

# Synthesis and Properties of a Water-Soluble Single-Walled Carbon Nanotube–Poly(*m*-aminobenzene sulfonic acid) Graft Copolymer\*\*

By Bin Zhao, Hui Hu, and Robert C. Haddon\*

Poly(*m*-aminobenzene sulfonic acid) (PABS), was covalently bonded to single-walled carbon nanotubes (SWNTs) to form a water-soluble nanotube–polymer compound (SWNT–PABS). The conductivity of the SWNT–PABS graft copolymer was about  $5.6 \times 10^{-3} \text{ S cm}^{-1}$ , which is much higher than that of neat PABS ( $5.4 \times 10^{-7} \text{ S cm}^{-1}$ ). The mid-IR spectrum confirmed the formation of an amide bond between the SWNTs and PABS. The  $^1\text{H}$  NMR spectrum of SWNT–PABS showed the absence of free PABS, while the UV/VIS/NIR spectrum of SWNT–PABS showed the presence of the interband transitions of the semiconducting SWNTs and an absorption at  $17\,750 \text{ cm}^{-1}$  due to the PABS addend.

## 1. Introduction

Carbon nanotubes possess outstanding materials properties,<sup>[1,2]</sup> but they are difficult to process and insoluble in most solvents. Recently polymers such as poly(vinyl pyrrolidone) (PVP), poly(styrene sulfonate) (PSS),<sup>[3]</sup> poly(phenylacetylene) (PPA),<sup>[4]</sup> poly(*meta*-phenylenevinylene) (PmPV),<sup>[5]</sup> polypyrrole (PPy),<sup>[6]</sup> poly(*p*-phenylene benzobisoxazole) (PBO),<sup>[7]</sup> and natural polymers<sup>[8]</sup> have been used to wrap carbon nanotubes and render them soluble in water or organic solvents. Most of these polymer-wrapping methods depend on the physical adsorption of polymers to the surface of the carbon nanotubes in order to promote the solubility of the nanotubes. Sun and co-workers reported the covalent functionalization of carbon nanotubes with poly(propionylethylenimine-*co*-ethylenimine) and poly[(vinyl acetate)-*co*-(vinyl alcohol)];<sup>[9]</sup> these polymer-bound carbon nanotubes were found to be soluble in water and chloroform. Functionalization of multi-walled carbon nanotubes (MWNTs) with a polystyrene copolymer has also been reported by the same group.<sup>[10]</sup>

Conducting polymers are of interest in fields such as energy storage, sensors, electronic devices, electromagnetic interference shielding, and the inhibition of corrosion. Among the conducting polymers, polyaniline (PANI) has drawn special attention due to its high stability toward air and moisture, high electrical conductivity, and unique redox properties. Recently PANI has been used to make composite materials with single-walled nanotubes (SWNTs).<sup>[11]</sup> It was found that thin films of such PANI–SWNT composite were printable via laser ablation with high resolution, while retaining appropriate conductivity

( $2 \text{ S cm}^{-1}$ ). Another PANI–MWNT composite has been produced that exhibits an order of magnitude increase in conductivity over neat PANI.<sup>[12]</sup> PANI derivatives (e.g., polyanisidine (POAS)) have been used to wrap MWNTs to form a POAS–MWNT nanocomposite,<sup>[13]</sup> and this material is soluble in organic solvents such as chloroform.

In order to broaden the application of SWNTs and PANI, it is necessary to tailor their solubility properties. Several substituted PANIs soluble in organic solvents have been prepared, such as alkyl-,<sup>[14]</sup> alkoxy-,<sup>[15–18]</sup> and alkyl-*N*-substituted<sup>[19]</sup> PANIs. The most important work in this direction is the synthesis of the sulfonated PANIs (SPAN).<sup>[20–24]</sup> SPANs are of interest because of their unique electroactive properties, self-doping, thermal stability, characteristic optical properties, and water-solubility. SPANs have potential applications in rechargeable batteries,<sup>[25,26]</sup> light-emitting diodes,<sup>[27]</sup> junction devices,<sup>[28]</sup> and in the electrochemical control of electrolyte acidity and enzyme activity.<sup>[29]</sup> However, because the sulfonic acid functionality is a strong electron-withdrawing group, the conductivity of SPAN ( $10^{-3}$  to  $10^{-7} \text{ S cm}^{-1}$ ) is much lower than that of PANI ( $10^{-1}$  to  $10 \text{ S cm}^{-1}$ ). In this paper, we report the covalent functionalization of SWNTs with a water-soluble conducting polymer, poly(*m*-aminobenzene sulfonic acid) (PABS). The functionalization is based on the acyl chloride-activated amidation of nanotube-bound carboxylic acids with the amine-rich PABS. The PABS-functionalized SWNTs (SWNT–PABS graft copolymer) are soluble in water and some organic solvents and have a much higher conductivity than neat PABS.

