

Probing the Cooperative Nature of the Conductive Components in Polystyrene/Poly(3,4-ethylenedioxythiophene):Poly(styrene sulfonate)–Single-Walled Carbon Nanotube Composites

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ABSTRACT The percolation threshold of single-walled carbon nanotubes (SWCNTs) introduced into polystyrene (PS) *via* a latex-based route has been reduced by using conductive surfactants. The use of the conductive polymeric latex, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), in conjunction with SWCNTs leads to conductive composites with loadings of both constituents below their own individual percolation thresholds. The high concentration of PEDOT:PSS in the final composites raises the concern that the composite conductivity is a result of the presence of the PEDOT:PSS alone. To elucidate the cooperative nature of the two conductive components, the contribution of the SWCNTs to the overall composite conductivity is investigated by replacing the original high-quality SWCNTs with SWCNTs of a lower quality. Percolation thresholds recorded for systems utilizing the lower quality tubes stabilized with nonconductive surfactants were over 2 wt % SWCNTs (4 times that of previously reported systems). The introduction of PEDOT:PSS was, once again, found to lower the percolation threshold (to 0.3 wt %) and to increase the ultimate conductivity up to the level of a pure PEDOT:PSS/PS blend. In the PS/PEDOT:PSS–SWCNT systems, the role of the SWCNT network is proposed to be limited to the formation of a template or scaffold on which a (more or less) continuous PEDOT:PSS layer deposits. The ultimate conductivity is therefore determined by the PEDOT:PSS alone.

KEYWORDS: nanocomposite · carbon nanotubes · conductive polymers · percolation

The use of carbon nanotubes (CNTs) in the production of CNT–polymer nanocomposites can yield materials with varying conductivities that exhibit vastly different percolation thresholds.¹ CNTs are near perfect electron conductors, and for this reason, one might imagine that the maximum achievable conductivities for CNT–polymer composites would not vary much when similar tubes are used. When conductivities are measured for CNT–polymer composites, and even for CNT mats (often called buckypapers), they are always orders of magnitude lower than the conductivity measured for an individual CNT. This is solely due to imperfect contacts present between adjacent CNTs. These give rise to *constriction resistance* and *tun-*

neling resistance.² For the case of polymer-based CNT composites, an additional resistance can arise from interfacial polymer layers present within the CNT junctions. Systems that are prepared from aqueous dispersions of CNTs also have an additional component, the surfactant. If the surfactant is not displaced from the CNT walls after the final processing steps, an insulating shell remains around every CNT that could be detrimental for the intertube charge transport in the final product.³ Theoretically, it was shown that the presence of a conductive polymer within the intertube junctions may significantly lower the contact-potential barrier.⁴ This in turn will increase the ultimate conductivity of the final CNT composite.

The ability of such “conduction bridges” formed by a conductive polymer between adjacent tubes has also been shown to alter the observed percolation threshold.^{5–7} In these works, different relationships between the composite morphology and the determined percolation thresholds (and ultimate conductivities) were observed. Composites prepared with DNA-wrapped, single-walled carbon nanotubes (SWCNTs) embedded in poly(aniline) (PA) show a distinct morphology-dependent percolation threshold and network structure.⁵ When DNA-stabilized SWCNTs were simply blended with the conductive polymer, high threshold values were observed. For systems in which the PA is grown on the surface of the SWCNT, low thresholds and high ultimate conductivities were observed. A similar investigation revealed that the pres-

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ence of the PA directly on the SWCNT surface is not a prerequisite for high conductivities.⁷ This is similar to what has been observed for composites prepared with SWCNTs and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS).⁶ In the reported works to date, the cooperative role of the CNTs and the conductive polymers with respect to the composite's final conductivity is not often addressed. The ability of conductive polymers to exhibit pseudo-percolation thresholds when blended into insulating polymers is well-documented.⁸ Values below 1 wt % of conductive polymer can yield highly conductive materials.^{9,10} The contribution of the CNTs to the final composite conductivity is often debatable, especially when the conductivity of the composite is similar to that of a blend of the used conductive and insulating polymers. The ultimate means to investigate the contribution of the CNTs in CNT-based composites containing a conductive polymer component would be to replace the CNTs with a nonconductive filler with a similar aspect ratio. Fillers such as boehmite fibers¹¹ and silica whiskers¹² come close to CNT dimensions, but they have vastly different surface chemistry, which is highly likely to induce altered morphologies. A second option is to use an alternative source of CNTs with similar aspect ratios, but simultaneously exhibiting poorer conductivities, due either to an increased number of defects or to a larger fraction of semiconducting tubes.

