Chem. Mater. **2007,** *19,* 291−300

Copolymer of Single-Walled Carbon Nanotubes and Poly(*p*-phenylene benzobisoxazole)

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Received September 18, 2006. Revised Manuscript Received October 30, 2006

The use of single-walled carbon nanotube (SWNT) copolymers in polymeric formulations may lead to better alignment of fibers, thereby producing higher performance materials. Although poly(*p*-phenylene benzobisoxazole) (PBO) fibers are some of the strongest organic polymer fibers known, the introduction of SWNTs into the PBO backbone might lead to improvements in their physical properties. Therefore, copolymerization of short (average length 60 nm) carboxylic acid functionalized SWNTs with PBO oligomers was successfully carried out in a mixed solvent of polyphosphoric acid and methanesulfonic acid (MSA) in the presence of P_2O_5 at 3.3 wt % concentration and 150 °C. The SWNTs were homogeneously distributed throughout the films of copolymerized products, as determined by Raman spectroscopy using the diagnostic radial breathing mode and D and G band emissions. Morphological differences between the copolymerized product and a physical mixture were readily seen using atomic force microscopy. The precipitated copolymerized nanotubes were separated by centrifugation from the MSA suspension of the products of short SWNTs and PBO oligomers. That benzoxazole moieties could be formed between the carboxylic acids of ultra-short (US) SWNTs and *o*-aminophenol derivatives was established by the condensation of US-SWNTs with *o*-aminophenols, and subsequent analysis of the products.

Introduction

In the rapidly growing field of nanotechnology, single-walled carbon nanotubes[1] (SWNTs) are suggested as the most electrically (ballistic conductance, 1 $\mu\Omega\cdot$cm) and thermally (∼3000 W/m K) conductive, light-weight (density ∼ 1.4 g/cm^3), and strongest (100 × stronger and 6 × lighter than steel) materials.[2−4] They also exhibit unique electromagnetic properties. Unfortunately, due to their rigidity and chemical inertness, SWNTs are difficult to process into useful articles, limiting their potential applications. Due to their high aspect ratio and the strong van der Waals attraction between them, full-length purified SWNTs tend to aggregate into a dense, robust network of ropes (usually 10−25 nm in diameter and several μm in length) that have limited solubility in either organic or non-fuming acidic media. Their intertube adhesion is 0.5 eV/nm. It has been shown, however, that the solubility of SWNTs can be improved by shortening their length and through chemical functionalization.[5−17] To fully exploit the potential of SWNTs in macroscopic functional articles such as fibers or films and to overcome the critical issues of limited solubility, dispersivity, and processibility of SWNTs, we prepared a new block copolymer system wherein short functionalized SWNTs (average length 60 nm) are covalently bonded to acid-soluble polybenzazoles, a commercial family of materials (specifically poly(*p*-phenylene benzbisoxazole) (PBO))[18−20] of well-defined length (less than 50 monomer units). The key concept is to synergistically combine the unprecedented properties of short SWNTs with the processibility of PBO. Additionally, we expect that the SWNT−

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10.1021/cm062227k CCC: $37.00

PBO copolymer will lead to better alignment of the polymer fibers, enhancing the physical properties of the formed materials. In-situ PBO synthesis in the presence of full-length purified SWNTs has been reported, but the formation of covalent SWNT−PBO bonds was not reported.[21] In the present work, novel copolymers were synthesized in acidic media from functionalized, shortened SWNTs and end-functionalized oligomeric PBO.

Experimental Section

Materials. 2-Aminophenol, 2-amino-4-chlorophenol, terephthaloyl chloride, methanesulfonic acid, and phosphorus pentoxide were purchased from Sigma-Aldrich Co. 4-Aminobenzoic acid and polyphosphoric acid (84.5% as P_2O_5) were purchased from Acros Organics. Diaminoresorcinol dihydrochloride was donated by Dow Chemical Co. The materials were used as received unless specified.

SWNT Cutting. SWNTs were cut into shorter lengths according to the previously reported procedures.[22,23] The SWNTs used in this study were produced by the high-pressure CO (HiPco) process.[24] The raw SWNTs were purified using SF_6/O_2 oxidation.[25−27]

Preparation of Ultra Short SWNTs (US-SWNTs) 1 (Length <60 nm). Purified SWNTs were first disentangled in oleum (20% SO_3) for 72 h by an immersion blender to ensure complete superacid intercalation.[22] Subsequently, a mixture of oleum (20% SO_3) and 70% nitric acid was slowly added into the SWNT/oleum dispersion to make a mixed solvent of oleum/nitric acid at volume ratio of 3:1. The SWNT dispersion was stirred at 65 °C for 2 h to cut the nanotubes. The resulting US-SWNTs were washed with NanoPure water (Barnstead International, Dubuque, IA), methanol and diethyl ether, and then vacuum-dried at room temperature. The US-SWNTs **1** were highly carboxylated (1 COOH group in every 4 SWNT carbons from the XPS data). The length was estimated to be <60 nm by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The US-SWNTs were then used in a model reaction via copolymerization with typical PBO monomers.

Preparation of Short SWNTs 2 (Average Length 60 nm). Short SWNTs are not heavily carboxylated on the sidewalls like the US-SWNTs. To produce short SWNTs, the sidewalls of purified SWNTs were fluorinated at 150 °C.[8] The fluorination creates damaged sites that can then be exploited by acid oxidation[23,28] or pyrolysis, leading to the cutting of SWNTs into short lengths (<100 nm).[23,29] Defluorination of the SWNTs was achieved by reacting the fluorinated nanotubes with hydrazine. The defluorinated SWNTs were oxidized in 96% sulfuric acid with ammonium persulfate at RT for 1 h. The oxidized SWNTs were washed with NanoPure water, hexane, and ethanol and then dried under vacuum at 45 °C to produce short SWNTs **2**. The cut, short nanotubes were then used in the copolymerization with PBO oligomers. In order to analyze the lengths of the nanotubes, portions of the purified SWNTs (before cutting) and the cut SWNTs **2** were both separately functionalized by the Billups method,[10b] resulting in the covalent attachment of dodecyl groups to the sidewalls. The resulting functionalized SWNTs, in $CHCl_3$ suspension, were dispersed on mica for AFM imaging. The average length of the cut, functionalized SWNTs was 60 nm. The dodecyl alkylated SWNTs were only used to verify tube length using AFM; they were not further used in the synthetic work.

