Electrical Properties of Soluble Carbon Nanotube/Polymer Composite Films

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A series of multiwalled carbon nanotube (MWNT) esters with various alkyl chains of *n*-butyl, *n*-hexyl, *n*-octyl, *n*-dodecyl, and *n*-hexadecyl has been synthesized via a concise method, and their solubilities in chloroform were determined by UV−vis absorption spectroscopy. The MWNT ester/polysulfone (PSF) composite films were made by drop casting, and their morphologies was checked by scanning electron microscopic method. The surface and volume conductivities of these films were measured. It was found that while longer alkyl chains can result in better properties such as better solubility in chloroform, better dispersibility in polymer matrix, and better electrical conductivity performance, the *n*-octyl modified MWNT ester always plays the inflection role, exhibiting the percolative character. While the surface electrical conductivity of the composite films is ohmic, the electrical conductivity along the thickness direction is nonohmic, which may provide the possibility to realize the unique electrical properties of carbon nanotubes on a macroscopic scale.

Introduction

Since their discovery, carbon nanotubes (CNTs) have attracted tremendous attention due to their unique properties such as extremely high mechanical strength and high electrical and thermal conductivity.[1−5] These properties together with their intrinsic high-aspect ratio, small diameter, and light weight make CNTs the ultimate carbon fibers for high-performance and multifunctional polymer composites, which could capitalize on their extraordinary properties on a macroscopic scale.[2,6−9] As for the electrical properties of CNT/polymer composites, it was reported that use of CNTs as conductive fillers in a polymer matrix implies a very low percolation threshold.[10−12] However, as CNTs are generally insoluble in common solvents and polymers, they tend to aggregate and disperse poorly in polymer matrix, resulting in deleterious effects. To overcome these difficulties, several methods have been developed to disperse CNTs in host polymers. For example, CNTs could be dispersed in certain polymer solutions via ultrasonication[13−27] or in the presence

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of surfactants.[9,28−32] The polymer wrapping on the wall of CNTs through noncovalent functionalization, e.g., $\pi-\pi$ interactions was also reported by several groups, which could make CNTs disperse in polymers.[10,33−36] Along with the rapid development of carbon nanotube chemistry, the direct polymerization of CNTs with specific molecules was also achieved.[37−42]

The other key approach of carbon nanotube chemistry is making CNTs soluble in aqueous and/or nonaqueous solvents,[43−45] which could provide a general way to allow homogeneous dispersion of CNTs in the host polymer matrix. The solubilized CNTs could also be made with customizing functional groups in order to make CNTs/polymer composites with special properties. However, so far most of the solubilized CNTs were obtained only on a milligram scale, which is far from the need of these kinds of practical applications.

We have been involved in developing methods that can obtain solubilized CNTs conveniently and in large scale. Recently, we have improved Haddon's method[46] of making solubilized CNTs by modifying the separation process via using two Soxhlet extractors in the procedure.[47] In this way, we can prepare bulk quantities of solubilized CNTs in the laboratory. We also developed a concise way to functionalize carbon nanotubes via the esterification reaction of the

carboxylate salt of carbon nanotubes and alkyl halides in the presence of a phase-transfer reagent in water.[48] The whole reaction is carried out in water and only needs several hours, which is simpler and more efficient than other methods described before. The above methods developed in our laboratory can make both single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) soluble; 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 solubilized MWNTs are practically significant which may meet the requirement of many applications. In this paper, a series of linear alkyl-modified MWNT esters has been synthesized. The solubility of these MWNT esters in chloroform was determined by UV−vis absorption spectroscopic method. The MWNT ester/polysulfone (PSF) composite films were made by the drop-casting method. The influence of the length of the alkyl groups on the morphology and the electrical conductivity of the composite films were also investigated.

Experimental Section

Materials. MWNTs were purchased from Shenzhen Nanotech Port Co. (China). These MWNTs were produced via the chemical vapor deposition method. The pristine MWNTs were purified according to literature method.[49] Briefly, 600 mg of the pristine MWNTs were suspended in 80 mL of concentrated sulfuric acid/nitric acid mixture (3:1 (v/v)) and sonicated for 10 h with a ultrasonicator (55 kHz, Cole-Parmer). The excess acid was removed by centrifuging. The resulting black solid was washed thoroughly with deionized water until the pH value of the water is ∼6. The purified MWNTs were dried at 50 °C in vacuo overnight. The purity of the MWNTs was checked by transmission electron microscopy (TEM). Polysulfone with an IV of 0.54 was produced by Shanghai Shuguang Chemical Factory (China).

