Large-Scale Preparation of Solubilized Carbon Nanotubes

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We report here a method that can be used to easily prepare bulk quantities of solubilized carbon nanotubes. The method is derived from Haddon's method in which we have modified the separation process by using two Soxhlet extractors in the procedure. Both primary and secondary amines could be used as starting materials to solubilize carbon nanotubes in our process, and the solubilized multiwalled carbon nanotubes (MWNTs) were fully characterized. Owing to the large quantity of solubilized MWNTs obtained, several basic properties such as the solubility and the percentage content of tubes in the solubilized samples have been determined and analyzed. Typical solubilized MWNT/polymer composites were also fabricated and their electronic and thermal properties were investigated.

Introduction

Carbon nanotubes (CNTs) are of great interest from both the fundamental and practical points of views.[1−3] Many applications based on this unique material have been proposed, such as high-strength composites,[4,5] electronic field emission materials,[6,7] optical limiting materials,[8−10] and optoelectronic components.[11−14] However, the research studies and applications of carbon nanotubes are hindered by processing and manipulation difficulties owing to their insolubility or poor dispersion in common organic solvents and polymeric matrixes. The solubilization of CNTs via covalent or noncovalent

methods is considered an efficient method to overcome these difficulties.[14] Several methods have been developed to solubilize CNTs, which also offer new opportunities for application.[14] For example, Haddon[15] first synthesized solubilized CNTs by amidation reaction of a long chain amine with nanotube-bound carboxylic acid groups. Prato et al.[16] took advantage of the 1,3-dipolar cycloaddition reaction of azomethine ylides and obtained highly solubilized CNTs. Tang[10] solubilized CNTs by in situ polymerizations of phenylacetylene catalyzed by certain metallorganic compounds in the presence of CNTs. However, so far most of the solubilized CNTs were obtained only on a milligram scale, which is far from the need of practical applications, for example, for the application of solubilized CNTs in CNTs/polymer composites.

We report herein a method of preparing bulk quantities of solubilized CNTs on the laboratory scale, which also could be easily developed for the industrial manufacture of solubilized CNTs. The method is derived from Haddon's method,[15] in which we have modified the separation procedure by using two Soxhlet extractors in the whole procedure. With our effective method, we can obtain tens of grams of solubilized CNTs at one time on the laboratory scale. Both primary and secondary amines could be used as starting materials. Single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) could be solubilized in the same manner. However, compared with the scarcity and high cost of SWNTs, MWNTs can be obtained in large quantity and at low cost from chemical vapor deposition (CVD) methods. Therefore, at present, the large-scale preparation of solubilized MWNTs (s-MWNTs) is practically significant and may meet the requirement of many applications. On the basis of our large quantity of

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† Institute of Chemistry, Chinese Academy of Sciences.
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(1) Special Issue on Carbon Nanotubes. *Acc. Chem. Res.* **2002,** *35* (12).
(2) Ajayan, M. *Chem. Rev.* **1999,** *99,* 1787.
(3) Yakobson, B. I.; Smalley, R. E. *Am. Sci.* **1997,** *85,* 324.
(4) Gong, X.; Liu, J.; Baskaran, S.; Voise, R. D.; Young, J. S. *Chem. Mater.* **2000,** *12,* 1049.
(5) Andrews, R.; Jacques, D.; Rao, A. M.; Rantell, T.; Derbyshire, F.; Chen, Y.; Chen, J.; Haddon, R. C. *Appl. Phys. Lett.* **1999,** *75,* 1329.
(6) Rao, A. M.; Jacques, D.; Haddon, R. C.; Zhu, W.; Bower, C.; Jun, S. *Appl. Phys. Lett.* **2000,** *76,* 3813.
(7) Gao, B. Z.; Yue, G. Z.; Qiu, Q.; Cheng, Y.; Shimodu, H.; Fleming, L.; Zhou, O. *Adv. Mater.* **2001,** *13,* 1770.
(8) Sun, X.; Yu, R. Q.; Xu, G. Q.; Hor, T. S. A.; Ji, W. *Appl. Phys. Lett.* **1998,** *73,* 3632.
(9) Chen, P.; Wu, X.; Sun, X.; Lin, J.; Ji, W.; Tan, K. L. *Phys. Rev. Lett.* **1999,** *82,* 2548.
(10) Tang, B. Z.; Xu, H. *Macromolecules* **1999,** *32,* 2569.
(11) Ouyang, M.; Huang, J.-L.; Lieber, C. M. *Acc. Chem. Res.* **2002,** *35,* 1018, and references therein.
(12) Star, A.; Stoddart, J. F.; Steuerman, D.; Diehl, M.; Boukai, A.; Wong, E. W.; Yang, X.; Chung, S.-W.; Choi, H.; Heath, J. R. *Angew. Chem., Int. Ed.* **2001,** *40,* 1721.
(13) Ago, H.; Petritsch, K.; Shaffer, M. S. P.; Windle, A. H.; Friend, R. H. *Adv. Mater.* **1999,** *11,* 1281.
(14) For recent excellent reviews, please see: (a) Bahr, J. L.; Tour, J. M. *J. Mater. Chem.* **2002,** *12,* 1952. (b) Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M. E.; Haddon, R. C. *Acc. Chem. Res.* **2002,** *35,* 1105. (c) Hirsch, A. *Angew. Chem., Int. Ed.* **2002,** *41,* 1853. (d) Sun, Y.-P.; Fu, K.; Lin, Y.; Huang, W. *Acc. Chem. Res.* **2002,** *35,* 1096.

