (a). The samples were prepared by dropping redispersion of MWCNT-PS in CHCl_3 onto holey carbon-coated copper grids and then drying under vacuum.

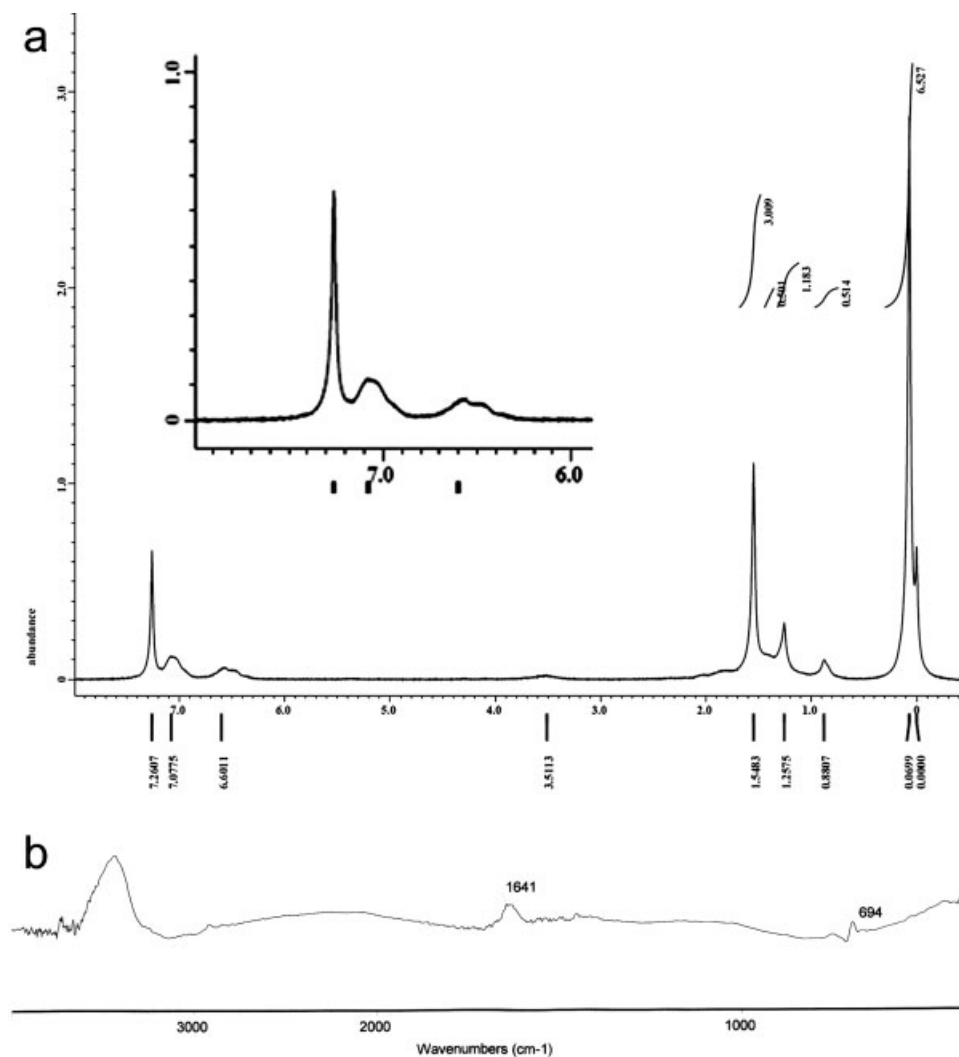


Figure 6 (a) ^1H NMR spectrum of MWCNT-PS. The inset shows a chemical shift value around 7.0, which belongs to the hydrogen atoms of benzene ring. The sample was prepared by re-dispersing MWCNT-PS (after removing solvents) in CDCl_3 using mild sonication; (b) FTIR spectrum of MWCNT-PS. The peak at 694 cm^{-1} belongs to the C-H bending vibration of single substituted benzene ring.

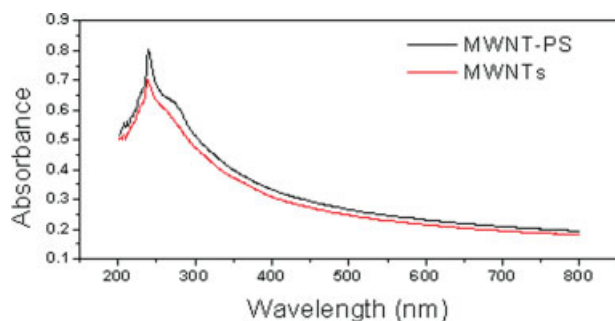


Figure 7 UV-vis absorption spectra of pristine MWCNT and MWCNT-PS in CHCl_3 . The reference solution was CHCl_3 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

above processing. As shown in Figure 10, in sharp contrast to pristine MWCNTs, MWCNT-PS can be dispersed in common solvents via slight sonication to obtain a quite well dispersion, which reveals the major advantage of this modification method and provides conveniences for further applications.