A series of alkyl bromide (RBr, R = n-C$_n$H$_{2n+1}$, n = 4, 6, 8, 12, and 16, respectively) was purchased from Beijing Chemical Plant. Tetra-n-octylammonium bromide (TOAB) was purchased from Alfa. All chemical reagents were commercially available and were used as received.

To make the MWNT esters, 60 mg of the purified MWNTs were sonicated in NaOH aqueous solution (10 mM, 90 mL) for 2 min and converted into the sodium salt form. To this black homogeneous suspension, 100 mg of TOAB and 1.5 mL of alkyl bromide (RBr) were added in and the mixture was heated at 80 °C for 4 h under vigorous stirring. The suspension became clear and colorless, and black precipitation was observed. The precipitation was collected and dissolved in an excess amount of CHCl$_3$. After filtration to get rid of unreacted MWNTs if there was any, the solution was washed with 15% NaCl aqueous solution three times and dried with anhydrous CaSO$_4$. The resulting chloroform solution was concentrated to about 2 mL via a rot-vap and then precipitated into 100 mL of ethanol. After centrifuging, the resulting solid was dried in vacuo at 50 °C overnight. The esters were obtained as black solids.
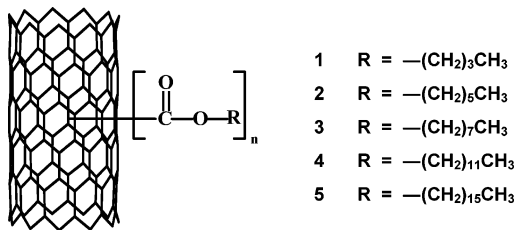
Through this general method, five esterified MWNTs with different linear alkyl chains were obtained (Chart 1). Ester **1**, R =

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Chart 1. Structures of MWNT Esters

1	R = —(CH$_2$)$_3$CH$_3$
2	R = —(CH$_2$)$_5$CH$_3$
3	R = —(CH$_2$)$_7$CH$_3$
4	R = —(CH$_2$)$_{11}$CH$_3$
5	R = —(CH$_2$)$_{15}$CH$_3$

n-butyl, yield 26.6 mg; ester **2**, R = *n*-hexyl, yield 43.2 mg; ester **3**, R = *n*-octyl, yield 47.0 mg; ester **4**, R = *n*-dodecyl, yield 45.5 mg; ester **5**, R = *n*-hexadecyl, yield 53.3 mg. To make these MWNT esters comparable, all of the experiments were performed using the same batch of purified MWNTs.

The MWNT ester/PSF composite films were fabricated as follows: 200 mg of PSF was dissolved in 20 mL of chloroform and 10 mg of the corresponding MWNT ester (**1**−**5**, respectively) was added, and the mixture was dispersed in the solution via sonication for 1−2 min. A 3 mL aliquot of the resulting solution was then dripped onto clean glass substrates and dried in air at room temperature to form a black thin film. The average thickness of the films is ~45 μm.

Measurement. UV−vis absorption spectra were recorded with a computer-controlled Shimadzu UV-2501PC spectrophotometer.

Transmission electron microscopy (TEM) analysis was conducted on a JEOL JEM-2010 transmission electron microscopy system. The operation voltage is 200 kV.

Scanning electron microscopy (SEM) was measured on Hitachi S-4300F scanning electron microscopy system. Standard specimens were cryogenically fractured in liquid nitrogen. The fracture surface was sputter-coated with gold before observation.

The room-temperature surface resistance and volume resistance of the composite films were measured using the two-probe technique with Advantest R8340 ultrahigh resistance meter. For the surface resistance measurement, the samples were cut into thin rectangular slabs with typical dimensions of 12 × 4 mm^2. The electrical contact was made using a silver paste. The volume resistance was measured across the thickness direction. The surface resistivity and the volume resistivity were converted into surface conductivity and volume conductivity, respectively.