In this work, two types of SWCNTs, namely, HiPCO SWCNTs and Carbolex SWCNTs, were evaluated in a SWCNT-PS/PEDOT:PSS system. First, the quality of the two SWCNT types was investigated using thermogravimetric analysis (TGA). Second, the dispersion of Carbolex SWCNTs in an aqueous solution of PEDOT:PSS was evaluated using ultraviolet visible light (UV-vis) spectroscopy.¹³ This was compared to dispersions prepared with sodium dodecyl sulfate (SDS), as well as to previously reported dispersions using HiPCO SWCNTs.⁶ These dispersions were further characterized by transmission electron microscopy (TEM), Raman spectroscopy, and UV-vis-near-infrared (NIR) spectroscopy. Buckypapers were prepared using both SDS-stabilized HiPCO and Carbolex dispersions. Conductivities of these papers were measured to determine the intrinsic conductivities of both SWCNT types. Polystyrene (PS)-SWCNT composites were prepared *via* a latex-based route, using Carbolex SWCNTs dispersed with either SDS or PEDOT:PSS. The percolation threshold for both Carbolex systems was determined and compared to those previously recorded for HiPCO-based PS-SWCNT nanocomposites. The cooperative nature of the conductive components in the SWCNT-PS/PEDOT:PSS systems was evaluated. We, perhaps somewhat surprisingly, find that in the composite with PEDOT:PSS the SWCNTs do not predominantly contribute to the conductivity and plausibly act as a scaffold

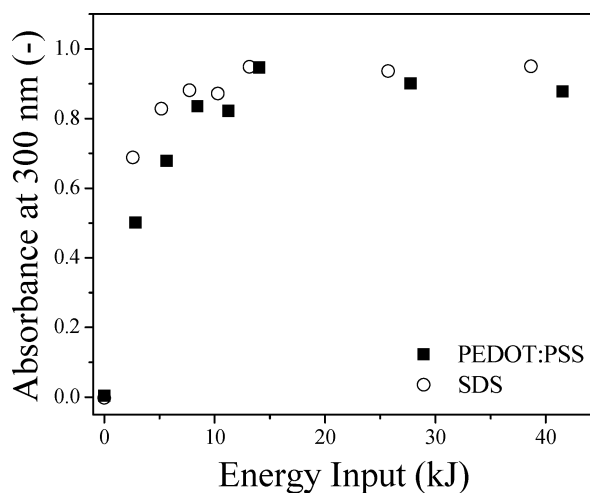


Figure 1. UV-vis exfoliation profiles for two 0.1 wt % Carbolex SWCNT exfoliations performed with SDS and PEDOT:PSS as surfactants. Samples were diluted 150 times, and blanks were made accordingly.

that facilitates the formation of an electrically percolating network of the PEDOT:PSS.

