Nanotechnology

Polymer-Grafted Multiwalled Carbon Nanotubes through Surface-Initiated Polymerization**

D. Baskaran, Jimmy W. Mays, and Matthew S. Bratcher*

Extensive research is focused on surface modification of carbon nanotubes mainly to enhance their chemical compatibility and dissolution properties.[1–5] Previously, the covalent grafting of organic or polymeric molecules on to carbon nanotubes has been accomplished by the "grafting-to"

[*] Dr. D. Baskaran
Department of Chemistry
University of Tennessee
552 Buehler Hall, Knoxville, TN 37996 (USA)
Fax: (+1) 865-974-9304
E-mail: baskaran@novell.chem.utk.edu
Prof. J. W. Mays
Department of Chemistry
University of Tennessee
552 Buehler Hall, Knoxville, TN 37996
and
Chemical Sciences Division
Oak Ridge National Laboratory, Oak Ridge, TN 37831 (USA)
Dr. M. S. Bratcher
U.S. Army Research Laboratory
Weapons and Materials Research Directorate
AMSRL-WM-MA, APG, MD 21005 (USA)

[**] We acknowledge U.S. Army (DAAD19-01-2-002) and DOE (DE-AC05-00OR22725) for financial support. We also thank Dr. John Dunlap, University of Tennessee,for doing TEM and SEM images.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

  DOI: 10.1002/ange.200353329

technique by using esterification and amidation reactions.[1] However, the loss in conformational entropy of the polymer significantly suppresses chains from diffusing to and reacting with the carboxylic acid sites of single or multiwalled carbon nanotubes (SWNTs or MWNTs), which leads to inefficient grafting.

On the other hand, noncovalent functionalization methods, such as polymer wrapping and "pi–pi" stacking on the surface of carbon nanotubes, are difficult to correlate quantitatively with properties due to the presence of excess polymer and the slippage of stacked molecules.[2,6,7] Growth of polymer chains from covalently attached surface initiators by using the "grafting-from" strategy is the best way to produce polymer brushes on any surface. So far, silicon, gold, and clay surfaces have been used to grow polymers through surface-initiated polymerization (SIP).[8] Carbon nanotubes have nonreactive surfaces and, hence, they have not been used for SIP. Herein, we report the surface-initiated atom-transfer radical polymerization (ATRP) of styrene (S) and methylmethacrylate (MMA) from MWNTs. To our knowledge, SIP from MWNTs through a covalently attached initiator has not been previously attempted, and this is the first report that demonstrates the growth of homopolymers and block copolymers in levels up to 70 wt % from the surface of MWNTs.

We used surface-bound carboxylic acid groups (≈1 mol %) on MWNTs (NanoLab, Watertown, MA) to attach the ATRP initiator (**2**). Scheme 1 outlines the strategy used for growing polymer chains from the surface of MWNTs. First, the MWNTs treated with thionyl chloride (**1**) were reacted with excess hydroxyethyl-2-bromoisobutyrate (**2**) in toluene in the presence of triethylamine at 100 °C for 24 h under an atmosphere of pure nitrogen. The tubes were washed thoroughly with ethanol until the filtrate showed an absence of **2** by thin layer chromatography (TLC) and dried.

The attachment of **2** to the MWNTs to give **3** (Scheme 1) was confirmed from the characteristic C–H and carbonyl stretching vibrations centered at 2922 cm^{-1} and 1737 cm^{-1}, respectively in the FTIR spectrum. The quantity of the initiator attached to the surface was determined from the thermogravimetric analysis (TGA) of **3**, which showed a 6.3 % weight loss at 241 °C corresponding to the decomposition of the initiator fragments (Figure 1 A, b). The mole percent of the initiator ($[I]_{MWNT} = 0.36$ mol % with respect to carbon) on MWNT surface was calculated by using the weight % and the initiator fragment molecular weight (210 g mol^{-1}).[9]