Results and Discussion

The nitrosulfuric acid was used to purify pristine MWNTs. This method can not only remove the majority of amorphous carbon and metal particles (which came from the metal catalyst used to make the nanotubes) but also introduce carboxylic acid groups on the surface of nanotubes. Figure 1 shows a typical large-scale TEM image of the purified MWNTs used in our experiments. It can be seen clearly that there are almost no amorphous carbon and metal particles after the purification procedure, which guarantees the electrical properties obtained in our study are not affected by conductive impurities.

Since the five MWNT esters synthesized were obtained from the same batch of purified MWNTs using the same method, the only difference among these samples is the different alkyl chains attached to the MWNTs, which could result in different properties. The influence of the different alkyl chains on the solubility of MWNTs was studies by UV−vis absorption spectroscopic method under room temperature as described before.[47] Obviously, the solubility of
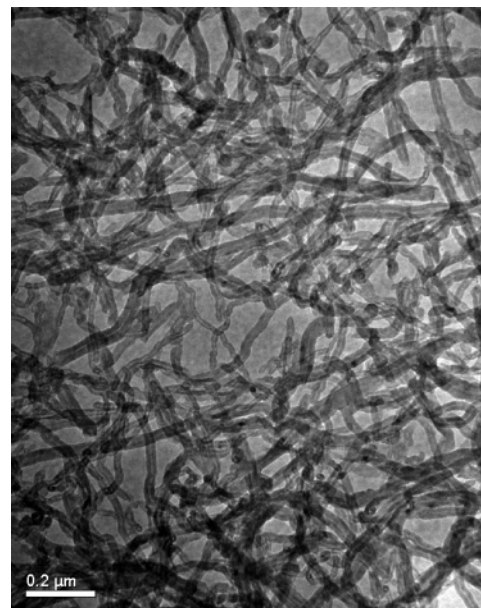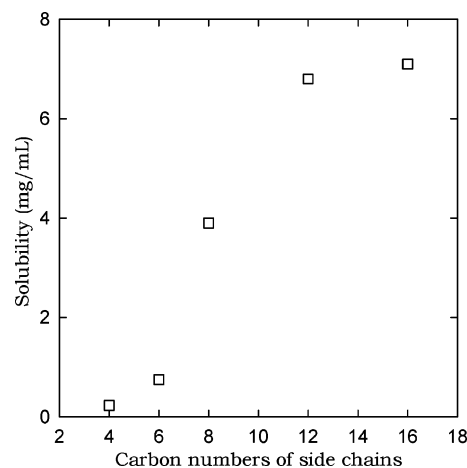

Figure 1. Typical large-scale TEM image of purified MWNTs.

Figure 2. Solubilities of MWNT esters in CHCl$_3$ vs carbon numbers of side chains.

these MWNT esters strongly depends on the length of the attached linear alkyl chains. The attachment of longer alkyl chains gives better solubility (Figure 2). The solubility of ester **1** and ester **2** is determined as 0.1 and 0.8 mg/mL, respectively, which means these two esters do not solublize well in chloroform. However, the solubility of ester **3** shows a dramatic increase up to 3.9 mg/mL. For esters **4** and **5**, the solubility is 6.8 and 7.1 mg/mL, respectively. Thus the attachment of eight carbon alkyl chains can make MWNTs soluble, and longer alkyl chains can give MWNTs better solubility. From Figure 2, it can also be deduced that although 12- and 16-carbon alkyl chains can make MWNTs solubilize better, it is not necessary to attach longer alkyl chains on the MWNTs just to increase the solubility. It was reported by Georgakilas et al.[50] that the solubility of their covalent side-wall functionalized SWNTs was ~50 mg/mL, much higher than those of the functionalized MWNTs obtained in this study. Considering that the substitutions attached to SWNTs in their work are also common organic