(15) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998,** *282,* 95.
(16) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2001,** *124,* 760.

s-MWNTs, several basic properties of *s*-MWNTs such as their solubilities in certain solvents and the percentage content of MWNTs in the solubilized samples have been determined. Typical *s*-MWNT/polymer composites were also fabricated and their electronic and thermal properties were investigated.

Experimental Section

Materials. MWNTs produced from a chemical vapor deposition (CVD) method were bought from Sun Nanotech Co. Ltd (Nanchang, China). The pristine MWNTs were purified according to a literature method.[17] Briefly, 50 g of pristine MWNTs were refluxed 24 h in 800 mL of concentrated nitric acid. The excess concentrated nitric acid was removed by centrifuging. The resulting black solid was washed thoroughly with deionized water until the pH value of the water was about 5−6. The purified MWNTs were dried at 50 °C in a vacuum overnight. To make the *s*-MWNTs, the purified MWNTs were stirred in 500 mL of fresh distilled thionyl chloride at 70 °C for 24 h to convert the surface-bound carboxylic acid groups into acyl chloride groups. After centrifugation, the remaining solid was washed with anhydrous tetrahydrofuran (THF) and then dried at room temperature under vacuum. A mixture of the resulting solid and 30 g of didecylamine (DDA) or octadecylamine (ODA) was stirred under N_2 atmosphere at 80 °C for 96 h. After cooling to room temperature, the resulting solid mixture was placed in a porous paper thimble (made by a regular filter paper from Hangzhuo Xinhua Paper Plant, Hangzhou, China; pore size ∼30 μm) of a Soxhlet extractor. A 300 mL portion of ethanol was employed as extraction solvent to remove the excess amine. After 24 h, the ethanol solution was discarded, and 300 mL of chloroform was used as extraction solvent to obtain the *s*-MWNTs. After another 24 h, a black chloroform solution with apparent precipitation was obtained. The solvent was removed on a rotary evaporator, the resulting black solid (DDA-modified MWNTs, denoted as MDDA, or ODA-modified MWNTs, denoted as MODA) was dried at room temperature under vacuum, yielded 20 g of the product.

The MODA/polysulfone (PSF) composite films with various concentrations of MODA specified by weight percentage were fabricated as follows: 100 mg of PSF was dissolved in 10 mL of chloroform and the corresponding MODA of various weight percentages (0.5, 1, 2, 2.5, 3, 4, 5, 7, and 10% respectively) was added to each of the solutions to form a series of homogeneous solutions. The chloroform solutions were dripped onto clean glass substrates and dried in air at room temperature to form black thin films. The MODA/polystyrene (PS) composite films with various concentrations of MODA specified by weight percentages (1, 5, and 10%) were prepared with the same method as that of preparation of the MODA/PSF composites. To make a comparison, MWNTs/PSF and MWNTs/PS composite films were also prepared from purified MWNTs with certain polymers, respectively, with the same methods.

Measurement. UV/Vis absorption spectra were recorded with a computer-controlled Shimadzu UV-2502PC spectrophotometer. Raman spectra were obtained with 632.8-nm excitation (He−Ne laser) on a Renishaw RM 2000 micro-Raman spectrometer. FT-IR spectra were collected using a Bio-Rad FTS600 spectrometer.

