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Addition of Carbon Radicals Generated from Organic Peroxides to Single Wall Carbon Nanotubes

Polona Umek,*,†,‡ Jin Won Seo,† Klara Hernadi,§ Ales Mrzel,‡ Peter Pechy,|| Dragan D. Mihailovic,‡ and László Forró†

Institute of Physics of Complex Matter, Faculty of Basic Sciences, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland, Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia, Department of Applied and Environmental Chemistry, University of Szeged, H-6720 Szeged, Rerrich B. tér 1, Hungary, Institute of Molecular and Biological Chemistry, Faculty of Basic Sciences, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

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Single wall carbon nanotubes (SWNT) were functionalized via addition of carbon radicals, which were generated by thermal decomposition of diacyl and dibenzoyl peroxides. Reaction products were investigated with TEM, Raman scattering, TGA, UV−Visible spectroscopy, FTIR, and ^{1}H NMR. In Raman spectra of functionalized SWNT materials one of the radial breathing modes with a maximum at 260 cm^{-1} diminished completely. At the same time, the intensity ratio between the G- and D-bands decreased in comparison to that in the spectrum of raw SWNT material. From TGA measurements we conclude that SWNTs were derivatized up to 2.9−6.1 wt. % with functionalizing moieties. The loss of van Hove singularities in UV−Visible spectra of functionalized SWNTs also indicates a covalent modification of SWNTs.

Introduction

Single wall carbon nanotubes (SWNTs) exhibit many unique mechanical[1] and electrical properties,[2,3] which depend on their diameter, chirality, and orientation. Because of their extraordinary mechanical properties (strength and flexibility) SWNTs, like conventional fibers, may be used as a reinforcing material in a polymer matrix to form advanced nanocomposite materials.[4] The main reason that progress in this field of SWNT research has been limited up to now is the smooth surface of SWNTs, which leads to very weak adhesion between nanotubes and polymer matrix.[5,6] If functionalized nanotubes would be in the composite instead of the as-produced SWNTs, the interaction between nanotubes and polymer matrix could be significantly improved.

First attempts in functionalization of carbon nanotubes were limited to a few reactions of oxidation with different oxidants,[7,8,9] which resulted in opened and shortened nanotubes. After this so-called acidic treatment, carboxylic groups are found on open edges and also on places where five- or seven-membered rings existed.[10] With further functionalization of carboxylic groups the disperasability of carbon nanotubes (CNTs) in different solvents was improved,[11,12] but to achieve good incorporation of modified CNTs into the polymer matrix the functional moieties should be more uniformly attached to the sidewalls of CNTs.

Up to now several derivatization approaches on the sidewalls of SWNTs have been successful, such as hydrogenation via Birch reduction,[13] fluorination,[14] 1,3-dipolarcyclo addition of azomethine ylides,[15] ozonization,[16] and electrochemical reduction of aryl diazonium salts.[17,18] Addition of radicals generated in situ from

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* To whom correspondence should be addressed. E-mail: polona.umek@epfl.ch or polona.umek@ijs.si.

† Institute of Physics of Complex Matter, Swiss Federal Institute of Technology.

‡ Jozef Stefan Institute.

§ University of Szeged.

|| Institute of Molecular and Biological Chemistry, Swiss Federal Institute of Technology.

(1) Wong, W. E.; Sheehan, P. E.; Lieber, C. M. *Science* **1997**, *277*, 1971.

(2) Saito, R.; Fujita, M.; Dai H.; Dresselhaus, G.; Dresselhaus M. S. *Phys. Rev. B* **1992**, *46*, 1804.

(3) Tans, S. J.; Devoret, M. H.; Dai H.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekker, C. *Nature* **1997**, *386*, 474.

(4) Collins, P. G.; Avourius, Ph. *Sci. Am.* **2000**, *283*, 38.

(5) Ajayan, P. M.; Stephen, O.; Colliex; C.; Trauth, T. *Science* **1994**, *265*, 1212.

(6) Lau, K.-T.; Hui, D. *Carbon* **2002**, *40*, 1597.

(7) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y.-S.; Lee, R. T.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253.