Model Reaction: Condensation of *o*-Aminophenols with US-SWNTs. The US-SWNTs **1** were used for a model reaction to give a product in which the covalent bond between the carboxylic acid of the SWNTs and the *o*-aminophenol moiety could be more easily detected (Scheme 1). In a typical procedure, 20 mg of **1** was homogeneously dispersed under N_2 by heating at 130−190 °C with stirring in 20 mL of PPA (84.5% as P_2O_5) or PPA/methanesulfonic acid (MSA) for 0.5−3 h. *o*-Aminophenol derivatives including 2-aminophenol **3** (13.4 mmol), 2-amino-4-chlorophenol **4** (1.44 mmol), or recrystallized diaminoresorcinol dihydrochloride **5** (2.95 mmol) were added to the US−SWNT/acid suspension at 100, 150, or 190 °C (see Table 1), and the reactions were carried out for 1 d. The functionalized SWNTs **6a**−**c** were washed with water, methanol, and acetone and then dried under vacuum at room temperature.

Synthesis of 2-(4-Aminophenyl)benzoxazole 7. 2-(4-Aminophenyl)benzoxazole **7** was synthesized using a procedure from the patent literature (see Supporting Information).[30]

Synthesis of 2-(4-Amidophenyl)benzoxazole Functionalized, US-SWNTs 9. US-SWNTs **1** (35 mg) were dispersed in 15 mL of thionyl chloride to convert the carboxylic acid moieties into acid chlorides (Scheme 2). The reaction mixture was stirred at 70 °C for 1 d. Excess thionyl chloride was removed under vacuum, and then 20 mL of anhydrous 1-methyl-2-pyrrolidinone (NMP) was added to the acid chloride functionalized US-SWNTs **8**. The product **8** was stirred in NMP for 5 min to obtain a good dispersion of the nanotubes. Subsequently, 1.67 g of **7** was added to the suspension of **8**. The reaction mixture was stirred under N_2 at room temperature

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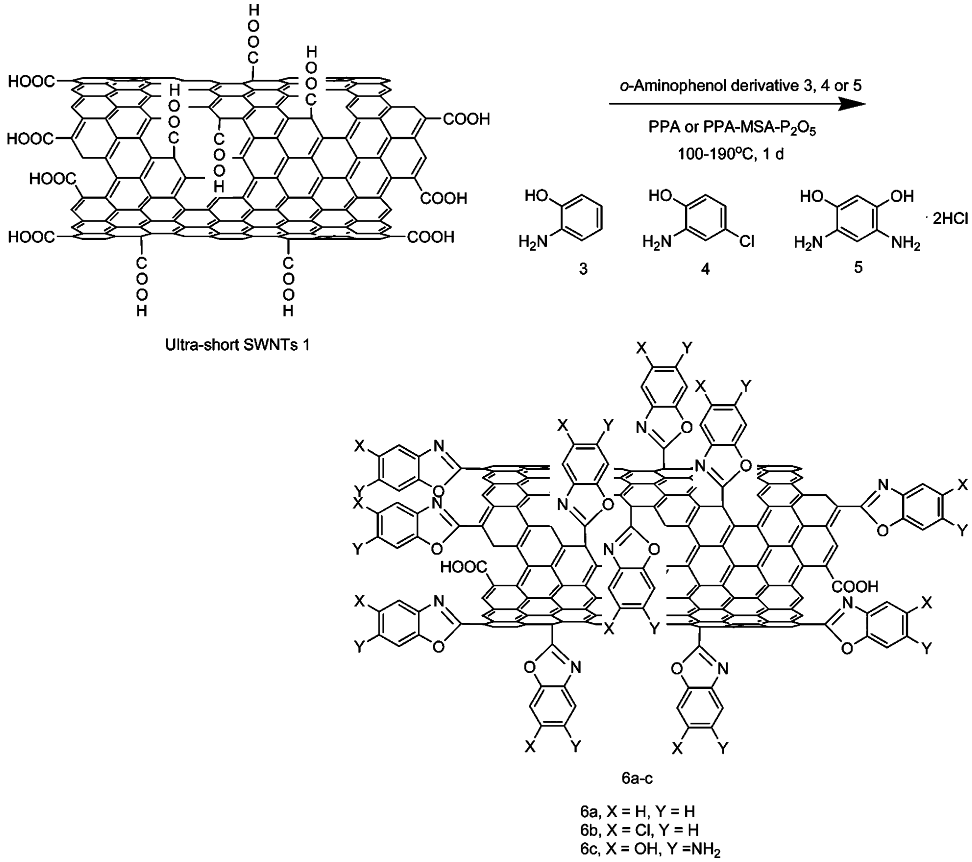
Scheme 1. Reaction of US SWNTs 1 with *o*-Aminophenols 3−5 To Produce 6a−c: Model Reaction for Copolymerization of SWNTs and PBO



6a, X = H, Y = H
6b, X = Cl, Y = H
6c, X = OH, Y = NH_2

Table 1. Results of Model Reaction for Copolymerization of US-SWNTs and PBO

o-aminophenol derivative	solvent	concn (wt %)	temp (°C)	TGA weight loss (%)	XPS elemental composition (%)
6a	PPA	5.0	150	40	C 1s 65.7, O 1s 30.4, N 1s3.9
6a	PPA	5.0	190	34	C 1s 57.3, O 1s 38.0, N 1s 4.7
6a[a]	PPA/MSA	5.0	100	40	C 1s 68.9, O 1s 27.6, N 1s 3.6
6a[a]	PPA/MSA	5.0	150	40	C 1s 64.7, O 1s 29.5, N 1s 5.8
6b	PPA	1.0	150	41	C 1s 64.0, O 1s 26.6, N 1s 5.3, Cl 2p 4.1
6c	PPA	2.0	150	40	C 1s 51.4, O 1s 38.5, N 1s 10.1

[a] Weight ratio of PPA/MSA: 16/84. P_2O_5 was used at weight ratio of MSA/P_2O_5 of 10/1.

for 1 d to give **9**. The functionalized US-SWNTs **9** were isolated by the addition of water and filtration; the collected solid was washed with water, methanol, and acetone and then dried under vacuum at room temperature. TGA weight loss: 34%; XPS analysis: C 1s 75.1%, O 1s 20.3%, N 1s 4.6%. The degree of functionalization was estimated from the XPS elemental composition to be 1 functional group for every 15 carbons of the US-SWNTs.

Synthesis of Aryl Sulfonated, Short SWNTs 10. Sidewall functionalization of short SWNTs (average length 60 nm) **2** was carried out by the procedure previously reported.[7h] 0.25 g (20.8 mmol) of **2** was treated with 14.4 g (83.0 mmol, 4 equiv) of sulfanilic acid in a reaction mixture comprising 100 mL of H_2SO_4 (fuming, 20% free SO_3), 5.74 g (83.2 mmol, 4 equiv) of sodium nitrite, and 0.68 g (4.1 mmol, 0.2 equiv) of 2,2′-azobisisobutyronitrile (AIBN) (Scheme 3). This gave benzenesulfonic acid-functionalized, short SWNTs **10**. The product **10** was characterized by UV−vis spectroscopy as being devoid of van Hove singularities.[7a,b,f] The SWNTs **10** were also water-soluble, confirming that sidewall attachment of aryl sulfonated groups was achieved. TGA weight loss: 31%; XPS analysis: C 1s 74.8%, O 1s 21.5%, S 2p 2.9%. Degree of functionalization was estimated from the elemental composition, one functional group in every 18 carbons of the SWNTs **2**.