Thermogravimetric analysis (TGA) experiments were performed with a heating rate of 10 °C/min in a N_2 atmosphere on a TA Instruments Perkin-Elmer 7 thermogravimetric analyzer. Transmission electron microscopy (TEM) analysis was conducted on a Hitachi H-800 transmission electron microscopy system. The operation voltage was 100 kV.

The room-temperature conductivity of the composite films was measured using the two-probe technique with parallel indium contacts. The ohmic behavior was checked in each case.

Scheme 1. Flow Chart of Large-Scale Preparation of Solubilized MWNTs
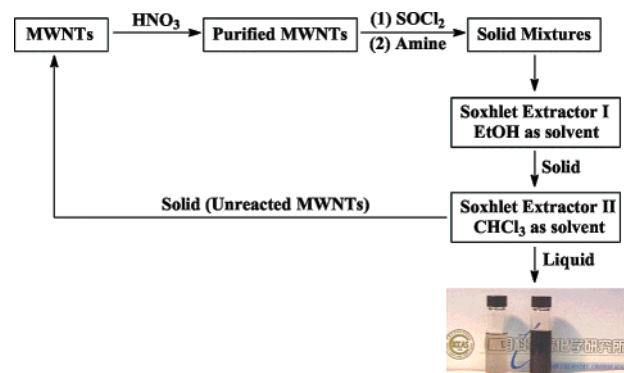
Results and Discussion

The solubilization of CNTs through the nanotube-bound carboxyl acid groups was first realized by Haddon et al.[15] and followed by other research groups.[14d,18−21] Although the reaction is not complicated, tedious work is usually needed to obtain even a milligram of solubilized samples. For example, to remove the excessive reactant of amine or alcohol, sonication is often needed, which makes the solubilized CNTs readily suspend in solvents such as ethanol, and they will hardly deposit even after heavy centrifuging. The ordinary method to separate the solubilized CNTs from those that are insoluble is pressure- or vacuum-filtration, in which the filter membrane or paper is easily blocked by the CNTs. Here, we introduce the Soxhlet extractor to eliminate these problems. The Soxhlet extractor is a convenient and efficient apparatus for extracting a solute by continuous passage of a boiling solvent. It has been widely used in the analyses of pharmaceutical materials and soil.[22] In our procedure, the Soxhlet extractor is used not only to simplify the process but also to realize the large-scale preparation of solubilized CNTs. First, the Soxhlet extractor was used to remove excessive amines by using ethanol as extraction solvent. Second, chloroform was employed to separate the solubilized CNTs from the unreacted CNTs. The unreacted CNTs could be easily recycled and used for another cycle of preparation of the solubilized CNTs, if necessary, which enabled the mass preparation of *s*-MWNTs in the laboratory level. This process is illustrated in Scheme 1.

Characterization. The black homogeneous solution of the *s*-MWNTs in certain organic solvents is a simple visual indication of MWNTs in the solutions. The typical UV/Vis spectra of MDDA and MODA in room-temperature chloroform are shown in Figure 1.

The TEM images provide the most direct evidence for the presence of MWNTs in the colored solutions. As seen in Figure 2(top), the pristine MWNTs are very long (>10

(17) Liu, L. Q.; Zhang, S.; Hu, T. J.; Guo, Z. X.; Ye, C.; Dai, L. M.; Zhu, D. B. *Chem. Phys. Lett.* **2002**, *359*, 191.

(18) (a) Hamon, M. A.; Chen, J.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Adv. Mater.* **1999**, *11*, 834. (b) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, M. A.; Hu, H.; Cohn, R. W.; Eklund, P. W.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C. *J. Phys. Chem. B* **2001**, *105*, 2525.

(19) Pompeo, F.; Resasco, D. E. *Nano Lett.* **2002**, *2*, 369.

(20) Kahn, M. G. C.; Banerjee, S.; Wong, S. S. *Nano Lett.* **2002**, *2*, 1215.

(21) Basiuk, E. V.; Basiuk, V. A.; Banuelos, J.-G.; Saniger-Blesa, J.-M.; Pokrovskiy, V. A.; Gromovoy, T. Yu.; Mischanchuk, A. V.; Mischanchuk, B. G. *J. Phys. Chem. B* **2002**, *106*, 1588.