RESULTS AND DISCUSSION

SWCNT Exfoliations Using SDS and PEDOT:PSS. It has been shown, using UV-vis spectroscopy, that PEDOT:PSS can efficiently stabilize individual HiPCO SWCNTs in water.⁶ Applying the Lambert-Beer law and realizing that only individual CNTs show absorbance in the UV-vis range,¹⁴ we linked the final absorbance level in the exfoliation profile to the degree of CNT individualization (by ultrasonication) if the extinction coefficient (ϵ) is known for that specific solvent-CNT system. Due to the fact that extinction coefficients for Carbolex SWCNTs dispersed in an aqueous environment are unavailable, a quantitative comparison between the degrees of exfoliation for the Carbolex and HiPCO SWCNT dispersions is avoided. The exfoliation profile for the dispersion of Carbolex SWCNTs in water using either SDS or PEDOT:PSS as surfactants is given in Figure 1. The profile shows that the dispersion of Carbolex SWCNTs as a function of the ultrasonication energy input proceeds at a similar rate when using PEDOT:PSS and SDS. The final absorbance level reached, after correcting for the absorbance of the PEDOT:PSS surfactant at 300 nm, is comparable for both systems. The profiles given in Figure 1 differ in two ways from those previously reported for HiPCO SWCNTs: (1) the comparable final absorbance levels when comparing SDS- to PEDOT:PSS-stabilized SWCNT dispersions, and (2) a lower energy input requirement for maximal exfoliation (1 kJ *versus* 100 kJ). A lower energy input requirement for exfoliation could be due to a less entangled nature of the original SWCNTs and/or a higher degree of surface functionalization or increased number of surface defects. Functionalized tubes, or those with higher numbers of surface defects, usually require much

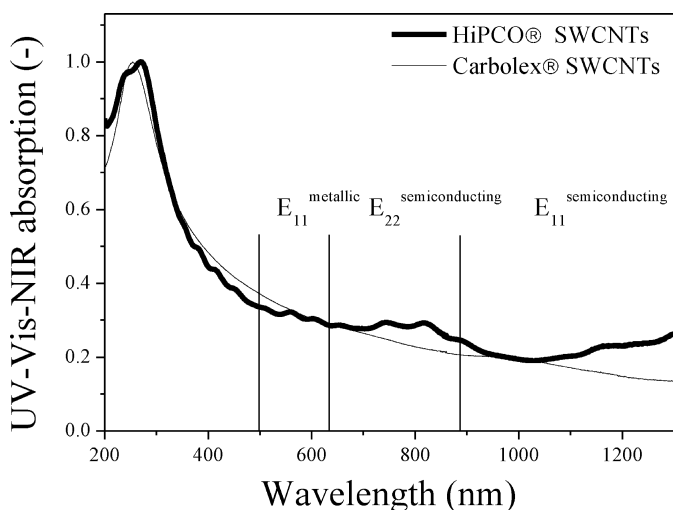


Figure 2. UV-vis-NIR absorbance spectra for Carbolex SWCNTs (thin line) and HiPCO SWCNTs (thick line) dispersed in water using SDS. Wavelength regions associated with specific permitted electronic transitions for metallic and semiconducting tubes are shown.

shorter ultrasonication times for achieving maximal individualization. The observed difference in the final absorbance level between the two surfactant systems for HiPCO SWCNTs was originally speculated to be due to the change in the extinction coefficient of the SWCNTs when the PEDOT:PSS is present.⁶ This implies that some interaction between the electronic states of the tubes and conductive surfactant is taking place. The absence of such a difference in the final absorbance level in the case of the Carbolex SWCNTs could indicate that the maximum level of individualization is lower for Carbolex SWCNTs when using PEDOT:PSS. This is unlikely in view of the high efficiency of our dispersion method and in view of the ease with which the Carbolex SWCNTs individualize. Alternatively, it could indicate that the presence of the PEDOT:PSS does not alter the extinction coefficient of the Carbolex SWCNTs. It is difficult to ascertain exactly which explanation is valid. Due to the fact that we ultimately would like to achieve a maximum individualization for both surfactant systems, we have not focused on the origin of this difference in exfoliation profile for the two SWCNT types.

Regions in the absorption spectrum that are linked to certain electronic transitions, common for metallic and semiconducting SWCNTs, are indicated in Figure 2. These UV-vis-NIR absorption spectra were taken of the final SWCNT dispersions prepared with SDS and both SWCNT types.

To study the quality of SWCNT dispersions, a π -plasmon background correction is often first performed on the original absorption spectra. Subsequently, the integrated area under the $E_{22}^{\text{semiconducting}}$ and E_{11}^{metallic} absorption bands is compared and analyzed.¹⁵ In the case of the Carbolex SWCNTs, such a background correction will result in a very small area in these regions. The featureless spectrum seen for the Carbolex SWCNTs is similar to that often seen for func-

tionized SWCNTs.¹⁶ This implies that the SWCNT surface chemistry could differ between the two CNT types, and the measurements point to a much higher surface quality of the HiPCO SWCNTs.