(8) Hwang, K. C. *J. Chem. Soc., Chem. Commun.* **1995**, 173.

(9) Rao, C. N. R.; Govindaraj, A.; Satishkumar, B. C. *J. Chem. Soc., Chem. Commun.* **1996**, 1525.

(10) Hirsh, A. *Angew. Chem.-Int. Ed.* **2002**, *41*, 1853.

(11) Sun, Y,-P.; Huang, W.; Lin, Y.; Fu, K.; Kitaygorodskiy, A.; Riddle, L. A.; Ju, Y. J.; Caroll, D. L. *Chem. Mater.* **2001** *13*, 2864.

(12) Hamon, A. M.; Chen, J.; Hu, H.; Chen, Y.; Itkis, M. E.; Rao, A. M.; Ecklund, P. C.; Haddon, P. C. *Adv. Mater.* **1999** *11*, 834.

(13) Pekker, S.; Salvetat, J.-P.; Jaakab, E.; Bonard, J.-M.; Forro L. *J. Phys. Chem B* **2001**, *105*, 7938.

(14) Mickelson, E. T.; Huffman, C. B.; Rinzler, A. G., Smalley, R. E.; Hauge, R. E.; Margrave, J. L. *Chem. Phys. Lett.* **1998**, *296*, 188.

(15) Georgakilas, V.; Kordatos, K.; Prato, M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760.

(16) Cai, K.; Bahr, J. L.; Yao, Y.; Tour, J. M. *Chem. Mater.* **2002**, *14*, 4235.

(17) Kooi, S. E.; Sclecht, U.; Burghard, M.; Kern, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1353.

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diazonium salts also yielded functionalized SWNTs.[19] Recently a new approach for functionalization of SWNTs with carbon radicals was reported by Dyke and Tour.[20] The approach itself is very promising for a large-scale functionalization of SWNTs because the reaction itself is preformed without any solvent.

In general, carbon radicals may be formed photochemically, thermally, in oxidation/reduction reactions by inorganic ions resulting in single electron transfer, and by electrolysis. For the thermal generation of carbon radicals, different precursors can be used, such as diacyl peroxides, benzoyl peroxides, t-butyl esters of peroxy compounds, aza compounds, and N-nitrozoanlilides. When the radicals are generated from organic peroxides, the reaction pathway and it's kinetic depend on reaction conditions such as solvent and temperature and also peroxides used as a source of radicals.[21,22]

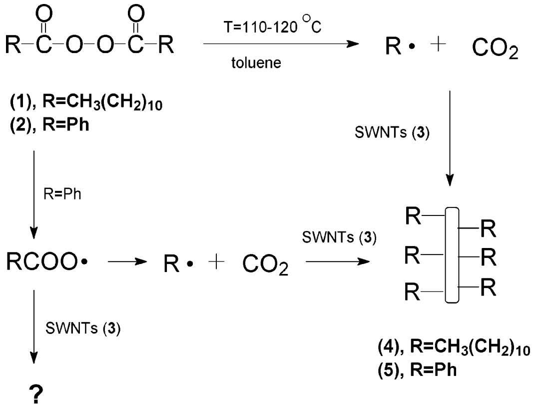
Here in this paper we present a new approach for addition of carbon radicals to SWNTs. Carbon radicals were generated by thermal decomposition of diacyl and dibenzoyl peroxides. Side product of the thermal decomposition using this kind of organic peroxides is CO_2, which makes the reaction very useful for large-scale functionalization of SWNTs.

Experimental Section

SWNTs (12.5 mg, origin HiPco, **3**) were dispersed in 15 mL of toluene with the help of an ultrasonic bath (5 min). Separately, 56.1 mg of lauroyl peroxide (**LP, 1**) was dissolved in 20 mL of toluene, and this was added to the SWNTs dispersed in toluene. The heterogeneous mixture was heated in an oil bath to the boiling point of toluene. After 3 h another portion of **LP** (56.1 mg) was added to the reaction mixture, and after 7 h the reaction was stopped. In the case of addition of phenyl radicals, 12.7 mg of SWNTs was dispersed in 20 mL of toluene. In addition to this dispersion, a solution of 50 mg of dibenzoyl peroxide (**DBP, 2**) in 20 mL of toluene was added and the heterogeneous mixture was also heated on the oil bath to the boiling point of toluene as described above. Subsequently, after 3 h, and again after 6 h, portions of **DBP** (50 mg) were added to the reaction mixture. Overall the reaction was stopped after 9 h. In both cases, the reaction mixture was cooled to room temperature and filtered. The black residue on the filter was washed with toluene and diethyl ether and later dried in a vacuum.