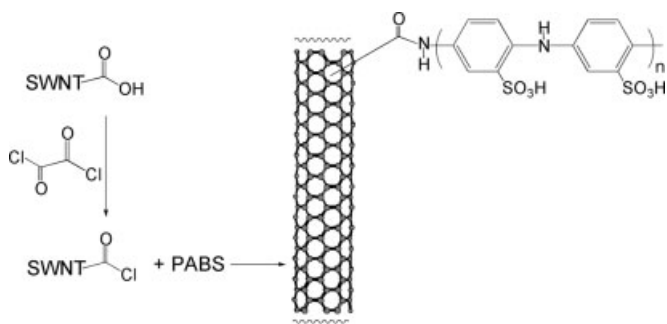
## 2. Results and Discussion

The methodology for chemical functionalization of the open ends of the carbon nanotubes has been mostly based on esterification or amidation of carboxylic acid groups that are introduced during acid treatment. There are two methods that have been used to convert carboxylic acid groups into amides. In the first method, the carboxylic acid was converted into an acyl chloride intermediate by treatment with thionyl chloride and subsequent reaction with an amine to give an amide.<sup>[30–35]</sup> The

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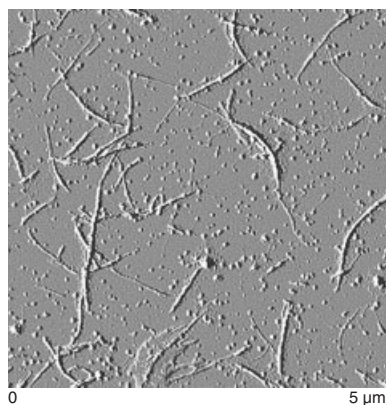
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second method can be regarded as a one-step reaction in which carboxylic acid functionalities of the carbon nanotubes reacted directly with amine in the presence of coupling reagents such as carbodiimide.<sup>[36–40]</sup> The method that we used to produce the SWNT–PABS graft copolymer is based on the first method, but makes use of oxalyl chloride instead of thionyl chloride (Scheme 1). Oxalyl chloride is a common reagent for the conversion of a carboxylic acid group into an acyl chloride at low or ambient temperature. The boiling point of oxalyl chloride is



**Scheme 1.** Reaction of SWNTs with PABS.

low (63 °C), so that after reaction the excess oxalyl chloride is easily removed. The SWNT–PABS is quite soluble in water and gives a black solution, whereas the color of PABS solution is dark purple. Dilute solutions of SWNT–PABS are gray-black, whereas neat PABS solution is purple. Figure 1 shows the atomic force microscopy (AFM) image of a sample of SWNT–PABS prepared from aqueous solution after 30 min of



**Figure 1.** AFM image of SWNT–PABS (from aqueous solution).

sonication. SWNT–PABS is partially soluble in organic solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), and aniline. The conductivity of SWNT–PABS was found to be about  $5.6 \times 10^{-3} \text{ S cm}^{-1}$ , which is much higher than that of neat PABS ( $5.4 \times 10^{-7} \text{ S cm}^{-1}$ ).<sup>[23,24]</sup>