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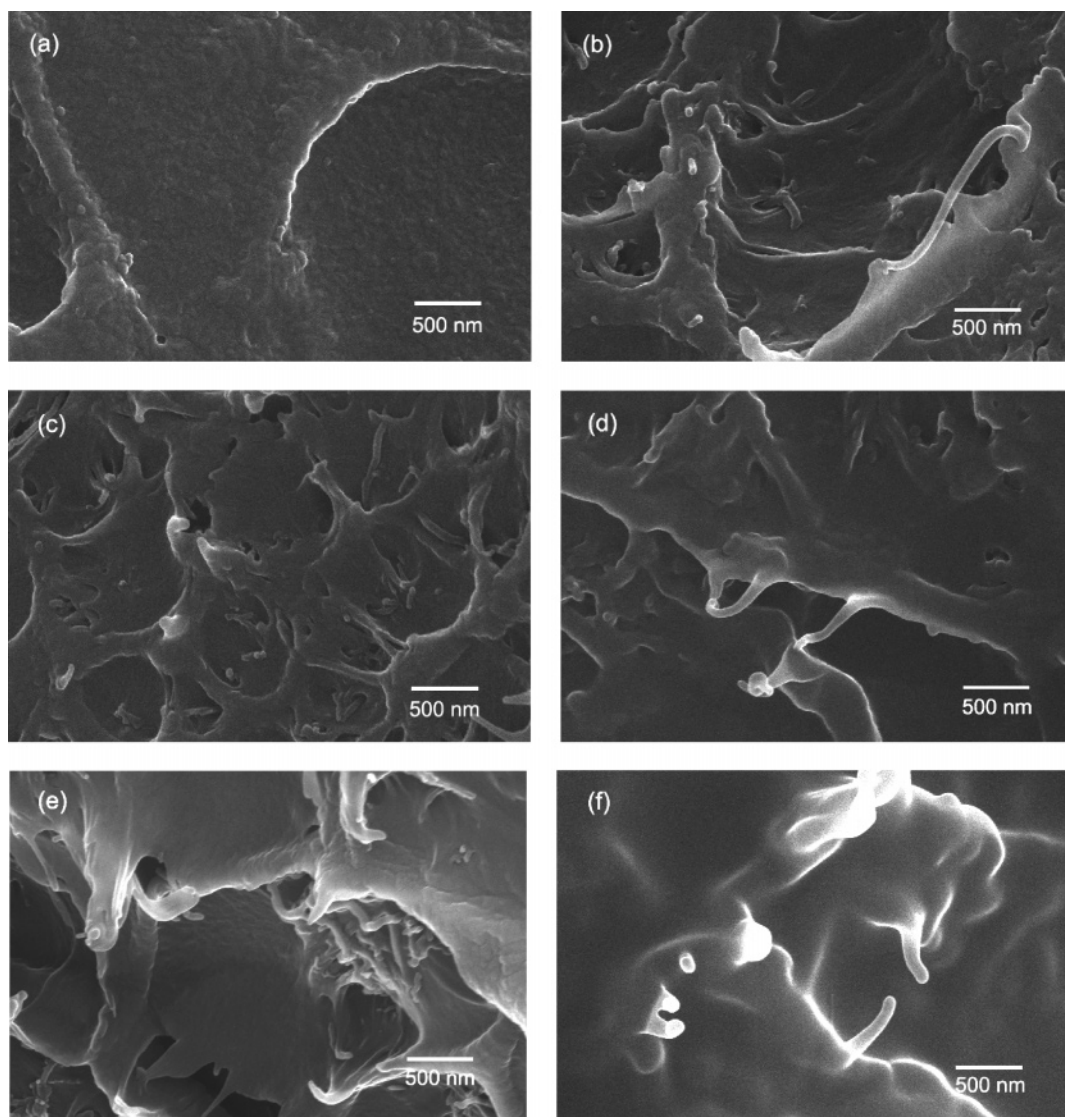
Figure 3. SEM images of fracture surfaces of PSF film (a) and MWNT ester/PSF films of **1**/PSF (b), **2**/PSF (c), **3**/PSF (d), **4**/PSF (e), and **5**/PSF (f).

groups, we believe this difference is dependent upon the intrinsic properties of CNTs, such as the type (multiwall or single-wall), the average length and diameter, and the reactivity of CNTs.