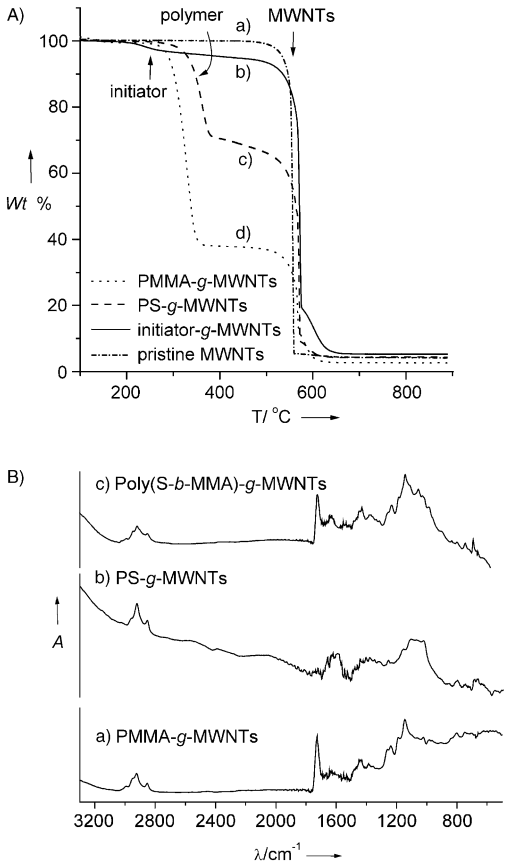
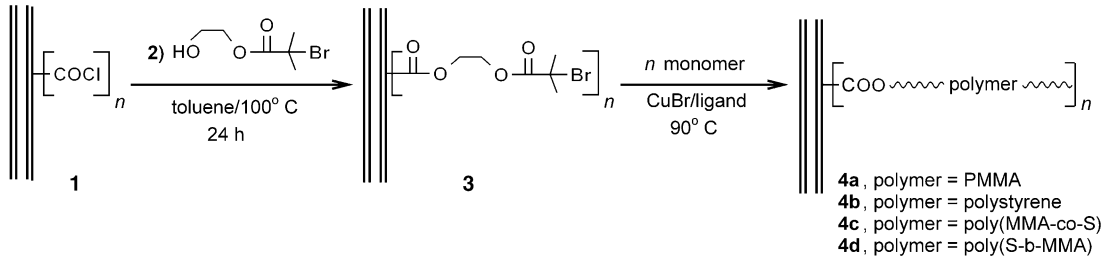


Figure 1. A) TGA of MWNTs recovered from the SIP after thorough washing with solvent; a) pristine MWNTs, b) initiator attached MWNTs, c) PS grown MWNTs (PS-*g*-MWNTs, Table 1, run 6), d) PMMA grown MWNTs (PMMA-*g*-MWNTs, Table 1, run 2). B) FTIR spectrum of various polymer grown MWNTs; a) PMMA-*g*-MWNTs (Table 1, run 1), b) PS-*g*-MWNTs (Table 1, run 5), c) P(S-*b*-PMMA)-*g*-MWNTs.

The SIP was performed in bulk by using known quantities of **3** in 1 mL of MMA or S in the presence of CuBr and pentamethyldiethylenetriamine (L) at a ratio of $[I]_{MWNT}$:[CuBr]:[L] = 1:1:2 at 90 °C for up to 24 h. After the polymerization, the heterogeneous reaction mixture was diluted with THF and the tubes were washed thoroughly with THF, then filtered (Whatman1) to remove soluble polymer. Washing was done until no polymer was found in the filtrate. The polymer functionalized MWNTs (**4**) were collected and dried under vacuum for 24 h at 40 °C. The yields



Scheme 1. Surface-initiated atom-transfer radical polymerization from MWNTs.