Synthesis of PBO Oligomers 11. PBO oligomers **11** were synthesized according to the patent literature (Scheme 4).[31] A slight excess of recrystallized diaminoresorcinol dihydrochloride was coupled with recrystallized terephthaloyl chloride to synthesize PBO oligomers that were *o*-aminophenol-terminated at both ends. To make PBO 15 mers (with an average degree of polymerization (DP) of 15): 4.48 g (21.0 mmol) and 4.00 g (19.7 mmol) were added to a solvent mixture of 33.2 g of polyphosphoric acid (PPA, 84.5% as P_2O_5) and 0.43 g of P_2O_5 (total P_2O_5 content in mixture = 84.7 wt %). The reaction mixture underwent dehydrochlorination at 45 °C for 16 h, after which time an oligomerization step was carried out at 95 °C for 8 h, 150 °C for 16 h, and 190 °C for 24 h. The reaction mixture was carefully poured into water to precipitate the product, which was filtered and dried. The product was then ground to a fine powder, suspended in refluxing water, the solid was filtered, and the filter cake was washed with water and acetone and dried under vacuum at 170 °C. This yielded PBO oligomers

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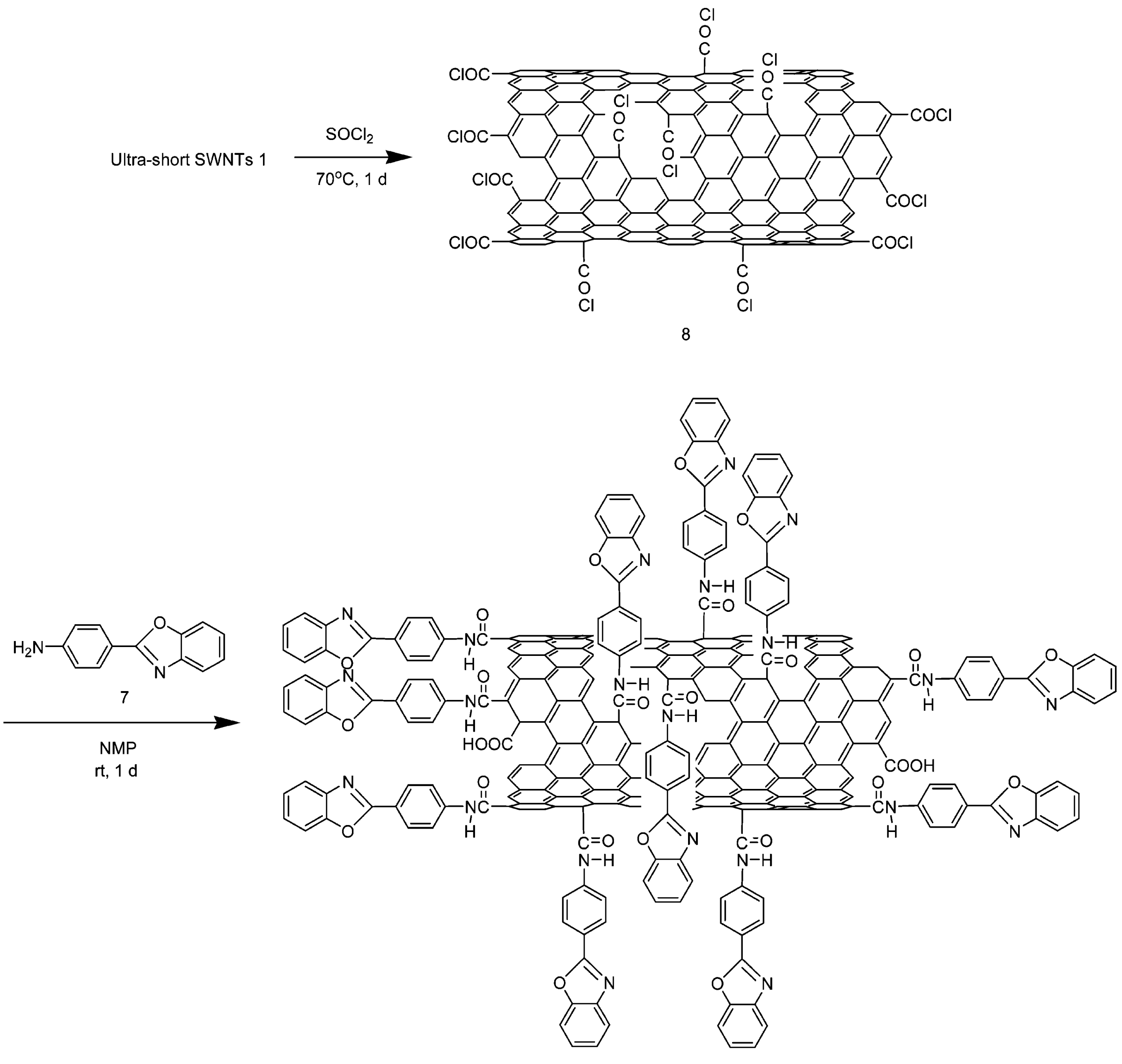
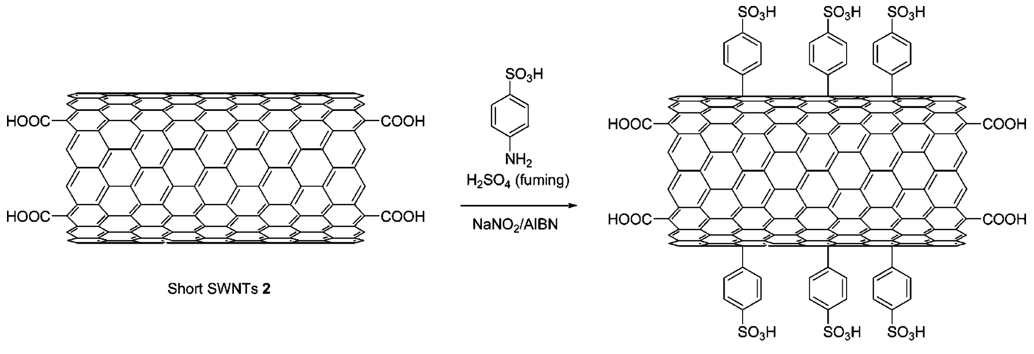
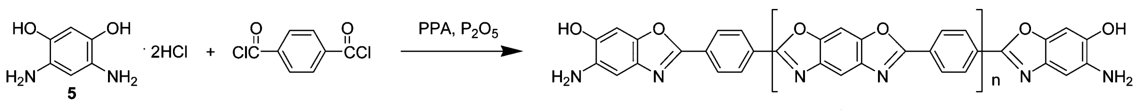
Scheme 2. Synthesis of 2-(4-Amidophenyl)benzoxazole Functionalized US SWNTs 9