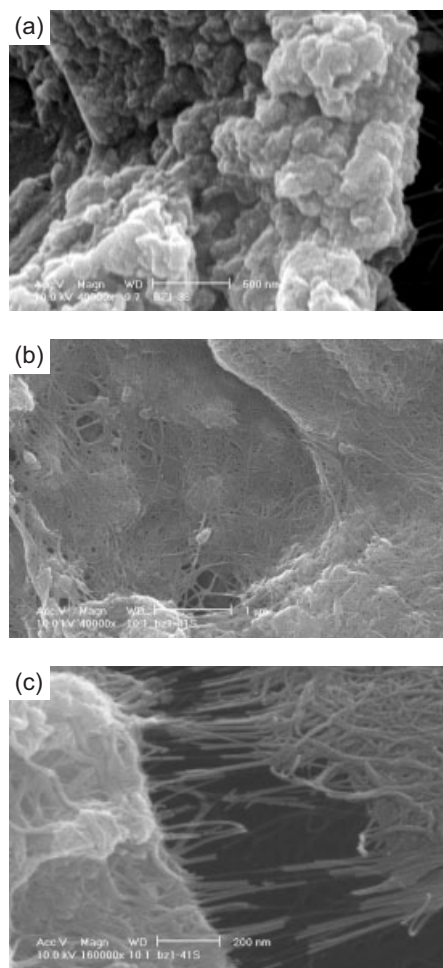
Energy-dispersive X-ray spectroscopic (EDS) studies of the SWNT–PABS graft copolymer showed atomic percentages of: C 63 %, N 7 %, O 21 %, S 7 %, Cl 2 %. The atomic percentages of C, N, O, and S are in the ratio of 9:1:3:1, and apart from carbon are consistent with the monomer formula of PABS ( $\text{C}_6\text{H}_5\text{NO}_3\text{S}$ ). It is therefore apparent that the EDS spectrum is

sensitive to both the PABS and the SWNT carbon atoms in the SWNT–PABS graft copolymer. Based on the monomer formula of PABS, about 42 at.-% of the carbon in the SWNT–PABS graft copolymer is present in PABS ( $C_{\text{PABS}}$ ), and the remaining 21 at.-% of carbon originates from the SWNTs ( $C_{\text{SWNT}}$ ). Thus the weight percentage of SWNTs in the SWNT–PABS graft copolymer ( $W_{\text{SWNT}}\%$ ) is obtained from

$$W_{\text{SWNT}}\% = [12 \times C_{\text{SWNT}}\%] / (12 \times C\% + 14 \times N\% + 16 \times O\% + 32 \times S\% + 35.5 \times Cl\%) = 17\% \quad (1)$$

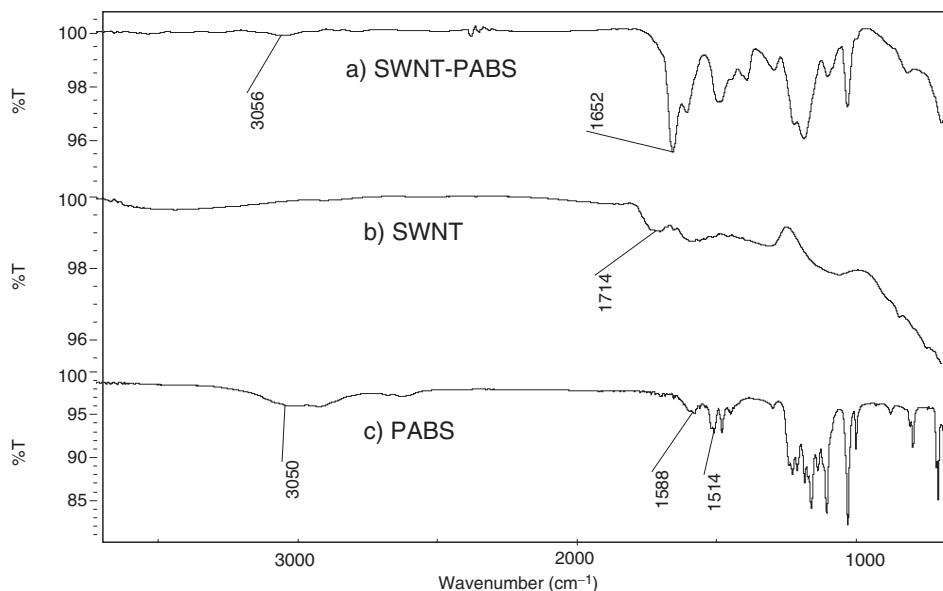
(the hydrogen makes a negligible contribution to the weight).