It should be interesting to know how the different alkyl substitutions in the MWNT esters we obtained can influence the electrical conductivities of MWNT/polymer composites. The MWNT ester/PSF composites were made by drop casting of the chloroform solution of the mixture onto clean glass substrates. The MWNT ester content in the mixture was kept as 5% (w/w) in each of the samples, respectively. After drying, black films which are uniform to the eye were formed. However, the corresponding film with purified MWNTs as doping shows clear black spots occasionally, which implies that the MWNT esters can disperse better than the purified MWNTs in PSF matrix. To further study the homogeneity of the films in microscale, the SEM method was employed to investigate the fracture surfaces of the composites together with that of pure PSF film (Figure 3). The pure PSF film indicates the typical fragile rupture. However, SEM images of composite films show different features. For the ester **1**/PSF and ester **2**/PSF composites,

MWNTs were observed pulled out from the matrix and left some holes, showing poor adhesion between the MWNTs and the matrix. The composite of ester **3**/PSF shows clearly that MWNTs are wrapped by the matrix, which indicates the good adhesion between MWNTs and matrix polymer PSF. As for ester **4**/PSF and ester **5**/PSF composites, a better adhesion of the MWNTs with polymer matrix is clearly observed. These results imply that a homogeneous dispersion of MWNTs can be achieved in the PSF matrix for MWNT esters with linear alkyl chains above eight. The introduction of longer alkyl chains on the surface of MWNTs can get MWNTs more compatible with the polymer matrix.

Both the volume and surface conductivity properties of the films were measured at room temperature by using a two-probe technique. Since there are two surfaces for the film, we define the top and bottom faces of the film as those faces exposed to the air and in contact with the substrate, respectively. As for the purified MWNT-doped PSF composite, the measurement of the conductivity did not give constant values, probably because of the heterogeneity of the sample.[47] Figure 4a shows the volume conductivity of MWNT ester/PSF composite films as a function of the carbon
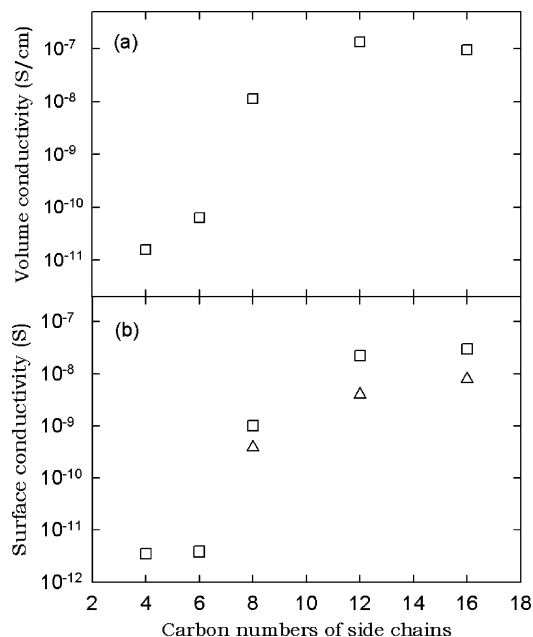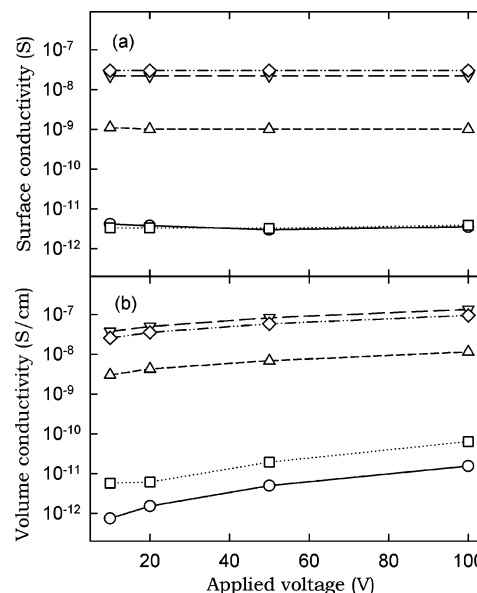
Figure 4. Volume conductivity (a) and bottom surface (square) and top surface (triangle) conductivity (b) variations with the carbon numbers of side chains.

number of linear alkyl chains. While ester **1**/PSF and ester **2**/PSF composites show similar conductivity between 10^{-12} and 10^{-11} S/cm, the conductivity of ester **3**/PSF composite films increases dramatically to $\sim10^{-8}$ S/cm. For ester **4**/PSF and ester **5**/PSF composite films, their volume conductivity values are between 10^{-7} and 10^{-8} S/cm. Thus a percolating network was formed for the ester **3**/PSF composite. Considering that the MWNT ester content is kept as 5% (w/w) for each of the samples investigated, the driving force for the better volume conductivity of MWNT ester/PSF composites is the better dispersion of MWNTs in the PSF matrix, which is due to the introduction of longer alkyl chains to the surface of MWNTs.