SWCNT Analysis. The quality and purity of the SWCNTs were further investigated using TGA, UV-vis-NIR spectroscopy, Raman spectroscopy, and by measuring intrinsic conductivities of buckypapers prepared from both SWCNT types. TGA mass loss curves for the HiPCO and Carbolex SWCNTs are given, along with the absolute value of their derivatives, in the Supporting Information. From the mass loss curves, it is found that the metallic impurity content for the Carbolex SWCNTs is significantly higher than that for the HiPCO SWCNTs. In the preparation of the PS-SWCNT composite films, no centrifugation is performed on the SWCNT dispersions. This fact, along with the results from the TGA, implies that the actual loading of SWCNTs will be lower than the weighed-in value. The amount of nongraphitic carbonaceous species appears to be less for the Carbolex SWCNTs. The temperature of the degradation of the CNTs is often taken as an indication for their degree of graphitization (surface perfection).¹⁷ From the derivatives of the mass loss curves, it appears that this temperature is not very different for the two SWCNT types studied here.

A typical Raman spectrum of a CNT mat or dispersion shows a few characteristic bands. These include the “graphene-like” or G-band observed between 1500 and 1600 cm^{-1} , the “disorder-induced” or D-band observed at 1300 cm^{-1} , and the radial breathing mode (RBM) observed between 100 and 500 cm^{-1} . A comparison between the G- and D-bands from two samples has been reported to indicate their relative degree of graphitization (SWCNT quality).¹⁸ Raman spectra recorded for SDS-stabilized dispersions of HiPCO and Carbolex SWCNTs are given in the Supporting Information. It appears that the D-band is broader for the Carbolex SWCNTs, but due to the poor baseline, it is not possible to make a definitive estimation of the relative SWCNT qualities. Qualitatively, it could be said that the D/G area ratio is slightly higher for the Carbolex tubes, indicating a lower degree of graphitization, which is expected to be reflected in a lower intrinsic conductivity (see further).

To further probe the SWCNTs' quality, their intrinsic conductivities were measured by preparing buckypapers from the respective dispersions. Conductivities of buckypapers prepared from HiPCO and Carbolex SWCNTs were approximately 1×10^5 and 1×10^3 $\text{S} \cdot \text{m}^{-1}$, respectively. The significant difference in intrinsic conductivities indicates that there is a difference in the electronic properties of the SWCNTs, which might also result in a different interaction with the conductive surfactant (as seen from the exfoliation profiles). The significantly lower intrinsic conductivity of the Carbolex SWCNTs could be attributed to more wall defects or

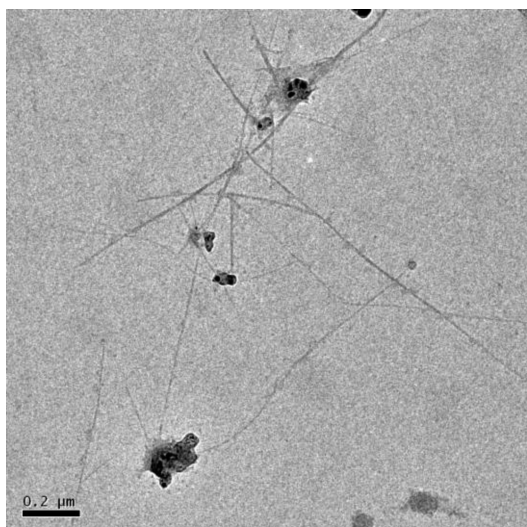


Figure 3. TEM micrograph of Carbolex SWCNT dispersions prepared with SDS.

a carbonaceous coating on the SWCNT wall. To determine the main cause of these lower conductivities would require further investigation, which is beyond the scope of this study. For the application intended here, this difference is very important, and on the basis of this difference in conductivity, we conclude that the quality of the HiPCO tubes is superior to that of the Carbolex tubes.