Scheme 3. Functionalization of 2 by Sulfanilic Acid to Produce 10

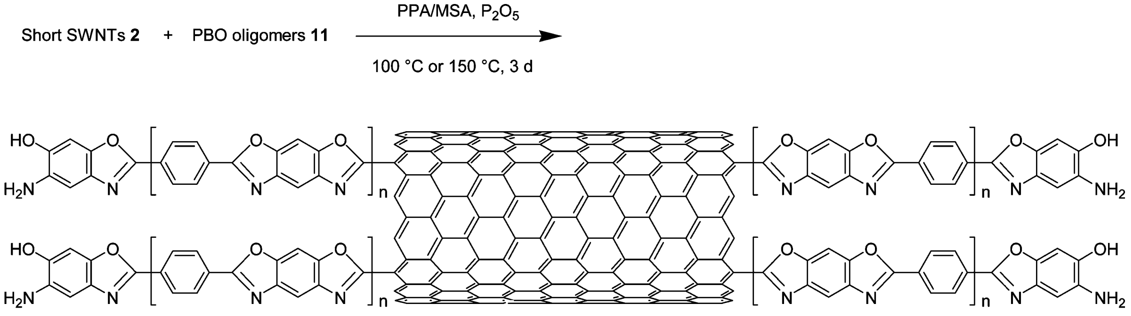


Scheme 4. Synthesis of PBO Oligomers 11



11 that had an inherent viscosity of 2.0 dL/g, which is in good agreement with inherent viscosity data for PBO oligomers terminated by 2-amino-4-chlorophenol having a DP of 15.[32] The inherent viscosity was measured in MSA (>99.5%) solution saturated by MSA anhydride at 25 °C, at a concentration of 0.05 dL/g in a cross-arm viscometer. The weight-average molecular weight of 6200 was calculated from the intrinsic viscosity using the equation, $[\eta]$ (dL/g) $= 2.77 \times 10^{-7} \times M_w^{1.8}$.[33]

Scheme 5. Synthesis of SWNT/PBO Copolymer 12



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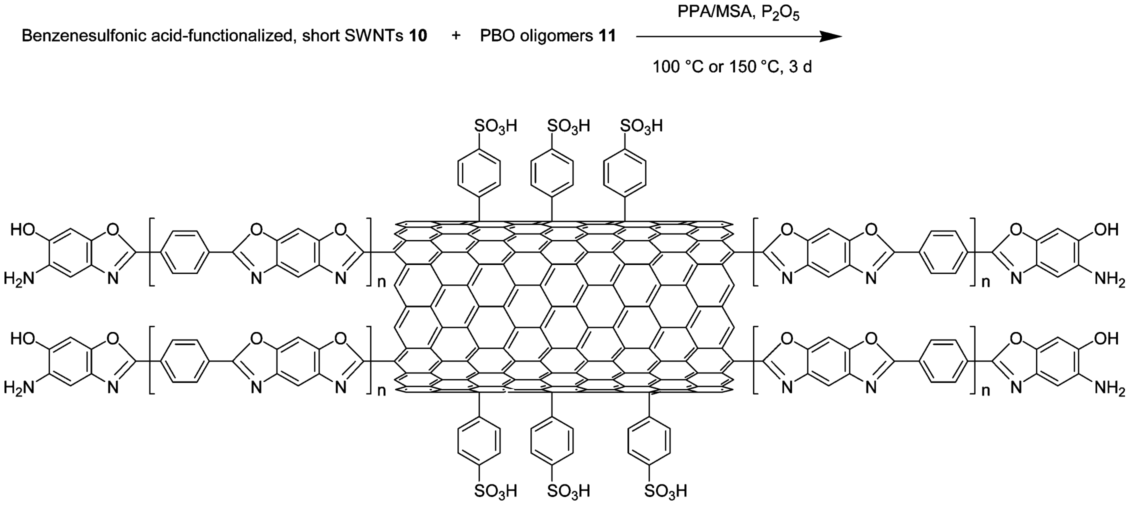
Scheme 6. Synthesis of SWNT/PBO Copolymer 13



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Copolymerization of PBO Oligomer 11 with 2 or 10. Carboxylated, short SWNTs **2** were copolymerized with PBO oligomers **11** (Scheme 5). In a typical procedure, 0.15 g of **2** was homogeneously dispersed under N_2 by heating at 150 °C with stirring in 10.0 g of MSA for 3 h, followed by mixing with 2.4 g of a PPA solution of 0.3 g **11** and 1.00 g of P_2O_5. The copolymerization was carried out at 150 °C for 3 d. The copolymerized product **12** was precipitated by slowly pouring the reaction mixture into water; the solid was collected by filtration onto a 0.45 μm PTFE filter; the filter cake was washed with water and acetone and then dried under vacuum at 100 °C. A similar procedure was used to synthesize copolymer **13**, see Scheme 6.

Fabrication of a Thin Film of a Physical Mixture of Aryl Sulfonated, Short SWNTs and PBO Oligomers. A suspension of aryl sulfonated, short SWNTs **10** was homogeneously dispersed in MSA by heating at 150 °C under N_2 with stirring for 3 h. The suspension was cooled to room temperature, followed by mixing with PBO oligomers **11**. After **11** dissolved, the mixture was poured into water and the precipitated solids were filtered, washed with water and acetone, and dried under vacuum at 100 °C. A thin film was made by press forming the mixture with an IR molding die.

Characterization. Tapping mode AFM images were obtained on a Digital Instruments Nanoscope IIIA. The lengths of short SWNTs **2** were measured using the SIMAGIS software nanotube length analysis package (Smart Imaging Technologies, Houston, TX). About 500−1000 nanotubes were measured to obtain statistically meaningful results. Raman spectra were recorded on a Renishaw Raman microscope with 633 nm excitation. ATR-IR spectra were collected on thin films. UV−vis spectra were collected in a DMF suspension of SWNTs. A powder was pressed onto 0.5 mm thick soft indium foil, and XPS data were collected on a PHI Quantera SXM Scanning X-ray Microscope with monochromatic Al Kα X-radiation (1486.6 eV). TGA analysis was done in argon up to 850 °C at a heating rate of 10 °C/min. TGA samples had isothermal treatment at 100 °C for 30 min to remove small amounts of adsorbed solvents.