of **4** were greater than 100% (on the basis of **3**) indicating the presence of surface-grown polymer. The TGA analysis of **4a–d** in the presence of air showed two major decompositions in the temperature range at 225–400 °C and 500–625 °C corresponding to surface grown polymer and MWNTs respectively (Figure 1A, c and d). The surface grown poly (methyl methacrylate) (PMMA) decomposes at $T_d \approx 330$ °C and poly(styrene) (PS) decomposes at $T_d \approx 360$ °C (Table 1). The

Table 1: Surface-initiated poly(methyl methacrylate) and poly(styrene) from MWNTs.[a]

Run	$[C]_{MWNT}$ [mmol][b]	$[I]_{MWNT}$[b] [10^3 mmol]	t [h][c]	Polymer-*g*-MWNTs		
				%[d] of polymer	T_d[d] of polymer	T_g[e] of polymer
Monomer-methyl methacrylate (9.36 mmol)						
1	1.75	6.3	10	58.9	329	125.5
2	1.00	3.6	20	63.8	331	126.9
3	1.10	3.9	24	70.9	335	128.8
Monomer-styrene (8.73 mmol)						
4	0.48	1.7	24	18.3	349	110.4
5	0.70	6.1	24	23.9	358	107.0
6	5.00	16.0	20	33.0	362	106.5
7[f]	2.50	8.0	20	24.6	360	–

[a] ATRP condition: $[I]_{MWNT}$:[CuBr]:[L] = 1:1:2. SIP of MMA at 90 °C and S at 100 °C. [b] $[C]_{MWNT}$ = (grams of MWNTs/12) and total initiator present in the reaction, $[I]_{MWNT}$ = {(mol% of initiator by TGA/100)/12} × grams of **3**. [c] Bulk polymerization reaction time. [d] wt% of attached polylmer and the decomposition temperature determined from TGA curves. [e] obtained from DSC second heating. [f] copolymerization from a mixture of monomers.

FTIR spectrum of MWNTs recovered from the surface-initiated MMA polymerization (**4a**, PMMA-*g*-MWNTs) showed characteristic vibration bands for PMMA (in KBr: νCH_s at 2922, $\nu C{=}O_s$ at 1725, $\nu C{-}H_b$ at 1440 cm^{-1}; Figure 1B, a). Similarly the tubes recovered from the styrene polymerization (**4b**, PS-*g*-MWNTs) exhibited vibration bands characteristics to PS (in KBr: aromatic $\nu C{-}H_s$ at 3025, $C{-}H_v$ at 2922, 1662, 1028, and 694 cm^{-1}; Figure 1B, b). The amount of PMMA covalently attached in **4a** determined by TGA is as high as 70.9 wt% and in the case of **4b**, it varies from 18 to 33 wt% depending on the initiator concentration in **3** (Table 1). Existence of a correlation between $[I]_{MWNT}$ and the amount of polymer present on the surface shows that it is possible to control the molecular weight of the growing polymer chain. It was found that samples, **4a–d**, exist as lumpy aggregates, and after breaking the lumpy aggregates into powder they dissolve freely in organic solvents. Although the polymer growth from the surface was expected to break up the bundles in to either individual or smaller aggregates, interentanglement of the growing chains with tubes led to lumpy aggregates during polymerization. Dispersion of aggregated nanotubes into an organic solvent before functionalization was very difficult even after the nanotubes have been subjected to sonication. However, after functionalization, the tubes were soluble in THF, chloroform, dichloromethane, and toluene with mild sonication (1–2 min; see the Supporting Information). The UV/Vis spectrum of **4a–d** in $CHCl_3$ shows featureless absorbance starting from 290 nm decreasing monotonously up to 900 nm, which is characteristic of the dissolved MWNTs.[1b] The intensity of the absorbance is inversely proportional to the amount of polymer present in the tubes (see Supporting Information).