(22) Luque de Castro, M. D.; García-Ayuso, L. E. *Anal. Chim. Acta* **1998**, *369*, 1.
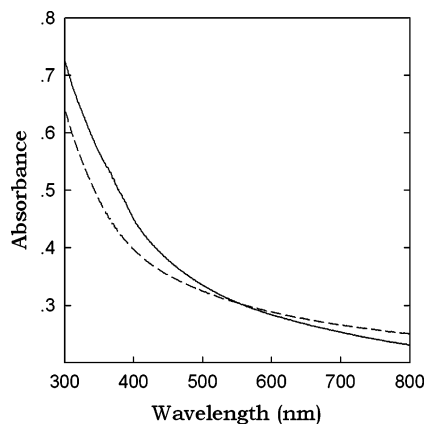
Figure 1. Absorption spectra of MODA (solid line) and MDDA (dashed line) in chloroform.
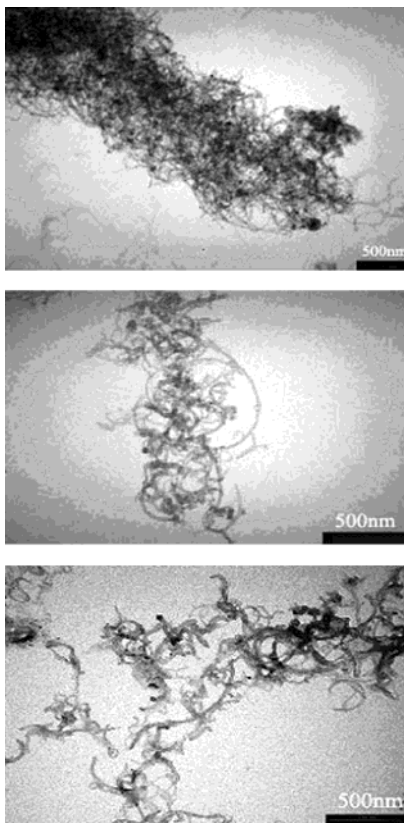

Figure 2. TEM images of pristine MWNTs (top), purified MWNTs (middle), and MDDA (bottom).

μm) and poorly dispersed and entangled together. However, the purified MWNTs (Figure 2(middle)) are obviously shorter than the precursor MWNTs, with an average length of ~2 μm, and the tube structures are well maintained. Figure 2(bottom) shows the morphology of the MDDA, which is similar to that of the purified MWNTs. It is notable that MDDA are well dispersed and the tube structures are well kept. The TEM of MODA also shows similar features.

The FTIR spectra of MODA and MDDA show the functionalities clearly. For example, we can see peaks at 2922 and 2851 cm^{-1}, which are due to C–H stretch modes of the alkyl chain. The C=O stretch of the amide appears at 1640 cm^{-1}. The peaks at 1574 and 1466 cm^{-1} are from the C=C stretch of the MWNTs and C–H bend of the alkyl chain, respectively.
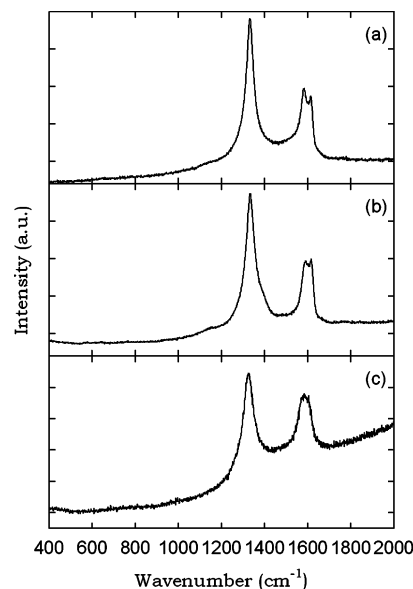

Figure 3. Raman spectra of pristine MWNTs (a), purified MWNTs (b), and MDDA (c).

The Raman spectra of pristine MWNTs, purified MWNTs, and MDDA are shown in Figure 3. All of the spectra have the same pattern, which implies that the solubilization procedure does not affect the graphite structure of the MWNTs, consistent with the TEM results discussed above. The first-order Raman spectroscopy shows a strong band at 1577 cm^{-1} (G lines) which is the Raman-allowed phonon high-frequency E_{2g} first-order mode, and a disordered-induced peak at 1326 cm^{-1} (D lines), which may originate from defects in the curved graphene sheets, tube ends, and turbostratic structure of graphene in the materials.[23,24] Generally the D lines are observed at 1346 cm^{-1} or 1350 cm^{-1}, G lines are observed at 1580 cm^{-1} for other carbon nanotubes.[25] The downshift is probably due to different carbon nanotube specimens and laser illuminated positions, as well as incident laser power.[26]