The isolated materials were characterized with transmission electron microscopy (TEM, Philips CM-20, 200 kV), infrared spectroscopy (FTIR, FTS 7000 Series), Raman scattering, proton nuclear magnetic resonance (^{1}H NMR, Bruker Avance DRX600AV), UV−Visible spectrometer (Varian CARY 50), and thermo gravimetric analysis (TGA, Derivatograph-Q). Samples for TEM were prepared by dispersion of material in methanol with the help of an ultrasonic bath. Raman scattering experiments were preformed at ambient conditions using argon excitation line (514.5 nm). The spectrometer was equipped with a SPEX triplemate/CCD detector. TGA analyses were preformed in nitrogen flow with a heating rate of 5 °C/min. Samples for characterization with the UV−Visible spectrometer were dispersed in dimethylformamide with help of an ultrasonic bath.

Scheme 1



Results and Discussion

As shown in Scheme 1 the reaction pathway of thermal decomposition of **LP** (**1**) and **DBP** (**2**) results in generation of undecyl and phenyl radicals. For the decomposition of benzoyl peroxide, initial homolysis of the O−O bond leads to benzoyl radicals, which fragment to yield phenyl radicals and carbon dioxide.[21,22] Formed benzoyl radicals are very reactive species and they have a high tendency to react with unsaturated systems, and because of this it was expected that both sort of radicals generated from **DBP** will readily functionalize SWNTs.

LP and **DBP** were added to the reaction mixture so that the molar ratio between generated radicals and carbon in raw HiPco SWNT material was 0.7 for added **LP** and 1.2 for added **DBP**, respectively. For addition of radicals generated from organic peroxides, no demanding chemical equipment is needed. Also, the isolation of functioanlized material is simple because once the reaction is finished there is no need for extra separation of either side-products or nonreacted species from the reaction mixture.

TEM images of raw HiPco SWNTs (**3**) and SWNT + DBP (**5**) are compared in Figure 1. Both samples contain dense bundle structure but the average bundle diameter is in the case of the functionalized sample smaller than that in the raw HiPco material. The second difference observed from these two images, is the bundle structure itself. The TEM image of raw SWNT material (Figure 1a) illustrates characteristic line contrast of SWNTs and clearly indicates a bundle structure, which is not so clear in the case of TEM images of product **5.** The same was observed in the TEM images of material **4**, which are not shown here. When the materials **4** and **5** were prepared for TEM with the glue technique (this means that the samples were not dispersed in any solvent before they were deposited on a TEM grid) the bundles were more covered with amorphous material which indicates that presence of amorphous material is not due to TEM grid preparation.

Before and after addition of undecyl and phenyl radicals SWNTs were characterized by Raman scattering. Figure 2a shows Raman spectra of **3**, **4**, and **5** in the high-frequency range. Spectra of **4** and **5** are normalized to the intensity of the D-band (1331 cm^{-1}) in the spectrum of raw SWNT material (**3**). The effect of functionalization is a lowered ratio of intensities between G- and D-bands in the spectra of SWNT materials **4** and **5**. In these two cases this ratio de-

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(18) Bahr, J. L.; Yang, J.; Kosnykin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536.

(19) Bahr, J. L.; Tour, J. M. *Chem. Mater.* **2001**, *13*, 3823.

(20) Dyke, C. A.; Tour, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 1156.

(21) Patai, S. Ed. *The Chemistry of Peroxides*; Wiley Interscience: New York, 1983.

(22) Chateaneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877.