The Raman spectrum of **4a** (run 3) and **4b** (run 6) samples shows characteristic tangential-mode peaks at ≈ 1566 cm^{-1} and a disorder-band peak at ≈ 1342 cm^{-1}.[10] These peaks are similar to the ones observed in pristine MWNTs except that the ratio of the peak intensity changes in **4a** and **4b** due to polymer grafting (Figure 2A). The presence of surface-

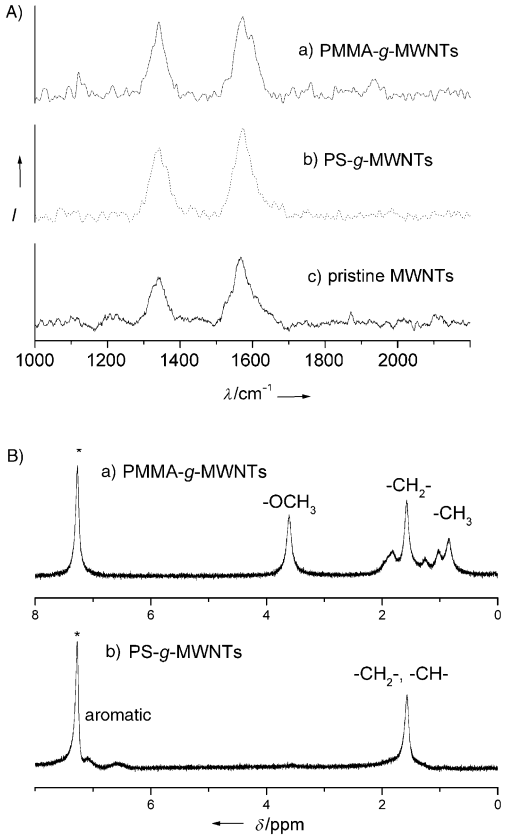


Figure 2. A) Raman spectra (514.5 nm excitation) of polymer grafted MWNTs; a) PMMA grown MWNTs (PMMA-*g*-MWNTs, **4a**, run 3), b) PS grown MWNTs (PS-*g*-MWNTs, **4b**, run 6), c) pristine MWNTs. B) ^{1}H NMR (300 MHz) spectrum polymer grafted MWNTs in $CDCl_3$; a) PMMA-*g*-MWNTs (**4a**, run 3) and b) PS-*g*-MWNTs (**4b**, run 6). The star indicates solvent signal.

initiated polymer was clearly seen in ^{1}H NMR of **4a** and **4b** (Figure 2B). The observed proton signals are entirely due to hairy polymer grown from MWNTs. However, considerable line broadening was observed as a result of the present of paramagnetic substances in the MWTNs.

A control experiment was also carried out under identical conditions with S (1 mL) and MWNTs (20 mg) that contained no initiator functionality. After 24 h, no polymer was found in the reaction solution and the washed MWNTs had no major polymer decomposition at ≈ 360 °C, thus confirming that the polymer formation from **3** is only from the initiator sites anchored on the surface of MWNTs (see Supporting Information).

Since the tubes are not monodisperse in terms of their length and can contain different levels of initiator functionality, some portion of the samples of **4a–d** is soluble in monomer solution due to a higher percentage of grafting especially for shorter tubes. Such a portion of polymer-*g*-MWTNs becomes separated while washing with THF. The recovered polymers appeared slightly grayish indicating the presence of MWNTs (0.1–0.2 wt% by TGA) and analysis by gel-permeation chromatography (GPC) showed very-large molecular-weight species ($300 < \bar{M}_w < 1000\ \mathrm{kg\,mol^{-1}}$) with broad distribution ($1.4 < \bar{M}_w/\bar{M}_n < 3$; $\bar{M}_w$ is the mass-average molar mass, $\bar{M}_n$ is the number-average molar mass) due to the presence of grafted tubes.