Results and Discussion

The block copolymerization is a condensation reaction between carboxylic acid moieties at the ends and defect sites of SWNTs and the *o*-aminophenol end groups of PBO oligomers. It has been reported that block copolymerizations of PBO oligomers with aromatic oligomers can be carried out in a mixed solvent of PPA and MSA with P_2O_5.[31] In our work, PBO oligomers with *o*-aminophenol moieties at both ends were synthesized by slight off-stoichiometry on AA and BB type monomers, diaminoresorcinol dihydrochloride and terephthaloyl chloride. Purified SWNTs were cut into short lengths and carboxylated by oxidation of the defect sites. Copolymerization of the short SWNTs and the PBO oligomers was studied.

Model Reaction. The formation of benzoxazole moieties by the reaction of the carboxylic acid functionality of US-SWNTs and *o*-aminophenol derivatives was studied. US-

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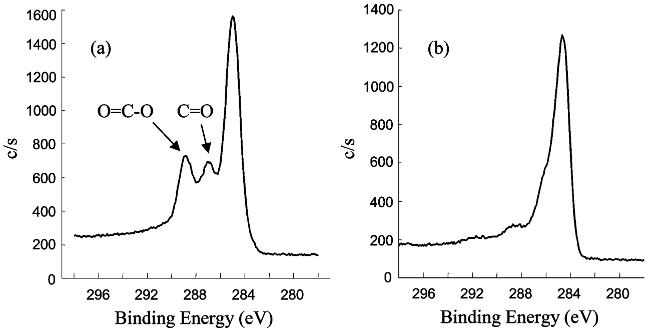

Figure 1. XPS spectra of C 1S of (a) US-SWNTs **1** and (b) product **6a** from US SWNTs functionalized by **3** in PPA at 150 °C.

SWNTs are highly carboxylated; a high yielding benzoxazole formation reaction would produce enough material to detect using standard analytical methods. The reaction conditions and results are in Table 1. The functionalized US-SWNTs **6a**−**c** showed good solubility in PPA and MSA. 2-(4-Amidophenyl)benzoxazole functionalized US-SWNTs **9** was synthesized for comparison.

Figure 1 shows XPS C 1s spectra of US-SWNTs (a) before (**1**) and (b) after functionalization by 2-aminophenol in PPA at 150 °C (**6a**). The carboxylic acid O═C—O peak at 289 eV is clearly detected in the spectrum of **1** due to a high degree of carboxylation.[22,34] The peak intensity at 289 eV significantly decreased after the functionalization, indicating covalent bonding between the carboxylic acid and 2-aminophenol. Decreases in the carboxylic acid peak intensities were similarly observed after all other functionalizations. Figure 2 shows ATR-IR spectra of (a) US-SWNTs **1** and (b−e) *o*-aminophenol derivatives **6a**−**c** and functionalized US-SWNTs **9**. The C═O and OH stretching modes of the carboxylic acid at 1705 cm^{-1} and 2500−3300 cm^{-1} were detected in the spectrum of **1** (Figure 2a).[22] The SWNTs C═C graphitic stretch was detected at 1581 cm^{-1} in Figure 2a. The C═O peak intensity at 1705 cm^{-1} significantly decreased after the functionalization (Figure 2b−e); in addition, the spectra show the characteristic oxazole absorption bands of the ═C—O—C and C═N stretching modes. A ═C—O—C stretch was observed at 1050−1100 cm^{-1} and a C═N stretch was observed at 1550−1600 cm^{-1} (overlapping the SWNTs C═C graphitic stretch). The peaks at ∼1350 cm^{-1} in Figure 2b−e were assigned to the C—N stretch, and the peaks at ∼1495 cm^{-1} were assigned to the aromatic ring C═C stretch of the functional groups attached to the US SWNTs. *o*-Aminophenol derivatives **6a**−**c** and **9** gave 34−41% weight loss by TGA. The TGA weight loss of **1** was 51% due to the large concentration of carboxylic acid groups. The weight loss of **6a**−**c** and **9** was 10−17% less than that of **1**. Thermally stable PBO oligomers gave 30% weight loss. These results support our finding that the functionalized US-SWNTs include thermally stable benzoxazole moieties, resulting in less weight loss. The products **6a**−**c** and **9** were soluble in PPA, MSA, and H_2SO_4 but insoluble in water. As previously reported,[22] US-SWNTs are water soluble, but this property changed after the functionalization, suggesting that the covalent attachment of **3**−**5** and **7** had indeed occurred. XPS analysis showed that these functionalized US-SWNTs contained 4−10% nitrogen. The nitrogen content of the US-SWNTs functionalized by **5** (**6c**) was about twice that of the other products. Approximately the same content of chlorine as nitrogen was detected for **6b**. The degree of functionalization was calculated from the elemental composition, which was one functional group in every six carbons of the functionalized SWNTs. Therefore, benzoxazoles were successfully formed between carboxylated US-SWNTs and *o*-aminophenol derivatives.

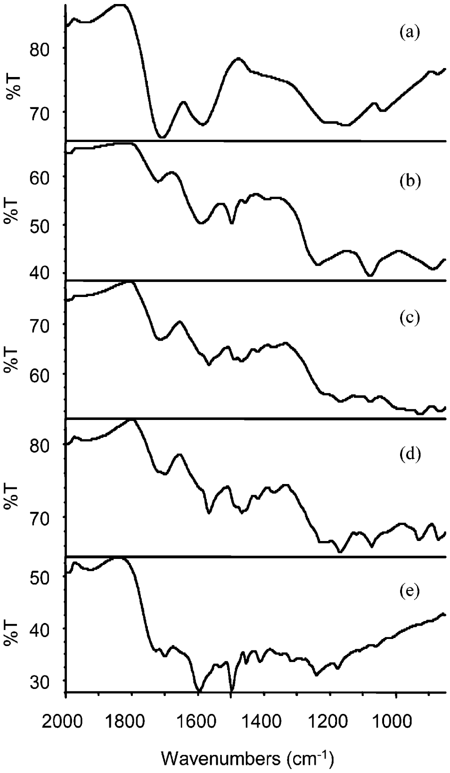

Figure 2. ATR-IR spectra of (a) **1**, (b) **6a**, (c) **6b**, (d) **6c**, and (e) **9**.