One further prerequisite for a valid comparison of nanocomposites based on HiPCO and Carbolex SWCNTs is that the aspect ratio of the two SWCNT types is not vastly different. The average SWCNT length for the Carbolex SWCNTs was examined using TEM. A TEM micrograph of SDS-stabilized Carbolex SWCNTs is shown in Figure 3. When comparing the SWCNTs presented in the TEM micrograph in Figure 3 to that previously reported for HiPCO SWCNTs (length between 0.5 and 1 μm , and diameter of approximately 1 nm),⁶ little difference between the lengths can be seen. On average, the Carbolex SWCNT length ranges between 0.5 and 1 μm , whereas the diameter is also around 1 nm. In Figure 3, the metallic catalyst residues are easily seen. On the basis of the similar CNT dimensions, it can be speculated that the percolation network morphology should not greatly differ between the two SWCNT types due to similar aspect ratios. Moreover, possible differences in the electrical properties of HiPCO- and Carbolex-based composites are most probably due to the intrinsic quality differences.

SWCNT—Polymer Composites: Conductivity and Morphology. Composites prepared with SDS-stabilized Carbolex SWCNTs have a percolation threshold value of 2.2 wt %, as can be seen in Figure 4.

For the SDS-based nanocomposites, the ultimate conductivity achieved above percolation is 0.1 S/m. Composites prepared with PEDOT:PSS-stabilized Carbolex SWCNTs show a much lower percolation threshold (0.32 wt %) when compared to those stabilized with

SDS (2.2 wt %) and show an ultimate conductivity value of 100 S/m. These percolation threshold values are different from those previously reported for similar systems (utilizing the same PS latex and conductive polymer) prepared with HiPCO SWCNTs.⁶ These results, along with those previously reported, are summarized in Table 1.

It appears that using the SDS-stabilized Carbolex SWCNTs leads to more than a quadrupling of the measured percolation threshold when compared to the SDS-stabilized HiPCO SWCNTs. This high threshold recorded for these tubes in combination with SDS could partly be due to the high concentration (approximately 40 wt %) of metallic impurities in the Carbolex SWCNTs (see TGA mass loss curves in Supporting Information), which implies a 40% overestimation of the Carbolex loading. If it is assumed that the percolation threshold for the Carbolex systems will always be roughly twice that of the HiPCO systems, due to the metallic impurities (which are considered to be nonconductive due to the extreme conditions they have been exposed to during processing), after taking into account the “corrected” SWCNT concentrations, the percolation threshold of the SDS-stabilized Carbolex SWCNT-based composites is still much higher than that of the corresponding HiPCO SWCNT-based composites. This implies that there are factors over and above composition differences causing a higher percolation threshold for SDS-stabilized Carbolex SWCNT-based composites. The way in which the SWCNTs appear to be “attached” to the metallic residues, as seen in the TEM micrograph in Figure 3, could also lead to different network structures.

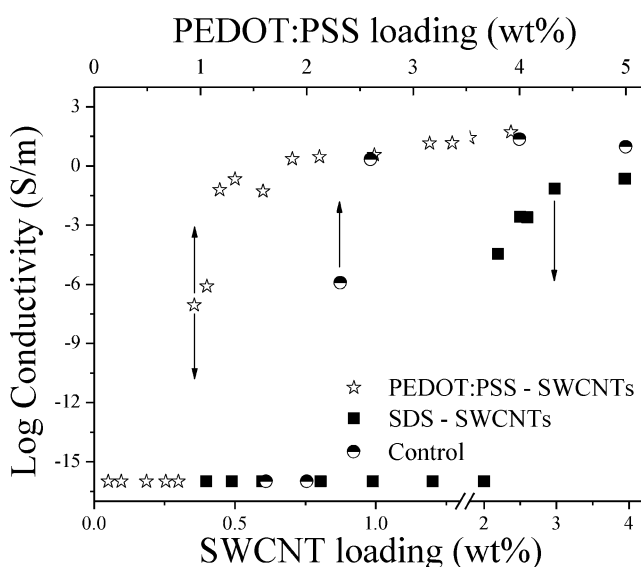


Figure 4. Percolation thresholds for composites prepared with SDS-stabilized Carbolex SWCNTs (squares) and PEDOT:PSS-stabilized Carbolex SWCNTs (stars) and the pseudo-percolation threshold of PS/PEDOT:PSS blends (circles). Arrows indicate applicable axes. For all nanocomposites, the same PS latex was applied.