Scanning electron microscopy (SEM) images of SWNT–PABS (Figs. 2b,c) show that the SWNT–PABS graft copolymer contains a large amount of SWNTs in a homogeneous form and indicate that PABS has not aggregated into the morphology that is observed in neat PABS (Fig. 2a).



**Figure 2.** SEM images: a) PABS; b) low-magnification image of SWNT–PABS; c) high-magnification image of SWNT–PABS.

Mid-IR spectra (Nicolet Magna-IR 560 E.S.P. spectrometer, attenuated total reflection (ATR) method) of PABS, SWNTs, and SWNT–PABS are shown in Figure 3. The spectrum of the shortened SWNT starting material shows an absorbance at  $1714 \text{ cm}^{-1}$ , which is due to the carbonyl stretch of the car-

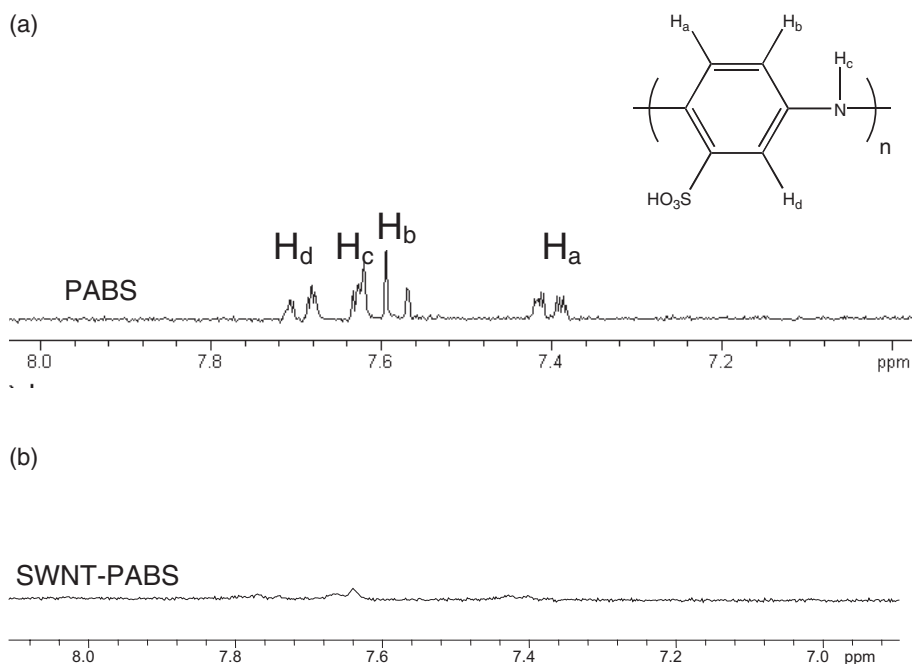


**Figure 3.** Mid-IR spectra (Nicolet Magna-IR 560 E.S.P. spectrometer, ATR method): a) SWNT–PABS; b) SWNTs; c) PABS.

boxylic acid group. The spectrum of SWNT–PABS is quite different. The strong absorbance at  $1652\text{ cm}^{-1}$  is due to the carbonyl stretch of the amide, which has been observed in other amide functionalized SWNTs.<sup>[31,32]</sup> The aromatic C–H stretch at  $3056\text{ cm}^{-1}$  can also be seen, together with signals at  $1580\text{--}1600\text{ cm}^{-1}$  (benzenoid ring stretch),  $1485\text{--}1500\text{ cm}^{-1}$  (quinonoid ring stretch),  $1100\text{--}1150\text{ cm}^{-1}$  (S=O stretch),  $1300\text{--}1345\text{ cm}^{-1}$  (O=S=O or C–N stretch), and  $693$  and  $616\text{ cm}^{-1}$  (S–O and S–C stretch), which are consistent with the presence of PABS. These results support the hypothesis that PABS is covalently bonded to the SWNTs via the formation of an amide bond.