Determination of the MWNT Content. Elemental analysis (EA) was used to determine the MWNT content in the solubilized samples. The MODA sample gives C, 85.85%; N, 1.55%; and H, 4.75%. Although the combustion of carbon is not complete due to the high thermal stability of the nanotubes, we can take the content of nitrogen as a standard to calculate the content of tubes in the solubilized sample. Because one nitrogen atom corresponds to one octadecyl ($C_{18}H_{37}$) chain and the molar ratio of N/$C_{18}H_{37}$ is 0.055, 1.55% content of nitrogen corresponds to ~28% weight content of octadecyl chains. Thus, the weight content of octadecylamino groups in MODA is ~30%, which implies the weight content of nanotubes in the solubilized sample is ~70%.

The content of tubes was also confirmed by thermogravimetric analysis (TGA). As shown in Figure 4(a), there is one inflection at 460 °C in the TGA curve of purified MWNTs, which indicates that the nanotubes

(23) Tan, P.; Zhang, S. L.; Yue, K. T.; Huang, F.; Shi, Z.; Zhou, X.; Gu, Z. *J. Raman Spectrosc.* **1997**, *28*, 369.
(24) Li, W.; Zhang, H.; Wang, C.; Zhang, Y.; Xu, L.; Zhu, K.; Xie, S. S. *Appl. Phys. Lett.* **1997**, *70*, 2684.
(25) Hiura, H.; Ebbesen, T. W.; Tanigaki, K.; Takahashi, H. *Chem. Phys. Lett.* **1993**, *202*, 509.
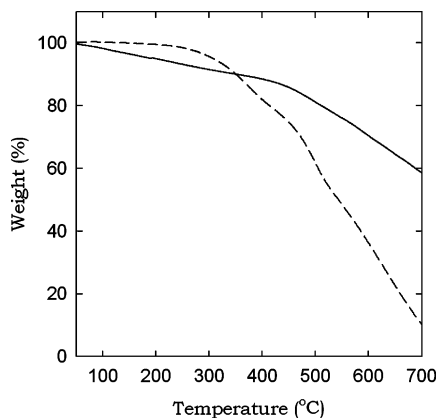(26) Ando, Y.; Zhao, X.; Shimoyama, H. *Carbon* **2001**, *39*, 569.

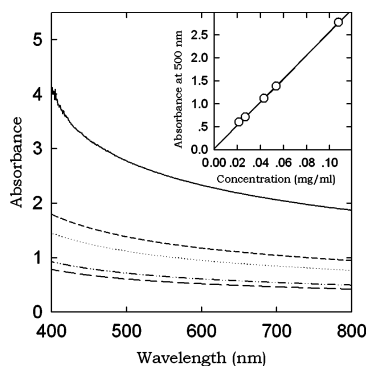**Figure 4.** TGA curves of purified MWNTs (solid line) and MODA (dashed line).

Figure 5. Absorption spectra of MODA in room-temperature chloroform at different concentrations. Inset shows the linear dependence of the absorption at 500 nm on concentration.

begin to decompose at 460 °C, as reported before.[27] As for the TGA curve of MODA (Figure 4(b)), there are two inflections at 250 °C and 460 °C, respectively. Compared with the TGA of purified MWNTs, the second inflection corresponds to the decomposition temperature of the nanotubes. The first inflection should be due to the decomposition of the attached octadecylamino groups. Thus, the second inflection in the TGA curve of MODA should be the onset of the weight loss of the tubes, indicating the removal of the attached octadecylamino groups, although at that temperature ODA may not be completely removed. Therefore, the weight loss corresponding to the second inflection of the TGA curve of MODA should be the weight content of alkyl chains, which corresponds to a value of ~30%. The weight content of tubes in the solubilized sample thus determined from TGA is 70%, which fits well with the elemental analysis results.