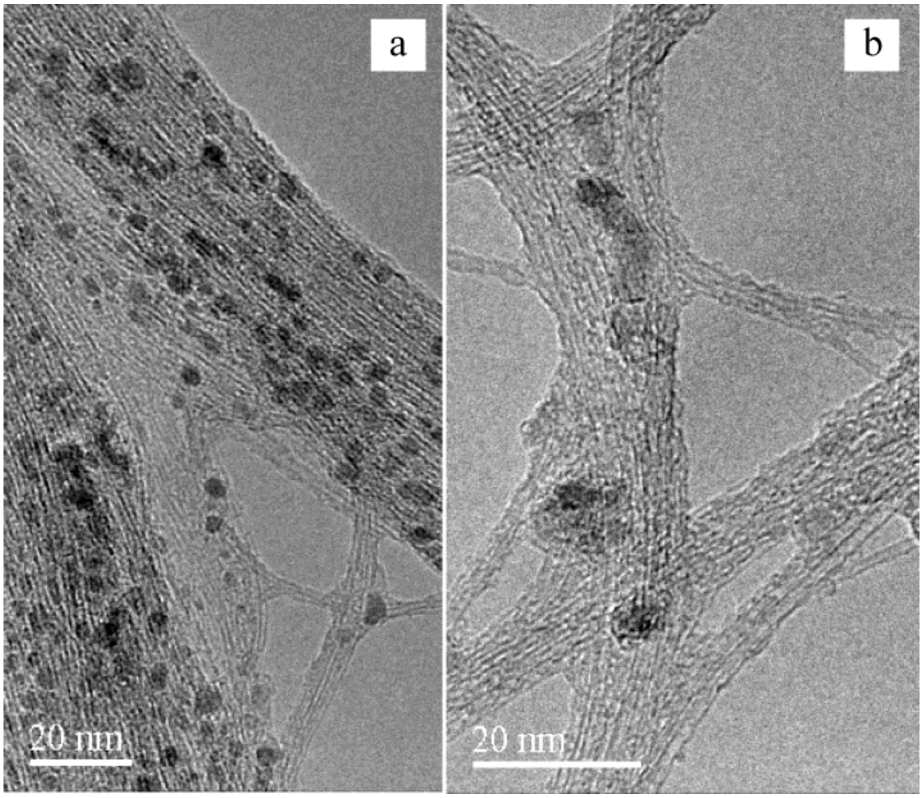

Figure 1. TEM images of (a) raw SWNT material (**3**), and (b) SWNT + DBP (**4**).

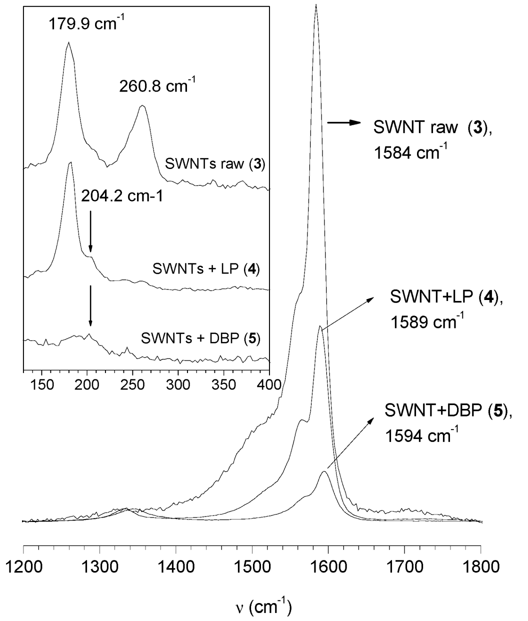

Figure 2. Raman spectra of SWNTs (**3**), SWNTs + LP (**4**), and SWNTs + DBP (**5**). Raman spectra in Figure a were normalized to the intensity of the D-band in spectrum of **1**. The inset shows spectra of **3**, **4**, and **5** in low-energy spectral range. The 514.5 nm Ar laser line was used for the excitation.

creased by half and by approximately 9 times, respectively. The lowered ratio in intensities between these two bands can be interpreted as an indication for increased number of sp^3 hybridized carbon atoms[18,23] in functionalized SWNT material and also as an indication that the amount of SWNTs in the investigated material have been decreased.[24–26] Another very interesting feature is that the maximums of G-bands were shifted to higher frequencies for functionalized materials; to be precise, they shifted to 1589 cm^{-1} and 1594 cm^{-1} for products **4** and **5**, respectively. In the spectrum of material **5** the D-band also shifted for 12 cm^{-1} to higher frequencies, whereas the D-band in the spectrum of material **4** did not shift. Moreover, the shoulder in the G-band (at around 1564 cm^{-1}) became more pronounced in the product **4**.