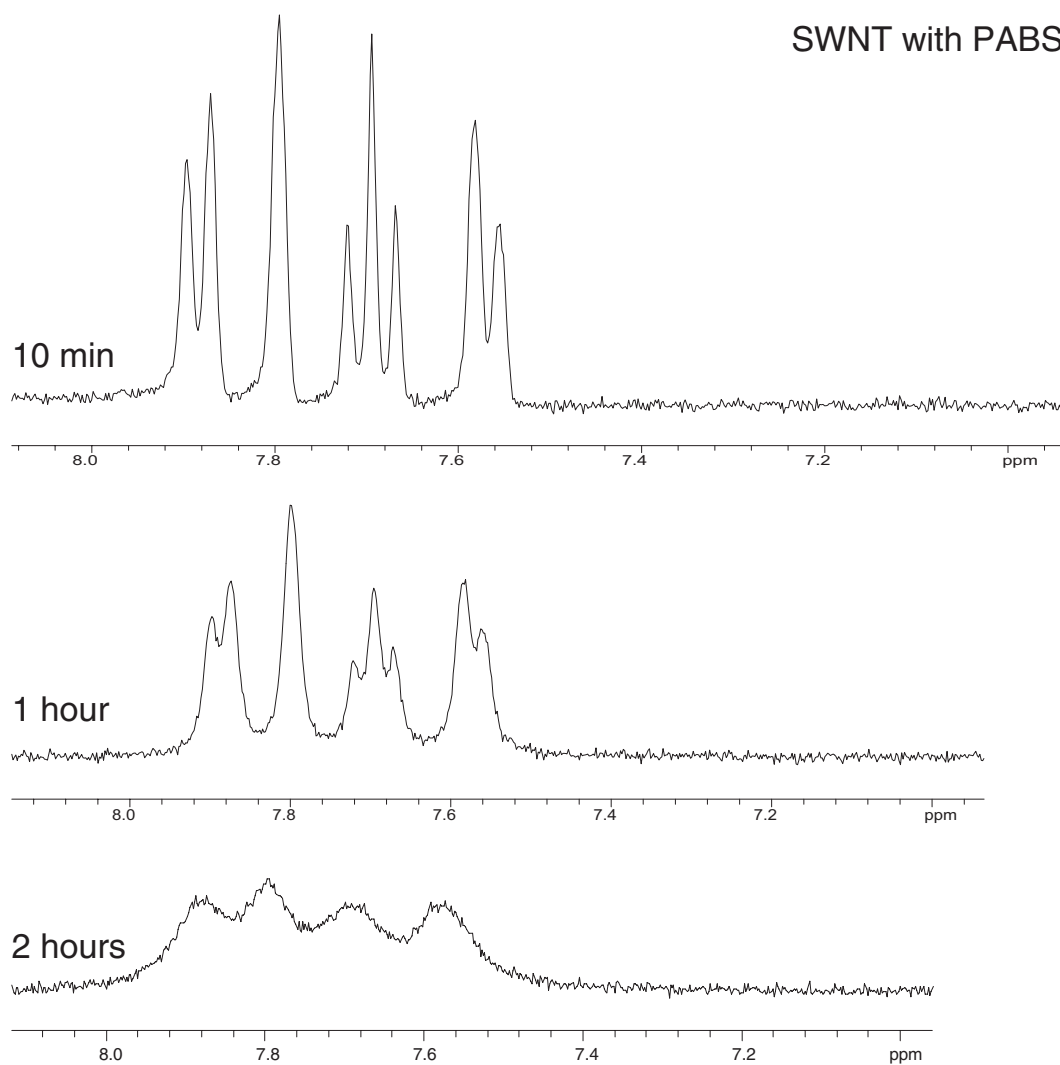
Proton NMR spectra (300 MHz,  $\text{D}_2\text{O}$ ,  $0.01\text{ mg mL}^{-1}$ ) of PABS and SWNT–PABS are shown in Figure 4. The spectrum