TABLE 1. Percolation Thresholds and Ultimate Conductivities Achieved for Carbolex- and HiPCO-Based SWCNT–PS/PEDOT:PSS Composites, As Well As the Pseudo-percolation Threshold of a PS/PEDOT:PSS Blend

SWCNT type	surfactant	percolation threshold (wt %)	ultimate conductivity (S/m)
Carbolex	SDS	2.2	0.1
	PEDOT:PSS	0.32	100
HiPCO ⁶	SDS	0.38	20
	PEDOT:PSS	0.18	500
–	PS/PEDOT:PSS	2.4	100

A higher concentration of semiconducting tubes can cause a raise in the percolation threshold. The lack of distinct electronic transitions associated with semiconducting SWCNTs in the UV–vis–NIR spectra of Carbolex SWCNTs cannot substantiate this hypothesis. A photoluminescence map of the two SWCNT types would be required to exactly determine the relative fractions of semiconducting and metallic SWCNTs. The observed differences in absorption spectra (see Figure 2) indicate that the Carbolex surface is of a poor quality. Adjacent SWCNTs may struggle to become electronically connected due to the presence of these functionalities, causing a higher percolation threshold.

The ultimate conductivity of the SDS-stabilized Carbolex SWCNT–PS nanocomposites is 2 orders of magnitude lower than that observed for the respective HiPCO SWCNT–PS nanocomposites (0.1 *versus* 20 S/m). This once again indicates a difference in intrinsic tube conductivities, as shown for the different buckypapers.

The most important observation that is made from Figure 4 and Table 1 is the presence of a percolation threshold for the PEDOT:PSS-stabilized Carbolex SWCNTs, which is lower than that of the corresponding SDS system. Furthermore, comparing the PEDOT:PSS/PS–SWCNT systems for both types of SWCNTs, a difference in percolation threshold is observed. Remembering the large difference in percolation threshold between the SDS systems for both SWCNT types, if the conductivity of the conductive “network” is a summation of contributions from the conductive polymer and conductive filler, one would imagine that the percolation threshold in the PEDOT:PSS–Carbolex system reported here would differ greatly from the PEDOT:PSS–HiPCO system. The observed difference in the percolation threshold, *viz.* 0.32 wt % for Carbolex systems and 0.18 wt % for HiPCO systems, is roughly 40% and can be explained by the difference in metallic impurity content for the two SWCNT types. The lack of a significant (over the observed 40%) difference in percolation threshold, as seen for the composites prepared with SDS as surfactant, implies that the electronic contribution of the SWCNTs is negligible in both systems involving PEDOT:PSS-stabilized SWCNTs. The structural role of the SWCNTs does, however, appear to be paramount.

The ultimate conductivity of the PEDOT:PSS/PS–SWCNT composites is similar to that of the control blends (PEDOT:PSS/PS), which is a first indication that this maximum conductivity is mainly determined by the conductive polymer, and that the contribution of the CNT network to the conductivity is only minor in our systems. It is important to note that the ultimate conductivity of HiPCO SWCNT–PS/PEDOT:PSS composites is on the same order of magnitude as the corresponding conductivity of Carbolex SWCNT–PS/PEDOT:PSS composites (100 *versus* 500 S/m). However, the difference between HiPCO SWCNT–PS/SDS and Carbolex SWCNT–PS/SDS composites is approximately 2 orders of magnitude (roughly the difference between intrinsic conductivity of the tubes, namely, 10^3 *versus* 10^5 S/m). The slight difference in ultimate conductivity between the PEDOT:PSS-stabilized SWCNT dispersions prepared from the two SWCNTs could be linked to a change in doping of the PEDOT by the SWCNT. For the lower quality sample of SWCNTs, the lower intrinsic conductivity could dope the conductive polymer to a lesser degree, causing a lower conductivity value.