Furthermore, PS-based polymers can also retain the merit that their inclusive PS macromolecular chains would preferentially attach to CNT surface. Acting like surfactants, block copolymers and graft copolymers with PS as one part can attach to the sidewalls of CNTs to compensate the inherent intertube attractions and form stable dispersions effectively through robust noncovalent interactions, as many researchers indicated in their experiments.²¹ Figure 11 presents optical microscopy and TEM images of MWCNT dispersion of two block copolymers (SBS, PS-PMMA) and a graft polymer, PS-g-(GMA-co-St).¹⁷ Clearly, the MWCNTs were well dissolved in these polymer solutions, forming macro-

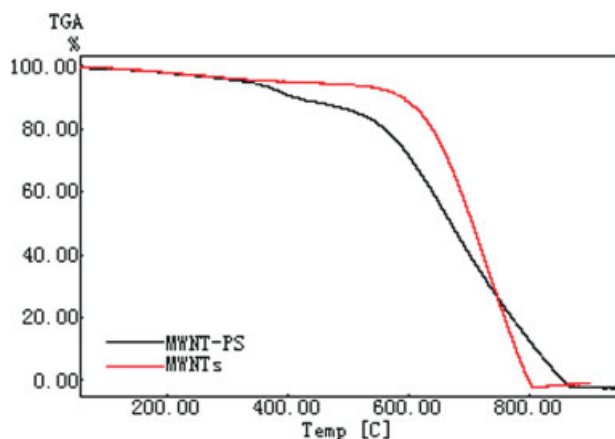


Figure 8 TGA traces for the pristine MWCNT and MWCNT-PS samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

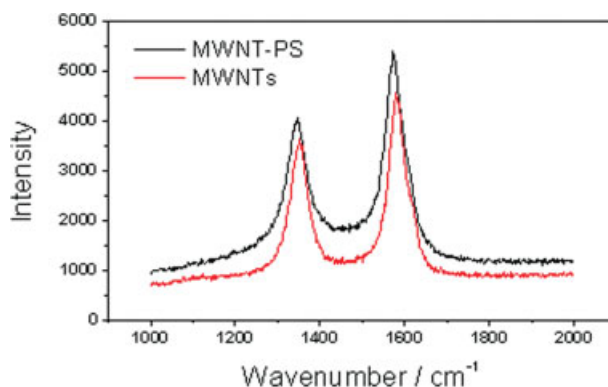


Figure 9 Raman spectra of pristine MWCNTs and MWCNT-PS samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

scopic transparent and homogeneous dispersions. With all these used polymers (PS, SBS, PS-PMMA, and PS-g-(GMA-co-St)), a wide range of choices are presented for effectively dispersing MWCNTs into organic solutions and modifying their surface properties. Based on these results, further applications that have different requirements for carbon nanotube dispersion may be satisfied with ease.

CONCLUSIONS

Based on systematic experimental results, evidences were presented that PS main chain would preferen-

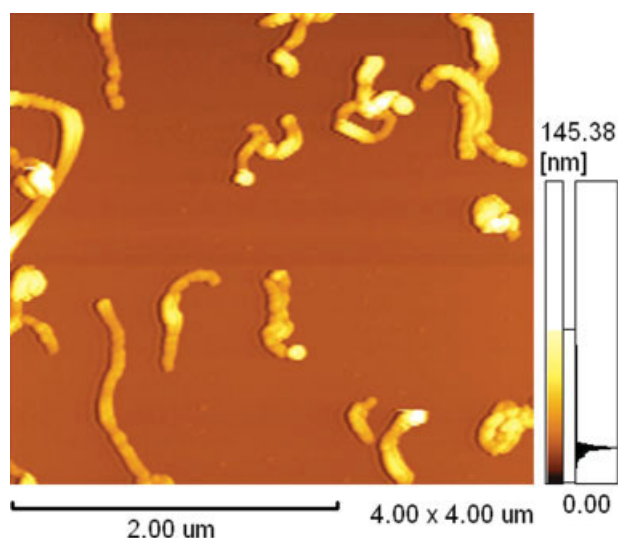


Figure 10 AFM image of typical re-dispersed MWCNT-PS. For sample preparing, MWCNT-PS was added into chloroform followed by slightly sonication (1 min). One drop of obtained dispersion was deposited between two freshly cleaved mica substrates and dried for observation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