More convincingly, the samples (**4a–d**) had a discontinuous thin amorphous layer (≈2–5 nm) in TEM and SEM images (Figure 3). As expected,[5] a large increase in the glass

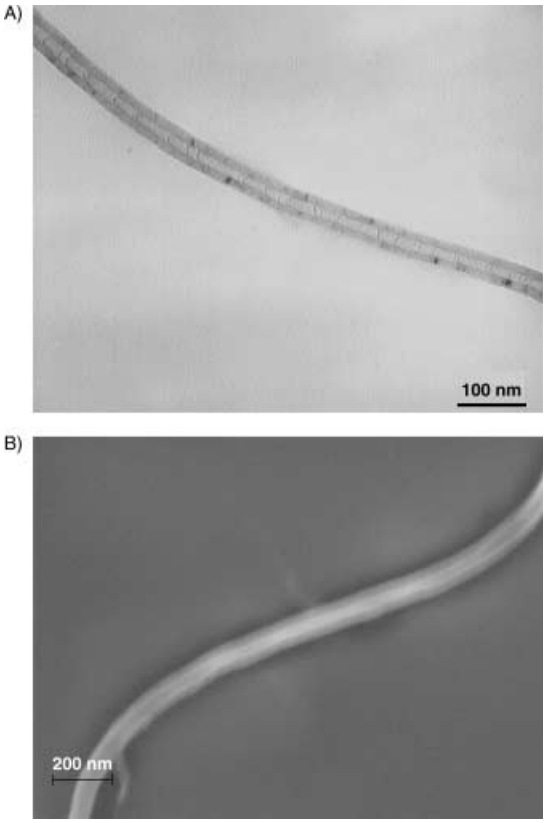


Figure 3. A) TEM and B) SEM images of PMMA-*g*-MWNTs exhibiting a fine coating of PMMA around the tubes (Table 1, run 2).

transition temperature (T_g) of the grafted PMMA and PS ($15 < \Delta T_g < 30\,^{\circ}\mathrm{C}$) was observed due to tethering (Table 1 and Supporting Information). Surface-anchored poly(S-*co*-MMA), **4c** was also synthesized by using copolymerization of a mixture of monomers (Table 1, run 7). The samples (**4a–d**) carry alkyl bromide at the dangling chain-ends. Thus, they can be used as MWNT-bound macroinitiators for block copolymerization. Accordingly, 10 mg of **4b** (Table 1, run 6) with 33 wt% PS was taken in an ampoule and mixed with MMA (1 mL) along with a solution of CuBr:L (1:2). After the SIP at 90 °C for 24 h and subsequent washing procedure, MWNTs grafted with poly(styene-*b*-methyl methacrylate) were obtained as a mixture of tubes in a gray sponge. It showed 63% wt loss in TGA at ≈335 °C, which is 29 wt% higher than the precursor and the FTIR spectrum shows the presence of carbonyl stretching at 1726 $\mathrm{cm^{-1}}$ along with other characteristic bands for PS and PMMA (Figure 1B, c; see the Supporting Information for TGA results). To understand the molecular characteristics of the grafted polymer, the polystyrene connected through ester linkage in **4b** (run 5) was cleaved by using KH in THF and analyzed by GPC.[11] The molecular weight of the detached PS was $\bar{M}_w = 1150\ \mathrm{g\,mol^{-1}}$ and the polydispersity, $\bar{M}_w/\bar{M}_n = 1.34$. Similarly, PS hydrolysized from run 6 gave $\bar{M}_w = 1600\ \mathrm{g\,mol^{-1}}$ with $\bar{M}_w/\bar{M}_n =$ 1.1(supporting information).

In conclusion, ATRP initiators anchored to MWNTs have been successfully used in the surface-initiated polymerization of S and MMA. Homo, block, and copolymer brushes consisting of PS and PMMA chemically bound on the surface of MWNTs at levels up to 70 wt% have been synthesized and thoroughly characterized. The SIP with other monomers, kinetics of the polymerization and the solution properties of polymer-*g*-MWNTs are under investigation.