In summary, we can say that the combination of poor-quality SWCNTs and a conductive “surfactant”, PEDOT:PSS, results in a conductive network with a low SWCNT percolation threshold and a maximum conductivity similar to that of a blend of the matrix and PEDOT:PSS. Replacing the lower quality SWCNTs with a higher quality grade exhibiting a 100-fold increase in intrinsic conductivity neither reduces the percolation threshold nor significantly enhances the maximum conductivity. Therefore, we postulate that the contribution to the conductive “network” in the PEDOT:PSS/PS–SWCNT system by the SWCNTs is minimal. The conductive surfactant overrules the effect of the SWCNT network, which merely facilitates the formation of a “percolating” conductive phase.

CONCLUSION

An investigation into the cooperative nature of the two conductive components in a SWCNT–PS/PEDOT:PSS composite was performed. Particularly, the contribution of the SWCNTs to the overall composite conductivity was the focus. A control system described in literature using high-quality SWCNTs was compared to systems using poor-quality SWCNTs. These SWCNTs exhibited lower intrinsic conductivities, but qualitatively, it can be said that their aspect ratio was similar to the first high-quality SWCNT used. It was observed that PEDOT:PSS could stabilize aqueous dispersions of the poor quality SWCNTs. The percolation threshold of these SWCNTs, initially stabilized with SDS in an aqueous dispersion, in PS was found to be over 1 wt %. As was seen in the control system (higher quality tubes), a large decrease in SWCNT percolation threshold upon the addition of PEDOT:PSS into the composite formula-

tion resulted. From this, it was postulated that the contribution of the SWCNTs to the overall composite conductivity is minimal, and that the role of the SWCNTs is more that of forming a template or scaffold for the

deposition of a connected PEDOT:PSS phase. The introduction of a conductive polymeric component into polymer–SWCNT composites is an effective means to lower the composite percolation threshold.

METHODS AND MATERIALS

Materials. Sodium dodecyl sulfate (SDS) (90%, Merck), sodium carbonate (SC) (Aldrich, 99%), and sodium peroxydisulfate (SPS) (90%, Merck) were used as received. The presence of any impurities in the surfactant used (SDS) is assumed not to influence the conductivity of the CNT networks. Styrene (99%, Merck) was passed over an inhibitor remover column. This was kept under refrigeration for later use. Water used in all reactions was double-deionized (DDI) water obtained from a purification system. An aqueous PEDOT:PSS dispersion, grade name Clevios P, was purchased from H.C. Starck and used as received. According to the supplier, the PEDOT:PSS dispersion contains 0.4 wt % PEDOT and 0.8 wt % PSS. HiPCO and Carbolex (AP grade) SWCNTs were purchased from Unidym Inc. and Carbolex Inc., respectively. Both were used as received.

Emulsion Polymerization. A PS latex was synthesized *via* conventional free radical emulsion polymerization. The reaction was performed in a RC1 reactor (Mettler Toledo) set at 70 °C, and the impeller speed was 400 rpm. The RC1 reactor was charged with 252 g of styrene, 26 g of SDS, 0.7 g of Na₂CO₃, and 712.2 g of H₂O. The reaction mixture was degassed for 30 min. A solution of SPS (0.45 g) and H₂O (10 g) was simultaneously degassed. The reaction was started with the injection of the initiator solution, and the reaction time was roughly 1 h. The latex was dialyzed for 4 days against DDI to remove excess surfactant (a large excess of surfactant was used in the emulsion preparation). The average particle size determined, by dynamic light scattering (DLS), was 64 nm. Size exclusion chromatography (SEC) showed M_n , M_w , and PDI values of 81 kg · mol⁻¹, 977 kg · mol⁻¹, and 12, respectively.