Copolymerization of Short SWNTs and PBO Oligomers. Cutting of SWNTs was carried out to increase the dispersion in PPA/MSA. Figure 3 shows the length distribution of the SWNTs before and after the cutting. The average length of the cut, short SWNTs was 60 nm. About 90% are shorter than 100 nm. It has been reported that treatment of SWNTs with strong acids or strong oxidizing agents opens the nanotubes and generates oxidized functional groups at the ends and defect sites.[5,6,35−39] It has also been shown that about 1−2% of the carbons in purified SWNTs are converted to carboxylic acids by the acid oxidation process.[40] The same

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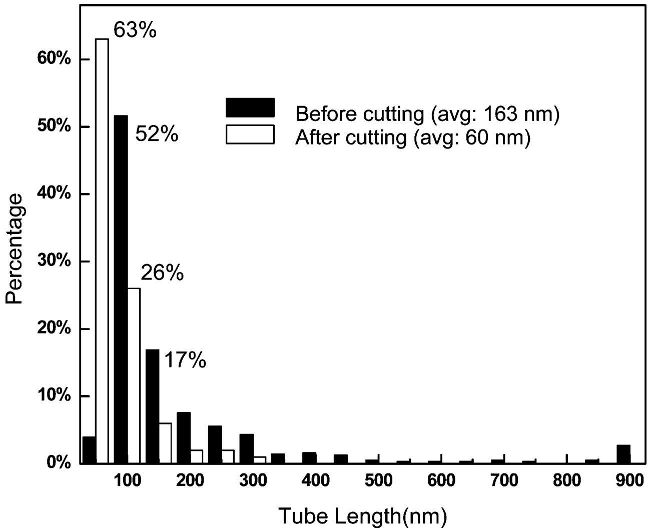

Figure 3. Length distribution of dodecyl functionalized SWNTs before and after cutting.

procedure was used to functionalize the cut, short SWNTs with carboxylic acid groups to produce **2**.

The UV−vis spectral analysis of the short SWNTs **2** showed van Hove singularities in the DMF suspension, indicating that the sidewalls were minimally perturbed. (For comparison, the US-SWNTs have severely compromised sidewalls.[22]) SWNTs/PBO blocks including short SWNTs **2** at the center and PBO oligomers **11** at the both ends were synthesized as the main product by using an excess of **11** over **2** (Scheme 5) to produce **12**. Copolymerization conditions are tabulated in Table 2. Two distinct reaction conditions, one at 100 °C and dilute concentration (0.36 wt %) and the other at 150 °C and higher concentration (3.3 wt %), were used for the block copolymerization. Aryl sulfonated short SWNTs **10** was used to increase the SWNT dispersion in PPA/MSA. AFM images of the functionalized, short SWNTs **10** showed that the short SWNTs **2** were exfoliated into individuals and small bundles by the sidewall functionalization process (see Supporting Information).[7e,h,j,k]

After copolymerization, the product was coagulated in water, washed with water and acetone, and dried under vacuum. A thin film was made by press-forming the product. Various areas of the films were examined by the focused beam of a 633 nm laser of the Raman spectroscope as shown in Figures 4 and 5. The diameter of the laser beam impinging on the surface was approximately 5 μm. Radial breathing modes (RBM) at ~230 cm^{-1}, a disorder mode (D band) at ~1290 cm^{-1}, and a tangential mode (G band) at ~1590 cm^{-1}, characteristic of SWNTs, were observed on those films along with fluorescence of PBO. As previously reported, a Raman spectrum of SWNTs/PBO (10/90) composite fibers by 785 nm excitation showed the G band superimposed over strong fluorescence of the PBO.[21a] For films of products synthesized at dilute concentration at 100 °C, RBM, D band, and G band with fluorescence of PBO were observed in almost half of the film's areas out of the 50 examined. Only fluorescence due to PBO was seen in the other examined areas of the films. A Raman spectrum of PBO oligomers **11,** which is indicative of the strong fluorescence, is shown in Figure 4b. These results might imply the presence of some aggregated SWNTs which were not covalently bonded to PBO. Also, a MSA suspension of the copolymers were not stable (i.e., they tended to flock out after several hours).

In contrast, when copolymerization of **2** or **10** with **11** was carried out at higher temperature and higher concentration, more stable suspensions of the copolymerized products **12** and **13** (respectively) in MSA were obtained. Raman spectra of the copolymerized product synthesized in higher concentration were the same in all of the 50 examined areas of the film. These results indicate that nanotubes with the characteristic RBM, D band, and G band were homogeneously distributed throughout the films. It has been reported that SWNT aggregates or bundles were not observed in SWNT/PBO (10/90) composite fibers, suggesting SWNTs exfoliation as individuals.[41] For the control experiment, a thin film was made from a corresponding mixture of **10** with **11**. Raman spectra of the film showed the presence of RBM, D band, and G band in almost half of the 50 examined areas. The other areas exhibited fluorescence from PBO. This result is supportive of the homogeneous distribution of nanotubes in the films from **12** or **13** synthesized at the higher concentration.

ATR-IR spectra of the copolymerized products at higher concentration showed the presence of peaks characteristic of PBO as shown in Figure 6. A C═N stretch at 1612−1619 cm^{-1}, ═C−O−C stretch at ~1050 cm^{-1} and an aromatic C−H stretch at 3000−3100 cm^{-1} were observed in all three spectra. AFM images of the copolymerized products in high concentration were compared with those of a corresponding mixture of the short SWNTs **2** or **10** and PBO oligomers **11** (Figure 7). It was observed that the copolymerized product in high concentration and the physical mixture have different morphologies, while the morphology of the copolymerized product in dilute concentration is similar to the physical mixture. The samples were spin-coated on Si from the MSA (>99.5%) suspensions at a concentration of ~ 0.05 mg/mL and dried under vacuum at 150 °C. Figure 7a shows ropelike aggregates of PBO oligomers **11** that range from hundreds to a few micrometers in length and 0.7−4.9 nm in height. As previously reported, the morphology of PBO prepared by quenching a dilute H_2SO_4 solution is fibril, and the molecular chains align along the fibril length direction.[42] It has also been reported that flat fibrils several nm thick were formed by quenching a dilute H_2SO_4 solution of poly(*p*-phenylene benzobisthiazole), a structural homologue of PBO.[43] The molecular chains were also oriented along the fibril length direction. Aryl sulfonated, short SWNTs **10** show small particles tens of nanometers in size and 1.9−6.7 nm in height, which are individuals and small bundles, as shown in Figure 7b. Figure 7c is a physical mixture of **10** and **11**. Long, ropelike structure coexists with small particles tens of nanometers in size. In contrast to this, the copolymerized product **13** shows the absence of those long, ropelike structures resulting from the segregation of PBO oligomers that are not covalently bonded to the SWNTs (Figure 7d). Short, rodlike structure and small particles were observed, ranging tens of nanometers to a couple of hundreds

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Table 2. Copolymerization Conditions to Make 12 or 13[a]

SWNTs used	wt ratio of **11** and SWNTs	molar ratio[b] of **11** to SWNTs	wt ratio of PPA and MSA	temp (°C)	concn (wt %) PBO + SWNTs[c]	concn (wt %) PBO	concn (wt %) SWNTs [c]	product
2	33/67	16	50/50	100	0.36	0.12	0.24	**12**
2	67/33	64	50/50	100	0.36	0.24	0.12	**12**
10	67/33	64	50/50	100	0.36	0.24	0.12	**13**
2	67/33	64	16/84	150	3.3	2.2	1.1	**12**
10	67/33	64	16/84	150	3.3	2.2	1.1	**13**

[a] Copolymerizations of **2** or **10** and **11** were carried out in a mixed solvent of PPA/MSA with P_2O_5 for 3 d. [b] Molecular weight of **2** or **10** was calculated assuming that the chiral index was (10, 10) and the length was 60 nm.[38] [c] For **10**, calculated based on weight of contained SWNTs, not the sidewall addends.