Experimental Section

MWNTs (Nanolab, Watertown, MA) containing ≈1 mol% carboxylic acid groups were used for the study. The tubes were purified by washing several times with THF and finally with water and dried under vacuum. The tubes had about 4–6 wt% iron catalyst as impurity. The amount of acid functionality was confirmed by titration, XPS, and prompt-gamma methods. CuBr (99.999%, Aldrich) was used as received. Pentamethyldiethylene triamine (L; Aldrich) was distilled over CaH_2 under vacuum. Hydroxyethyl-2-bromoisobutyrate was synthesized by using 2-bromoisobutyrylbromide with an excess ethylene glycol in dichloromethane in the presence of triethylamine. Methyl methacrylate and styrene (Aldrich) monomers were purified by distillation over CaH_2 and stored under a pure N_2 atmosphere in a refrigerator. Dichloromethane (Fisher) was distilled over CaH_2. Tetrahydrofuran (THF, Fisher) was distilled over Na/K alloy on a vacuum line. Prepurifed toluene was distilled in the presence of a small amount of styryllithum anion just before use.

Attachment of initiator on the surface of MWNTs (**3**): A sample of MWNTs (200 mg) was refluxed with 50 mL of thionyl chloride at 70 °C. After 24 h, the excess thionyl chloride was removed under vacuum. The activated MWNTs (MWNT–COCl) were washed with anhydrous THF and dried under vacuum. Hydroxyethyl-2-bromoisobutyrate (2.3 mL) in toluene (5 mL) was added to the flask that contained MWNT–COCl and the reaction was stirred at 100 °C for about 24 h under a pure N_2 atmosphere. After the reaction had finished, the solvent was completely removed under vacuum, the tubes were washed several times with ethanol (250 mL) and filtered. The initiator-attached tubes were dried at 40 °C for 10 hr under vacuum. FTRI (KBr): $\tilde{\nu} = 2958$ (C-H stretching), 2922 (C-H stretching), 2854 (C-H stretching), 1737 (C=O stretching), 1460 (C-H bending), 1260, 800 $\mathrm{cm^{-1}}$ (other CH vibrations). TGA: 6.3% weight loss at 240 °C.

Surface-initiated atom transfer styrene radical polymerization by using **3**: In a typical polymerization, **3** (20.5 mg, $[I]_{MWNT} = 6.1 \times 10^{-6}$ mol) was placed in a clean glass ampoule attached with a septum adaptor connected to both nitrogen and a vacuum system. Subsequently, styrene (1 mL) and a solution of CuBr (0.1 mL 6.1×10^{-6} mol) and ligand ([CuBr]:[L] = 1:2) in toluene were added into the ampoule with a syringe under N_2. Then the entire solution was degassed four times and sealed off under vacuum. The sealed

ampoule was placed in an oil bath that was maintained at 100 °C and the reaction stirred for 24 hr. It was noticed that after 4 h the polymerization solution with tubes became viscous and the tubes stuck to the walls of the ampoule. After 24 h, the reaction was quenched by cooling with liquid N_2 and the ampoule was opened. The heterogeneous polymerization solution was diluted with THF (30 mL) and kept stirring in a round bottom flask for few hours to dissolve the soluble polymer. The supernatant THF was filtered by using Whatman1 filter paper and washing with THF; this washing was repeated until the filtrate contained no polymer. The polymer grafted MWNTs (**4b**) were recovered as lumpy aggregates and dried at 40 °C for 24 h under dynamic vacuum (yield 25 mg, 121 % on the basis of the precursor MWNTs). The filtrate that contained the slightly grayish polymer (≈13 % on the basis of styrene) was recovered by precipitation in methanol.