The inset in Figure 3a shows the Raman spectra of SWNT materials **3**, **4**, and **5** in the low-frequency range. The band which appears in this range is called radial breathing mode (RBM) and its exact position depends on the diameter of the nanotubes[27,28] and also on the size of the bundles.[29] In the spectrum of raw SWNT material two RBMs are observed: one with a maximum at 179.9 cm^{-1} and another at 260.8 cm^{-1}. Although the RBMs in the spectrum of product **5** are completely diminished, one RBM is still clearly visible in the spectrum of **4** with a maximum at 179.9 cm^{-1}. This observation is in agreement with the prediction and observations that SWNTs with smaller diameters are

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[23] Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *313*, 91.

[24] Marcoux, P. R.; Schreiber, J.; Batail, P.; Lefrant, S.; Renouard, J.; Jacob, G.; Albertini, D.; Mevellec J.-Y. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2278.

[25] Umek, P.; Vrbanic, D.; Remskar, M.; Mertelj, T.; Venturini, P.; Pejovnik, P. Mihailovic, D. *Carbon* **2002**, *40*, 2582.

[26] Holzinger, M.; Hirsch, A.; Bernier, P.; Duesberg, G. S.; Burghard, M. *Appl. Phys. A* **2000**, *70*, 599.

[27] Tohji, K.; Goto, T.; Takahashi, H.; Shinoda, Y., Shimizu, N.; Jeyadevan, B. *Nature* **1996**, *383*, 679.

[28] Rao, A. M.; Richter, E.; Bandow, S.; Chase, B.; Eklund, P. C.; Williams, K. A.; Fang, S.; Sabuaswamy, K. R.; Menon, M.; Thess, A.; Smalley, R. E.; Dresselhaus, G.; Dresselhaus, M. S. *Science* **1997**, *275*, 187.

[29] Zhou, W.; Ooi, Y. H.; Russo, R.; Papanek, P.; Luzzi; D. E.; Fischer, J. E.; Bronikowski, M. J.; Willis, P. A.; Smalley, R. E. *Chem, Phys. Lett.* **2001**, *350*, 601.

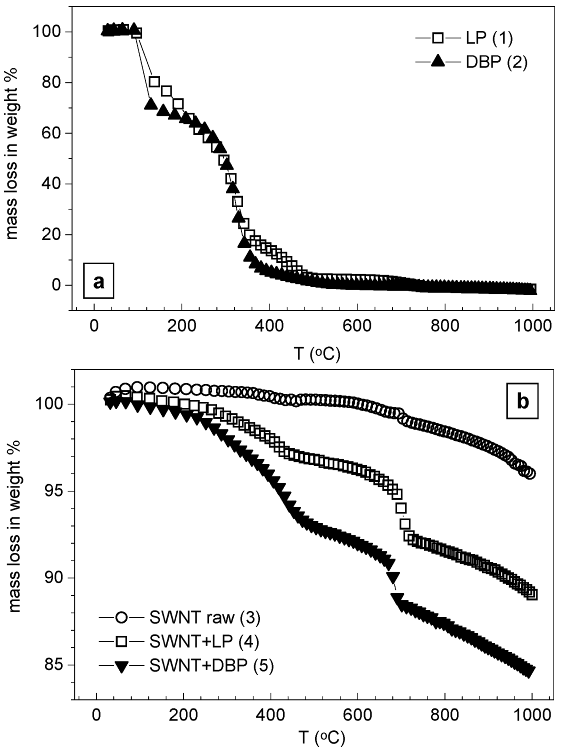

Figure 3. TGA results for (a) lauroyl peroxide (LP, **1**) and dibenzoyl peroxide (DBP, **2**); and (b) SWNTs raw (**3**), SWNTs+LP (**4**), SWNTs+DBP (**5**). Measurements were performed in nitrogen flow with a heating rate of 5 °C/min.

more reactive[23,28,30,31] but rather in contradiction with observations reported by Bahr et al.[18] and Marcoux et al.[23] In those two papers, the RBMs in Raman spectra corresponding to SWNTs with a larger diameter disappeared as a result of functionalization. Nevertheless, the difference of Raman spectra in low-energy region observed in products **4** and **5** suggests that the radicals, which were generated by thermal decomposition of **LP**, react more readily with the SWNTs of smaller diameter.