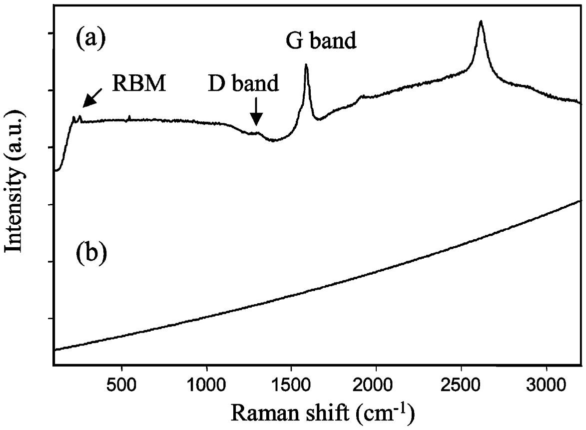

Figure 4. Raman spectra of (a) **12** at the weight ratio of 67/33 at 0.36 wt % concentration and (b) **11** (633 nm excitation).

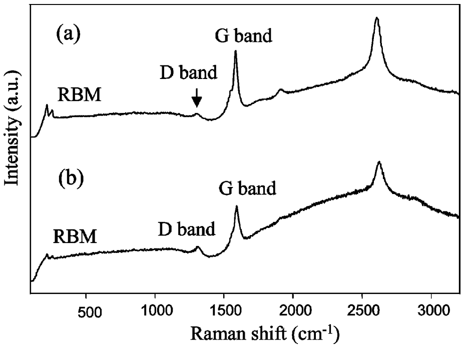

Figure 5. Copolymerized products (a) **12** and (b) **13** at 3.3 wt % concentration (633 nm excitation).

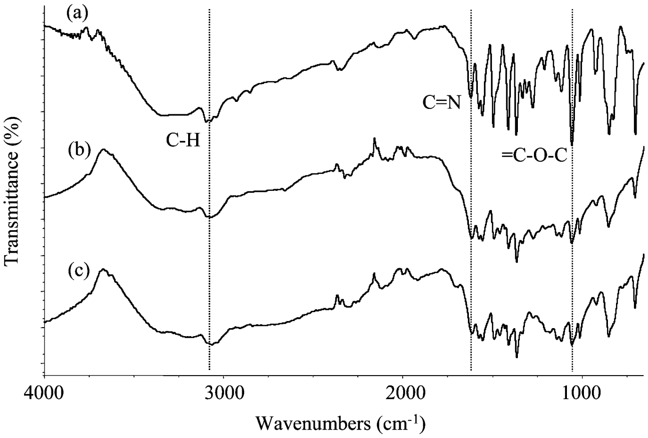

Figure 6. ATR-IR spectra of (a) PBO oligomers **11**, and (b) and (c) copolymerized products **12**, and **13**, respectively, at 3.3 wt % concentration.

of nanometers in size and 0.8−4.8 nm in height. The AFM of short SWNTs of average length 60 nm **2** (Figure 7e) shows small particles tens of nanometers in size comparable to the aryl sulfonated, short SWNTs **10** shown in Figure 7b. The particles are 2.3−14.3 nm in height, higher than **10**. It is notable that this morphological feature is different from the tens of nm high, large bundles spin-coated from the DMF suspension (see Supporting Information). This indicates that the morphology was significantly affected by the molecular constitution dispersed in the solvent,[44] and the short SWNTs were better dispersed in strong acids than in DMF. It has been reported that SWNTs disperse as individuals in superacids by protonation.[45−47] Figure 7f is a physical mixture of **2** and **11**. The AFM image is similar to a physical mixture of **10** and **11** (Figure 7c). On the other hand, the copolymerized product **13** shows the absence of the several μm long, ropelike structures that normally result from PBO oligomers (Figure 7g). These observed morphological features indicate formation of copolymers from the short SWNTs and PBO oligomers. A precipitate of **12** or **13** was separated by centrifuge from a MSA suspension of the reaction of **2** or **10** with **11** in high concentration. XPS analysis showed the elemental composition C 1s 83.1%, N 1s 2.6%, O 1s 14.3% for **12** and C 1s 78.5%, N 1s 2.9%, O 1s 17.2%, S 2p 1.4% for the product **13**. The degree of functionalization for each product was estimated from the elemental composition, assuming that the number-average DP for **11** was 15: there was one PBO oligomer for every 244 carbons in the **12** and 1 PBO oligomer for every 135 carbons in **13**. The peak intensity of the carboxylic acid moiety O=C−O at 289 eV decreased after the copolymerization, as seen in the model

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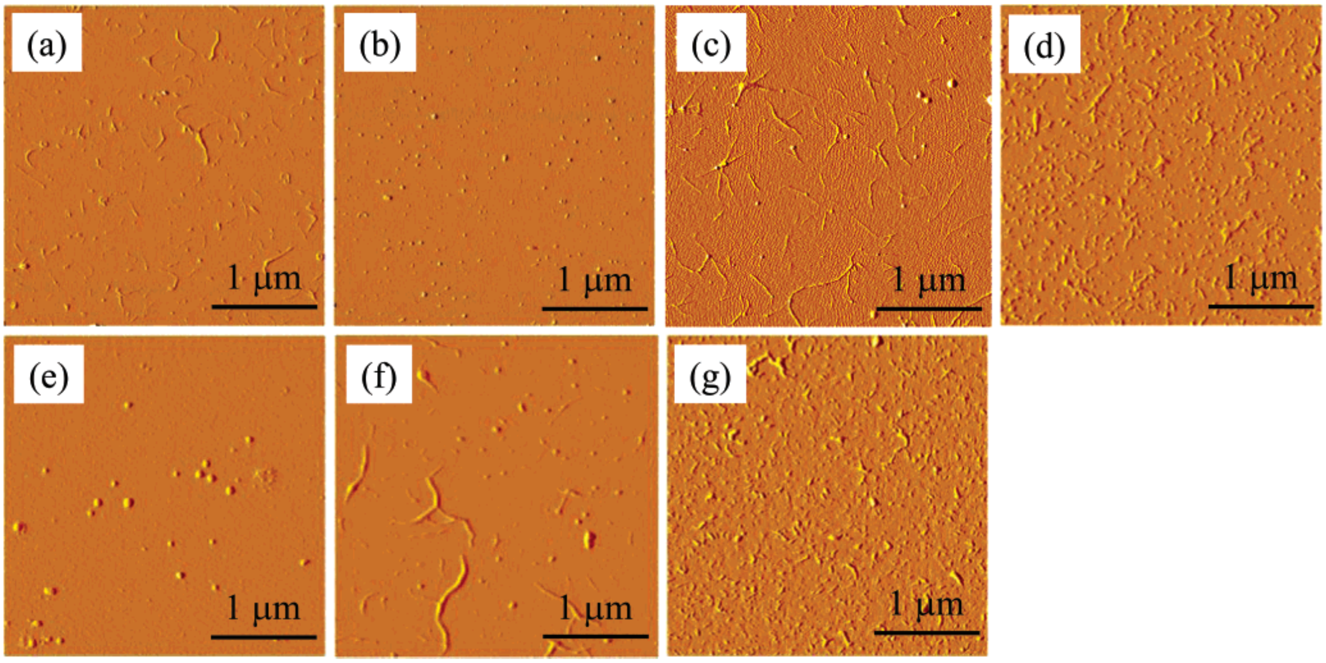