SWCNT Exfoliation. Two dispersions of 0.1 wt % (wrt the solution) Carbolex SWCNTs were prepared (maximum volume of 20 mL), one using an equal volume of a 0.2 wt % SDS solution, and the second using an equal volume of a 0.4 wt % PEDOT:PSS solution. Exfoliations of all of these SWCNT dispersions were performed using ultrasound provided by a Sonics Vibracell VC750 horn sonicator with a 10 mm diameter tip. The sonication power was maintained at 20 W during the exfoliation, and the solution was cooled in an ice-bath to prevent extensive SWCNT damage. Samples were taken at various times during sonication (diluted 150 times to achieve a concentration at which scattering can be ignored¹⁹) for further UV–vis spectroscopy. The absorbance of the samples at a set wavelength (300 nm) was recorded. The optimal exfoliation was determined by monitoring the increase in the absorbance at 300 nm with time. At a certain value of energy added, the UV–vis absorbance levels off, and this point was then taken as the required time for maximum exfoliation. Dispersions of a higher concentration, 0.25 wt %, were made using both surfactants (0.5 wt % SDS and 1 wt % PEDOT:PSS) for use in composite preparation.

SWCNT Analysis. UV–vis–NIR and Raman spectra of dilute dispersions of both the HiPCO and Carbolex tubes (prepared with SDS) were taken to compare the electronic transitions characteristic of SWCNTs and the quality factor of both SWCNT types. Buckypapers of SDS-stabilized Carbolex and HiPCO SWCNT dispersions were prepared by filtering the dispersions through a Sartolon polyamide filter (pore size of 0.45 μm) supplied by Sartorius Stedim. The conductivities of these papers were measured with four-point dc conductivity measurements. TGA was performed on the original SWCNTs to determine the relative amounts of carbonaceous and metal catalyst impurities. The degree of graphitization was also investigated using this technique.

SWCNT–Polymer Composite Preparation. Each of the two Carbolex SWCNT dispersions (with either PEDOT:PSS or SDS as surfactant) was used to prepare a range of PS–SWCNT composites. A control series of films was prepared by mixing varying amounts

of PEDOT:PSS latex with the PS latex (no SWCNTs are present in these films). The mixtures of the latex and SWCNT dispersions were freeze-dried overnight at 0.25 mbar on a Christ Alpha 2-4 freeze drier. This powder was then compression molded at 180 °C and 100 bar for 2 min on a 300G Collin Press. The final nanotube concentration is determined using the weighed amounts of CNT dispersion and latex and the CNT weight percentage of the CNT dispersion and solids content of the latex.

Analysis. UV–vis spectroscopy was performed on a Hewlett-Packard 8453 spectrometer (range of 200–1100 nm). UV–vis–NIR absorption spectroscopy was performed on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer (range 250–2500 nm). TGA measurements were performed on a Perkin-Elmer Pyris 6 TGA. A heating profile of 10 °C/min was used to scan a range of 30 to 900 °C. A N₂ atmosphere was maintained (flow rate of 20 mL/min). All results were analyzed using a Pyris 4.01 software package. A LABRAM (by Jobin Yvon) confocal Raman spectroscope equipped with an optical microscope was utilized. Samples were irradiated with a red high polarized laser (632 nm) supplied by Melles Griot. Graphite contact points were drawn on the PS–SWCNT composite film surfaces, and four-point direct current (dc) conductivity measurements were performed. The resistivities of the composites were measured with a Keithley 6512 programmable electrometer and a Keithley 220 Programmable current source. To calculate the final conductivities, film thickness measurements were performed using a piezoelectric thickness meter from Mitutoyo (LGA-110). For buckypapers, any porosity has been ignored. Transmission electron microscopy (TEM) was performed using a Sphera type Technai 20 (Fei Co.). This was operated with a 200 kV LaB₆ filament and a bottom mounted 1024 × 1024 Gatan CCD camera. A carbon-coated gold grid was used.

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Supporting Information Available: Thermogravimetric analysis (TGA) mass loss curves and Raman spectroscopy spectra obtained for Carbolex and HiPCO SWCNTs. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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