From TGA data of **LP** and **DBP** (Figure 3a) a total weight loss of 100% was derived for both peroxides when these were heated to 1000 °C in nitrogen flow. The weight loss occurring at low temperatures (80−130 °C) corresponds to the mass of CO_2, which was formed during the thermal decomposition of peroxy compounds **1** and **2** (Scheme 1). The second weight loss occurred in the temperature area between 230 and 400 °C, and it can be explained by the total decomposition of alkyl chains and phenyl rings. In contrast, Figure 4 b summarizes TGA results for SWNTs raw (**3**), and products **4** and **5**. For raw SWNTs, the weight loss during the heating was rather continuous with a total weight loss of ca. 4%. A small, hardly observable drop in mass can be seen at 701 °C. For functionalized SWNTs, the total weight losses in the whole heating range are about 11% and 15% in the case of products **4** and **5**, respectively. Their TGA curves reveal two drops in mass: the first occurs at temperature ranges between 240 and 440 °C and 230−480 °C for the products **4** and **5**, respectively, and corresponds to decomposition of alkyl chains and phenyl rings covalently attached to the side wall of SWNTs. For the product **4** this drop in mass corresponds to 2.9 wt. % of the whole analyzed material, whereas for the product **5**, 6.1 wt. % is estimated. This, first drop is rather smooth compared to the second one, which is abrupt and appears at around 701 °C. For the product **5** this second drop of mass shifted to lower temperatures, exactly to 683 °C, which can be due to the higher functionalization and also more damaged backbone structure of SWNTs, which is in agreement with Raman spectra. In our case, the amount of functional moieties attached to SWNTs obtained by addition of radicals is smaller than the one reported by Bahr and Tour[19] because the ratio of moles of generated radicals from **LP** and **DBP** to moles of carbon in raw HiPco material was smaller.

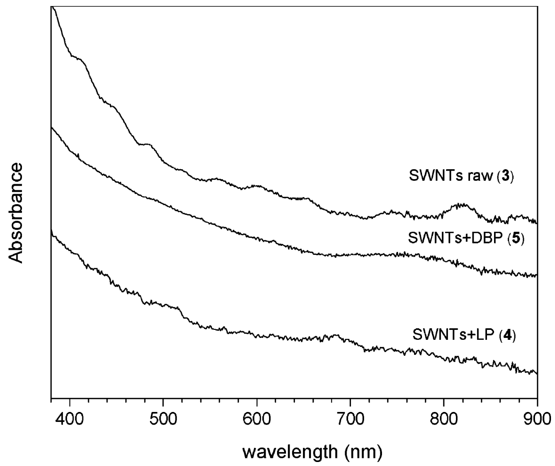

Figure 4. UV−Visible spectra of raw SWNTs (**3**), SWNTs+LP (**4**), and SWNTS+DBP (**5**). Spectra were measured in dimethylformamide between 400 in 900 nm.

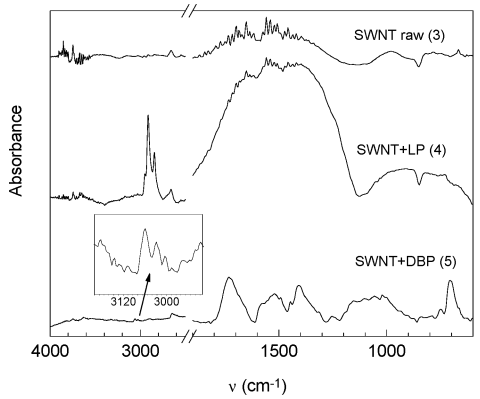

Figure 5. FTIR spectra of SWNTs raw (**1**), SWNTs+LP (**4**), SWNTS+DBP (**5**) measured in the range from 4000 to 700 cm^{-1}.