Figure 7. AFM images of (a) PBO 15 mers **11**, (b) aryl sulfonated, short SWNTs **10**, (c) physical mixture of **10** and **11**, (d) copolymerized product **13** from **10** and **11**, (e) short SWNTs **2**, (f) physical mixture of **2** and **11**, (g) copolymerized product **12** from **2** and **11**. All copolymerizations were carried out at 3.3 wt % concentration.

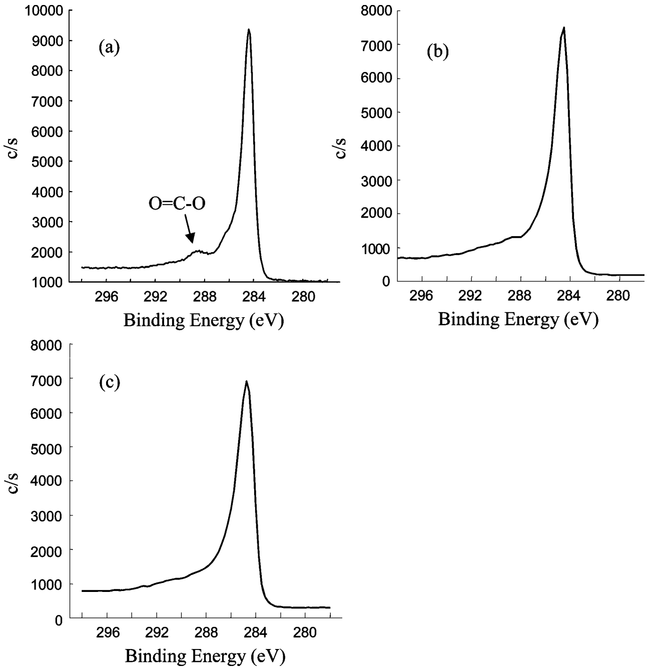

Figure 8. XPS spectra of C 1S of (a) short SWNTs **2** and copolymerized SWNTs precipitates from (b) **12** and (c) **13**.

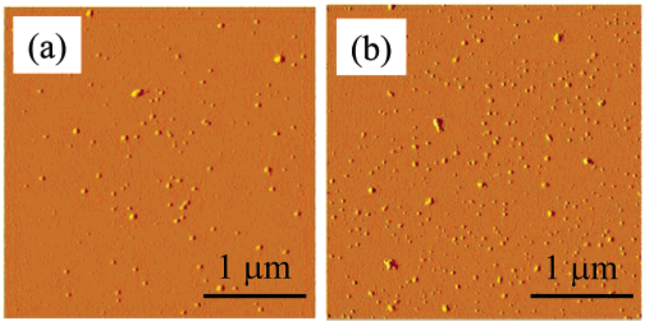

Figure 9. AFM images of copolymerized SWNTs precipitate from (a) product **13**, (b) product **12**.

reaction (Figure 8), which is indicative of the covalent bonding between short SWNTs and PBO oligomers.

The precipitate of **13** was insoluble in water, DMF and NMP. Aryl sulfonated, short SWNTs were water-soluble as mentioned above and also soluble in DMF and NMP, which are good solvents to disperse SWNTs, as previously reported.[48−50] The precipitate of **12** did not dissolve in DMF and NMP, while the short SWNTs **2** were soluble in both solvents. The change in solubility of the nanotubes before and after the copolymerization indicates covalent bonding of the PBO oligomers to the SWNTs. Figure 9 shows AFM images of the **12** and **13**. In both cases, small particles tens of nanometers in diameter were observed, ranging from heights of 1.5−6.8 nm for **13** (Figure 9a) and 1.6−10.8 nm for **12** (Figure 9b). The particle sizes were slightly smaller than the copolymerized products that did not undergo separation by centrifuge. The height of copolymerized SWNTs precipitate **12** was higher than that for **13**, but there appeared to be no morphological differences between precipitates **12** and **13** that we could detect at the resolution of the AFM. The precipitates of **12** or **13** showed RBM, D band, and G band in the Raman spectra (633 nm excitation), while fluorescence was not seen. These results indicate that the short SWNTs in **12** and **13** were covalently bonded to PBO oligomers. Therefore we can conclude that novel copolymers were successfully synthesized by polymerization of short SWNTs with PBO oligomers at 3.3 wt % concentration and 150 °C in a mixed solvent of PPA/MSA in the presence of P_2O_5.

Conclusion

Copolymerization of short SWNTs with PBO oligomers was successfully carried out at 3.3 wt % concentration and 150 °C in a mixed solvent of PPA and MSA in the presence of P_2O_5. Short SWNTs were homogeneously distributed with RBM, D and G bands in the films of copolymerized products. The morphological features of the copolymerized products are different from the corresponding physical mixture of short SWNTs and PBO oligomers. In addition, the solubility of the copolymerized nanotubes changed before and after the reaction, which is indicative of the attachment of PBO oligomers to the SWNTs. We are studying the production of fibers from copolymers **12** and **13** and will report on the results in a future publication.

Acknowledgment. Financial support for this work was provided by the Air Force Office of Scientific Research (Grant FA9550-05-1-0152). We thank Dr. Matteo Pasquali for helpful discussions.

Supporting Information Available: Synthetic procedure for **7** and AFM images of dodecyl alkylated SWNTs before and after cutting, and short SWNTs before (**2**) and after (**10**) sidewall functionalization by sulfonated aryl groups. This material is available free of charge via the Internet at http://pubs.acs.org.

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