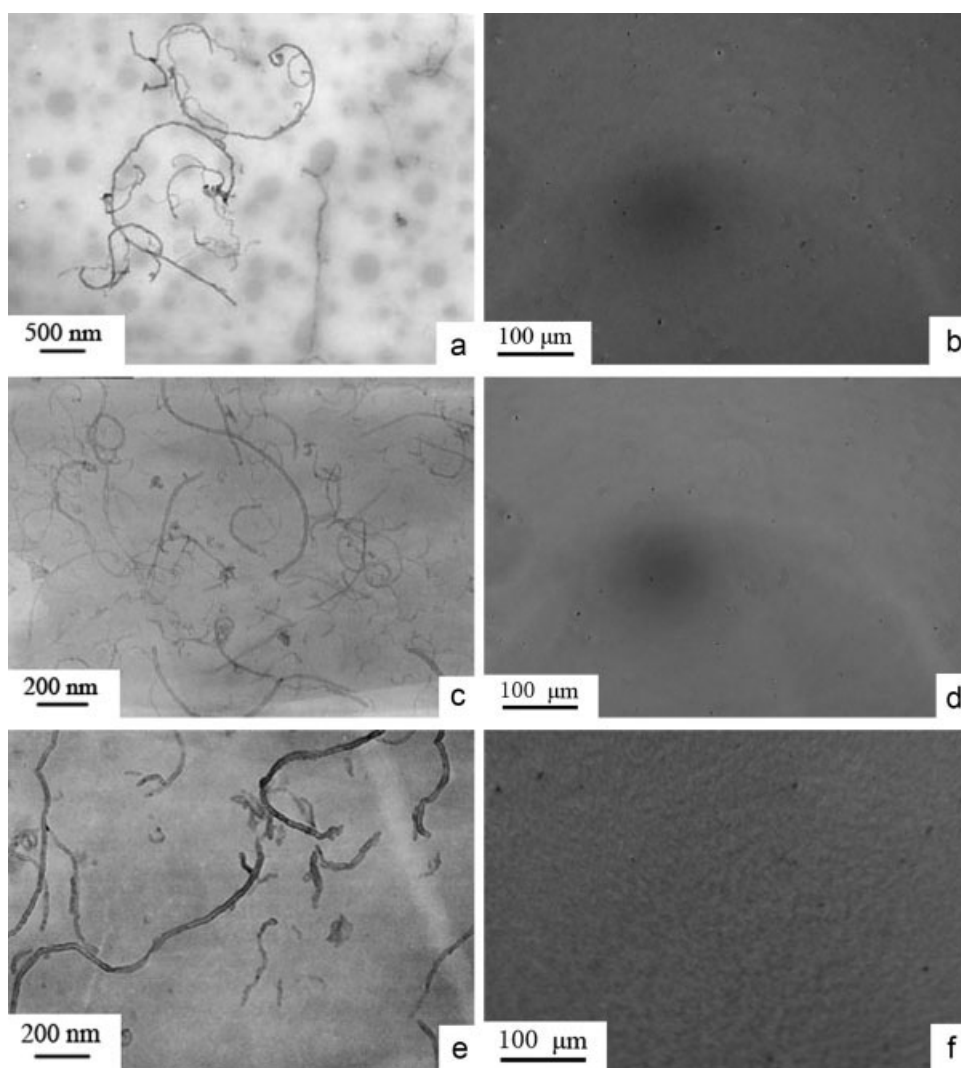


Figure 11 Optical microscopy and TEM images of MWCNTs dispersed in 1.0 wt % polymer solution (in chloroform). Sample preparation procedures are the same as PS (Fig. 4). Differences only rest with used polymers: (a) and (b) SBS; (c) and (d) PS-PMMA; (e) and (f) PS-*g*-(GMA-*co*-St).¹⁷

tially attach to carbon nanotube surface, which can be used to provide sufficient steric repulsion to stabilize debundled MWCNTs to form homogeneous dispersion. Even after careful washing with solvents, the attached PS could remain and the resulted composite MWCNT-PS can be easily redispersed in organic solvents. Extraordinary properties of MWCNTs may be kept undamaged in the process of dispersing and modifying. Copolymers that contain PS as one part also retain the characteristics of PS and can be used to disperse MWCNTs for further applications.

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