The UV−Visible spectra of raw SWNTs (**3**) and products **4** and **5** are shown in Figure 4. Findings are the same as those previously reported for functionalized SWNTs.[16,18−20] The absorption spectrum of product **5** shows a complete loss of the van Hove singularities what indicates covalent modification of the nanotubes. In the case of product **4** the absorption spectra still retains some visible features, which are less pronounced than those in the spectrum of **3**. This latter finding is in good agreement with Raman measurements and TGA results.

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(30) Rao, M. A.; Chen, J.; Richter, E.; Uschlecht, U.; Eklund, P. C.; Haddon, R. C.; Venkateswaran, U. D.; Kwon, Y.-K.; Tomanek, D. *Phys. Rev. Lett.* **2001**, *86*, 3895.

(31) Chen, Y.; Haddon, R. C.; Fang, S.; Rao, A. M.; Eklund, P. C.; Lee, W. H.; Dickey, E. C.; Grulke, E. A.; Pendergrass, J. C.; Chavan, A.; Haley, B. H.; Smalley, R. E. *J. Mater. Res.* **1998**, *13*, 2423.

FTIR spectroscopy was also used for characterization of functionalized SWNT materials **4** and **5** (Figure 5). The spectrum of product **4** clearly indicates significant C−H stretching in the alkyl chains at ca. 2915 cm^{-1}. In the other parts of the FTIR spectra no other significant changes can be found, probably because of high molar absorbtivity of SWNTs.[19] In the spectrum of **5** more absorption bands can be seen. Above 3000 cm^{-1} a weak stretching for sp^2 hybridized C−H bonds in aromatics rings (inset in Figure 4) is observed. At smaller wavenumbers a combination of two bands appears; the first and more intense one is found at 705 cm^{-1} and is accompanied by a less intense band at 750 cm^{-1}. This combination is typically found in FTIR spectra of monosubstituted benzenes. Regarding the pathway of thermal decomposition of **DBP** (Scheme 1) we expected that benzoyloxyl radical ($PhCO_2\bullet$) would react with SWNTs because aroyloxyl radicals add rapidly to unsaturated molecules.[21] In the spectrum of **5** (1730 cm^{-1}) a band is observed in the area where the stretching vibration of C═O bond appears. The stretching vibration of C═O group is always very intensivebut that is not the case for this band; because of this fact it cannot be confirmed that functional moieties attached to SWNTs contain ester groups.

In the ^1H NMR spectrum of **4**, which was recorded in $CDCl_3$, the peaks belonging to aliphatic protons were clearly visible between $\delta = 0.89$ and 1.38 ppm. Two triplets were observed: first for the terminal $-CH_3$ group in the alkyl chain, and the second for the $-CH_2-$ group, which are directly attached to the walls of SWNTs at 0.89 and 1.38 ppm, respectively. The signals belonging to the remaining protons in the alkyl chain were found between 1.27 and 1.33 ppm as a broad singlet. The ^1H NMR spectrum of SWNT + DBP (**5**) was recorded in d_6-DMSO. In this spectrum two broad singlets belonging to the phenyl protons were observed at $\delta = 7.46$ and 7.55 ppm in an intensity ratio of about 3 to 2. The peaks for protons in phenyl ring, which could be through carboxyl group covalently bonded to the sidewalls of SWNTs, were not observed. There are two reasons for this: first is that no benzoyl groups are attached to SWNTs and second is that the amount of attached benzoyl groups to sidewalls of SWNTs is very low.

In summary, we have shown that the addition of carbon radicals generated from diperoxy compounds is a reliable and easy way for functionalization of SWNTs. This is only the first step toward further derivatization of so-functionalized nanotubes because SWNTs functionalized with alkyl and phenyl moieties offer a wide variety of possible reactions for further functionalization. Functionalized SWNT materials exhibit better dispersability in organic solvents, which should also facilitate their incorporation into polymer matrix.

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