Determination of Solubility. The solubility of solubilized CNTs is of both practical and fundamental interest. Our solubilized MWNTs are essentially insoluble in polar and H-bonding solvents such as water, methanol, and acetone. However, they show relatively high solubility in chloroalkanes and aromatic solvents. The solubility of MODA in a variety of organic solvents was determined by UV/Vis absorption spectroscopy. A similar method has been used to determine the solubility of fullerene[28] and small-diameter SWNTs.[29] Typically, ~200 mg of accurately weighed MODA was completely dissolved in a certain amount of the selected solvent under study. The solution was separated into several portions and diluted to different concentrations,
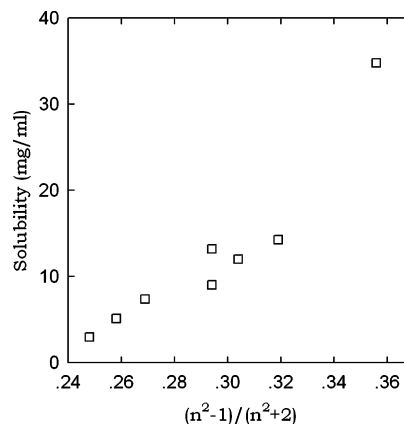

Figure 6. Room-temperature solubility of MODA as a function of the solvent polarizability parameter.

Table 1. Room-Temperature Solubility of MODA

solvent	mg/mL	n	$(n^2-1)/(n^2+2)$
carbon disulfide	34.8	1.63	0.356
1,2-dichlorobenzene	14.3	1.55	0.319
toluene	13.2	1.50	0.294
chlorobenzene	12.0	1.52	0.304
benzene	9.0	1.50	0.294
chloroform	7.4	1.45	0.269
dichlorofomethane	5.1	1.42	0.258
tetrahydrofuran	3.0	1.41	0.248

and their absorption spectra were measured (Figure 5). The absorption spectra are dependent on the solution concentration in a linear fashion, following the Lambert–Beer's law. Thus, a standard curve of absorbance–concentration dependence at certain wavelength (e.g., 500 nm) can be obtained (Figure 5 inset). A saturated solution of MODA in the same solvent was made and the solution was then diluted to a proper concentration in which the absorption at certain wavelength can match the standard curve. Then the solubility of MODA in this solvent could be calculated. The solubility of MODA in typical organic solvents is given in Table 1. The values given were averages of duplicate measurements.

As shown in Table 1, MODA shows best solubility in CS_2, which is similar to C_{60}.[30] MODA also has better solubility in aromatic solvents such as toluene, etc. We also find that the solubility of *s*-MWNTs has a certain relationship with the polarizability parameter of the solvent, which is expressed as $(n^2 - 1)/(n^2 + 2)$, where n is the index of refraction (Na_D line).[30] From Figure 6 we can approximately conclude that the solubility of solubilized MWNTs is increased along with n value of the solvent, similar to C_{60}.[30] Although their solubilities are lower than those of functionalized SWNTs reported by Prato et al.,[16] the relatively high solubilities of MODA in a variety of solvents still provide the possibility to easily disperse MWNTs, which allows us to fabricate MWNT/polymer composites and study their properties, as discussed below.

(27) Bom, D.; Andrews, R.; Jacques, D.; Anthony, J.; Chen, B. L.; Meier, M. S.; Selegue, J. P. *Nano Lett.* **2002**, *2*, 615.
(28) Sivaraman, N.; Dhamodaran, R.; Kaliappan, I.; Srinivasan, T. G.; Vasudeva Rao, P. R.; Mathews, C. K. *J. Org. Chem.* **1992**, *57*, 6077.
(29) Bahr, J. L.; Mickelson, E. T.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *Chem. Commun.* **2001**, 193.
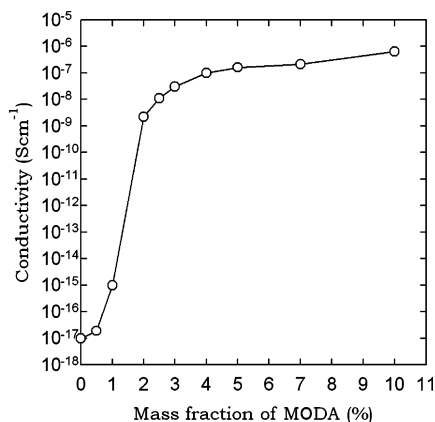(30) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379.

Figure 7. Dependence of the room-temperature MODA/PSF composite conductivity with the MODA content.

MODA/Polymer Composites. The large quantity and good solubility of *s*-MWNTs prepared in this work enabled us to fabricate MWNT/polymer composites. The *s*-MWNTs should show better dispersive homogeneity and interfacial compatibility compared with that of pristine or purified MWNTs, which may lead to better composite performance.