Hydrolysis of poly(styrene) from poly(styrene)-*g*-MWNTs (run **6**): In a typical hydrolysis reaction, 8 mg of KH was taken in 3 mL of THF and mixed with a dry sample of poly(styrene)-*g*-MWNTs (25 mg). The solution was stirred at 50 °C under nitrogen for 10 h. The resulting black solution was quenched with a small amount of methanol and the entire solution was filtered with a 0.2 μm Teflon membrane before being subjected to GPC analysis. The cleaved polymer recovered from the THF solution was 6 mg (yield 75 % on the basis of wt % of PS in the TGA of the precursor).

Supporting Information available: UV/Vis and DSC **4a**–**b**, GPC of cleaved polymer, TGA of P(S-*b*-MMA)-*g*-MWNTs.

Received: November 13, 2003 [Z53329]

Keywords: carbon · copolymerization · nanotubes · polymers

[1] a) J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund, R. C. Haddon, *Science* **1998**, *282*, 95 – 98; b) Y.-P. Sun, K. Fu, Y. Lin, W. Huang, *Acc. Chem. Res.* **2002**, *35*, 1096 – 1104.

[2] A. Star, J. F. Stoddart, D. Steuerman, M. Diehl, A. Boukai, E. W. Wong, X. Yang, S.-W. Chung, H. Choi, J. R. Health, *Angew. Chem.* **2001**, *113*, 1771 – 1775; *Angew. Chem. Int. Ed.* **2001**, *40*, 1721 – 1725.

[3] V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger, A. Hirsch, *J. Am. Chem. Soc.* **2002**, *124*, 2002.

[4] C. A. Dyke, J. M. Tour, *Nano Lett.* **2003**, *3*, 1215 – 1218.

[5] a) G. Viswanathan, N. Chakrapani, H. Yang, B. Wei, H. Chung, K. Cho, C. Y. Ryu, P. M. Ajayan, *J. Am. Chem. Soc.* **2003**, *125*, 9258 – 9259; b) S. Banerjee, M. G. C. Kahn, S. S. Wong, *Chem. Eur. J.* **2003**, *9*, 1898.

[6] M. J. O'Connell, P. J. Boul, L. M. Ericson, C. B. Huffman, Y. Wang, E. H. Haroz, C. Kuper, J. M. Tour, K. D. Ausman, R. E. Smalley, *Chem. Phys. Lett.* **2001**, *342*, 265 – 271.

[7] a) R. J. Chen, Y. Zhang, D. Wang, H. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 3838 – 3839; b) F. J. Gomez, R. J. Chen, D. Wang, R. M. Waymouth, H. Dai, *Chem. Commun.* **2003**, 190 – 191.

[8] a) M. D. K. Ingall, S. J. Joray, D. J. Duffy, D. P. Long, P. A. Bianconi, *J. Am. Chem. Soc.* **2000**, *122*, 7845 – 7846; b) T. Werne, T. E. Patten, *J. Am. Chem. Soc.* **1999**, *121*, 7409 – 7410; c) J.-B. Kim, M. L. Bruening, G. L. Baker, *J. Am. Chem. Soc.* **2000**, *122*, 7616 – 7617; d) Q. Zhou, X. Fan, C. Xia, J. W. Mays, R. Advincula, *Chem. Mater.* **2001**, *13*, 2465; e) Q. Zhou, S. Wang, X. Fan, R. Advincula, J. W. Mays, *Langmuir* **2002**, *18*, 332.

[9] The mole % of initiator present in the MWNTs was calculated as follows: $[I]_{MWNT} = \left[\frac{\left(\frac{\text{wt\% of initiator from TGA}}{\text{mol. wt of initiator fragment}}\right)}{\left(\frac{100}{\text{mol. wt fo carbon}}\right)}\right] 100.$

[10] A. M. Rao, A. Jorio, M. A. Pimenta, M. S. S. Dantas, G. Dresselhaus, M. S. Dresselhaus, *Phys. Rev. Lett.* **2000**, *84*,1820.

[11] K. Fu, W. Huang, Y. Lin, L. A. Riddle, D. L. Carroll, Y.-P. Sun, *Nano Lett.* **2001**, *1*, 439.