of PABS shows signals at  $7.4\text{--}7.8\text{ ppm}$ , which are due to the protons on the aromatic ring of PABS. On the other hand, the proton signals of SWNT–PABS graft copolymer are quite weak. This weakness in the proton signal suggests that there is no free PABS in the SWNT–PABS sample. In order to further investigate the nature of the interaction between PABS and the SWNTs, the SWNTs starting material was sonicated with PABS (weight ratio of 1:2 SWNT/PABS) for periods of 10 min, 1 h, and 2 h in  $\text{D}_2\text{O}$ , and the resulting suspension immediately examined by  $^1\text{H}$  NMR (Fig. 5). All of the samples show proton signals in the range  $7.4\text{--}7.8\text{ ppm}$ . It is interesting to find that proton signals broaden with increasing sonication time. It has been reported that the broadened  $^1\text{H}$  NMR signal of the polymer-



**Figure 4.**  $^1\text{H}$  NMR spectra (300MHz,  $\text{D}_2\text{O}$ ): a) PABS; b) SWNT–PABS.

## SWNT with PABS



**Figure 5.** <sup>1</sup>H NMR spectra (300MHz, D<sub>2</sub>O) of SWNT with PABS sonicated for: 10 min (top), 1 h (middle), and 2 h (bottom).

wrapped carbon nanotubes may be attributed to inhomogeneities in the local magnetic field.<sup>[3]</sup> Unlike in the spectrum of the SWNT–PABS sample, after sonication of the SWNT and PABS mixture the fine structure in the spectrum can still be discerned. However the protons in the SWNT–PABS graft copolymer, in which the PABS is covalently attached to the SWNTs, are much more strongly affected by the SWNTs, and it is the covalent attachment that is apparently responsible for the drastic change in the <sup>1</sup>H NMR spectrum of the PABS moiety.

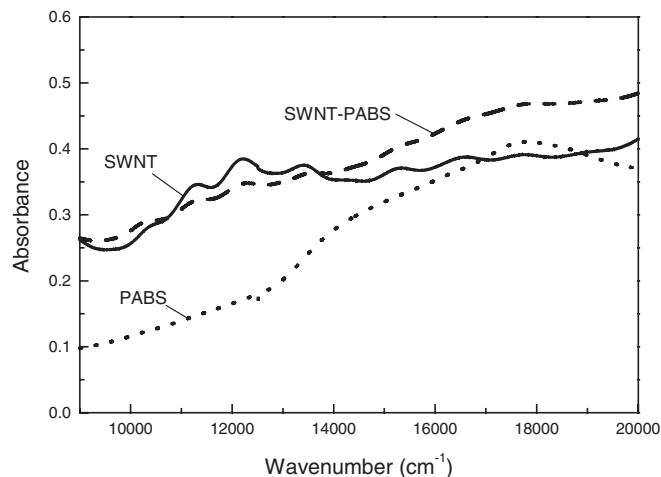
It is of interest to investigate the electronic properties of SWNT–PABS and Figure 6 shows the UV-vis-NIR absorption spectra (Cary 500 scan UV-vis-NIR spectrophotometer) of PABS, SWNT, and SWNT–PABS in DMF solution. The absorbance centered at 17 750 cm<sup>-1</sup> in the spectrum of PABS has been assigned to the n–π\* band transition.<sup>[24]</sup> The UV-vis spectrum of the SWNT–PABS graft copolymer shows bands characteristic of transitions between the second pair of singularities in the density of states (DOS) of the semiconducting SWNTs (S<sub>22</sub>, from 10 000 to 14 000 cm<sup>-1</sup>), although somewhat de-

creased in intensity. As expected from the NIR spectra of the individual components, the spectrum of SWNT–PABS is clearly a composite of both spectra.