A series of MODA/PSF composites with different MODA mass fractions was made by drop-casting a chloroform solution of the mixture on clean glass substrates. After the solution dried, a black homogeneous film formed which was uniform to the eye. However, the corresponding film with purified MWNTs as doping shows clear black spots occasionally. This implies that the solubilized MWNTs can disperse better than the purified MWNTs. The room-temperature electronic conductivity properties of the films were measured with a two-probe technique. As shown in Figure 7, with increased percentage of MODA, the conductivity of the composite increased remarkably. For example, when about 1% of MODA was added to the polymer, the conductivity of the composite could increase dramatically by 9 orders of magnitude. The behavior of conductivity is characteristic of percolation in composite systems, with a threshold of approximate 1.5% mass fraction. As for the pristine MWNT-doped PSF composites, the measurement of the conductivity did not give constant values, probably because of the bad homogeneity of the sample. Thus the doping of solubilized MWNTs can improve the electronic conductivity of PSF with a very small percentage, most probably due to the better electronic conductivity of MWNTs and the better homogeneous dispersion of solubilized samples.

The MODA/PS composites were also prepared in order to check the influence of doping of tubes on the thermal stability of the composites. To make a comparison, MWNTs/PS composites with different fractions of purified MWNTs in the polymer were also obtained with the aid of sonication. Similar to the MODA/PSF composites, the MODA/PS composite films are uniform to the naked eye, while the MWNTs/PS films contain many black spots. The sample films were subjected to TGA to measure their thermal stability and the resulting curves are shown in Figure 8. The masses remaining at 700 °C are almost entirely due to the undecomposed nanotubes, and are approximately in proportion consistent with the initial nanotubes loading, as pure PS is
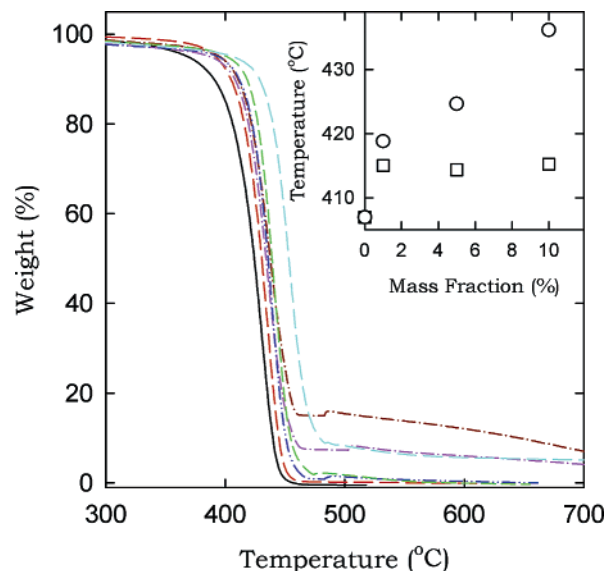

Figure 8. Weight-loss curves for PS, purified MWNT/PS, and MODA/PS composites in different nanotube loadings: black line, PS; red line, MWNT loading of 1%; blue line, MWNT loading of 5%; dark red line, MWNT loading of 10%; blue line, MODA loading of 1%; green line, MODA loading of 5%; cyan line, MODA loading of 10%. Inset shows the dependence of the decomposing temperature of the composites on the content of nanotubes. Circle: MODA-doped PS. Square: purified MWNTs-doped PS.

decomposed completely at ~460 °C. With the addition of both MODA and purified MWNTs, the decomposition temperatures of the composites are obviously increased compared with those of pure PS. The more nanotubes that were added, the higher temperature the composites could endure. It is worth noting that at the same percentage of MODA and purified MWNTs in the composites, the MODA-based polymer composites show higher thermal stability than the corresponding purified MWNT-based composites (Figure 8, inset). Thus, the solubilized CNTs can improve the thermal stability more efficiently than the purified CNTs, probably because of the better interfacial compatibility of the solubilized CNTs.

Conclusion

In summary, a method that can be used to prepare solubilized CNTs on a large scale was realized. The solubilized MWNTs prepared in this paper contain ~70% of MWNTs and exhibit good solubility in certain organic solvents. They also show good dispersive homogeneity and interfacial compatibility when used to make MWNT/polymer composites, and can efficiently improve the electronic conductivity or thermal stability of certain composites. We believe our large-scale preparation of solubilized MWNTs will have great utility in the application of MWNTs, especially in MWNT/polymer composites, which we are studying currently.