Figure 4b shows the bottom and top surface conductivity of the composite films, respectively. For composite films made from ester **1** and ester **2**, the top surface conductivity could not be detected in our experiments, probably because there are few conductive fillers (CNTs) on the surfaces. However, the bottom conductivities of both of these two films give a value $\sim0.5 \times 10^{-11}$ S. The electrical conductivity of the bottom surfaces of the other three composite films made by ester **3**, ester **4**, and ester **5** exhibits a relatively higher electrical conductivity than those of the top surfaces, giving the value of 1×10^{-9}, $\sim4 \times 10^{-8}$, and 5×10^{-8} S, respectively.

Both of the bottom surface and the volume conductivities of the MWNTs ester/PSF composite films were also measured versus different applied voltage (Figure 5). As shown in Figure 5a, the bottom surface conductivities are almost invariable as the applied voltage is increased, namely, the ohmic conductivity, which also indicates of the homogeneity of the bottom surface of the composite films. However, the volume conductivities are increasing as the applied voltage is increased, which indicates the nonohmic behaviors (Figure 5b). It implies the uneven distribution of MWNT esters along the thickness direction of the composite films. Thus, the films

Figure 5. Bottom surface conductivity (a) and volume conductivity (b) vs the applied voltage for **1**/PSF (circles), **2**/PSF (squares), **3**/PSF (up triangles), **4**/PSF (down triangles), and **5**/PSF (diamonds).

Chart 2. MWNT Distribution in Polymer Matrix[a]
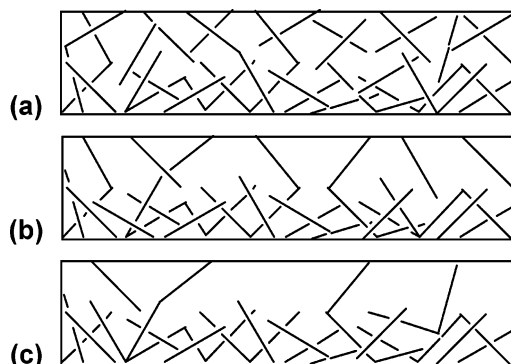
[a] The dispersion of MWNTs follows a degressive sequence from a to c.

obtained in our study are ohmic along the surface and nonohmic along the thickness direction. As the MWNT esters are the only conductive species in the composites, these results imply the presence of denser aggregated carbon nanotubes, possibly due to the settlement of MWNTs during film formation.[14a] The better solubility of MWNT ester **4** and ester **5** makes MWNTs disperse nearly uniformly throughout the whole polymer matrix (Chart 2a). However, the lower solubility of MWNT ester **1** and ester **2** reveals an indication of segregation of the MWNTs into a particular phase but lacking continuity though the matrix (Chart 2c). The moderate solubility of MWNT ester **3** results in the moderate distribution of MWNTs in the polymer matrix, as shown in Chart 2b. Thus, the dispersion of MWNTs in the polymer matrix is the reason for the different conductivity between the top and bottom faces as well as the nonohmic behaviors of the volume conductivity along the thickness direction.

Conclusion

In summary, we have synthesized a series of MWNT esters with various linear alkyl chains. The solubility of these

MWNT esters is increased along with the increase of the length of the alkyl chains. The SEM studies of MWNT ester/PSF composite films show that the longer alkyl chains give better dispersion of MWNTs in PSF matrix. Both the surface and volume conductivity study shows that better dispersion of MWNTs in polymer matrix results in better conductivity. The *n*-octyl-modified MWNT ester exhibits the percolative character. It is also found that the bottom surface electrical conductivity of the composite films is ohmic and the electrical conductivity along the thickness direction is nonohmic. This observation could provide the possibility of utilizing the unique microelectrical properties of carbon nanotubes on a macroscopic scale, such as electronic modulators.