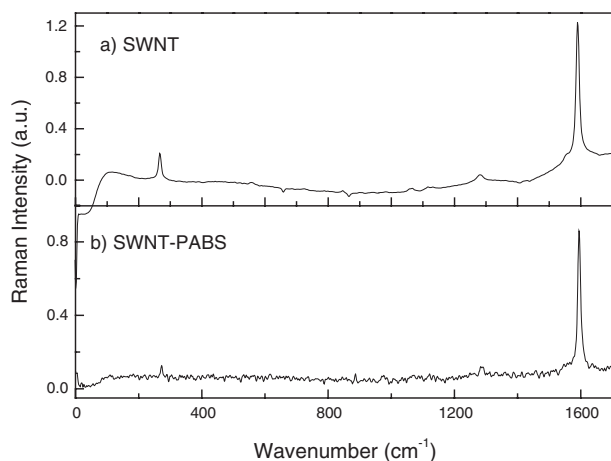
The Raman spectrum (Fig. 7) of SWNT–PABS shows two bands: the radial mode ( $\omega_r = 269 \text{ cm}^{-1}$ ) and the tangential mode ( $\omega_t = 1590 \text{ cm}^{-1}$ ). These characteristic peaks are same as in the pristine HiPco SWNTs, which indicates that the electronic structure of the SWNTs are not greatly perturbed on incorporation of PABS.

### 3. Conclusion

We report the synthesis of a SWNT–PABS graft copolymer. Based on IR spectroscopy we conclude that the PABS is covalently bonded to the SWNTs via an amide functionality. UV-vis spectroscopy further supports the covalent binding in the SWNT–PABS graft copolymer and <sup>1</sup>H NMR showed that there is no free PABS in this material. The SWNT–PABS graft co-



**Figure 6.** UV-vis spectra (Cary 500 scan UV-vis-NIR spectrophotometer) taken in DMF: SWNT (solid line); SWNT–PABS (dashed line); PABS (dotted line).



**Figure 7.** Raman spectra (Bruker RFS 100/s): a) SWNT; b) SWNT–PABS.

polymer is quite soluble in water and exhibits an order of magnitude increase in electrical conductivity over neat PABS.

#### 4. Experimental

**PABS:** PABS was prepared according to literature methods [23]. *m*-Aminobenzene sulfonic acid (ABS, 0.865 g) and aniline (15–20 mol% of ABS) were mixed in 1 M HCl with ammonium persulfate as the oxidation reagent. Aniline was used as the initiator for the ABS polymerization. The mixture was stirred at 0 °C for 6 h and then the solution was concentrated at room temperature, filtered, and the solid was washed with acetone. The solid that collected on the filter paper was redissolved in water and then reprecipitated by slow addition of the aqueous solution to a large excess of acetone. The black precipitate was collected by filtration and dried at room temperature (340 mg). The yield of final product was 40 %. The UV spectrum of PABS in 1 N NaOH showed absorptions at 290 nm and 510 nm, in agreement with the literature data [23].

**SWNTs:** HiPco SWNTs (Carbon Nanotechnologies Inc., 0.2 g) were sonicated in 80 mL of mixed acid (3:1 concentrated H<sub>2</sub>SO<sub>4</sub>/concentrated HNO<sub>3</sub>) for 4 h. The mixture was diluted with deionized (DI) water and filtered through 0.2 μm pore-size membrane. The solid was dried at room temperature and sonicated in a solution of 4:1 sulfuric

acid/hydrogen peroxide for 15 min. After dilution with DI water, the mixture was filtered and dried under vacuum at room temperature. The yield of final product was 79 %. Based on AFM analysis of the product, nearly 85 % of the SWNTs have a length of less than 600 nm.

**SWNT–PABS Copolymer:** The shortened SWNTs (12 mg) were sonicated in 20 mL of DMF for 30 min to give a homogeneous suspension. Oxalyl chloride (0.4 mL) was added drop-wise to the SWNT suspension at 0 °C under N<sub>2</sub>. The mixture was stirred at 0 °C for 2 h and then at room temperature for another 2 h. Finally the temperature was raised to 70 °C and the mixture was stirred overnight to remove excess oxalyl chloride. 120 mg of PABS dissolved in DMF was added to the SWNT suspension and the mixture was stirred at 100 °C for 5 days. After cooling to room temperature, the mixture was filtered through a 0.2 μm pore-size membrane and washed thoroughly with DMF and ethyl alcohol. The black solid (57 mg) was collected on the membrane and dried under vacuum overnight.

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