

Synthesis and Characterization of the Isolated Straight Polymer Chain Inside of **Single-Walled Carbon Nanotubes**

Zunfeng Liu^{1, *}, Xiaoyan Zhang¹, Xiaoying Yang², Yanfeng Ma¹, Yi Huang¹, Bin Wang¹, Yongsheng Chen^{1,*}, and Jing Sheng^{3,*}

¹ Key Laboratory for Functional Polymer Materials and Center for Nanoscale Science and Technology, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China ² School of Pharmaceutical Sciences, Tianjin Medical University, Tianjin 300070, China ³ School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

In this paper, a novel molecular wire comprising an isolated straight polystyrene (PS) chain encapsulated by a single-walled carbon nantube (SWNT) was prepared. The interaction of the PS chain with the SWNTs was systematically characterized using transmission electron microscopy (TEM). Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and Raman spectroscopy.

Keywords: Carbon Nanotube, Polymerization.

1. INTRODUCTION

Single molecular (SM) electronics is attracting great attention due to the potential applications in future computing technology and related fields.^{1,2} Carbon nanotubes (CNTs) have been investigated to be used as nanowire and molecular wire in a wide variety of devices, including transistors and sensors due to their high tensile strength. extraordinarily high electron mobility, and 1-d nanometer scale structure.²⁻⁴ Filling carbon nanotubes (CNTs) with metals might create intriguing multifunctional nanodevices such as electrical nanocables, nanomagnets, melt or cluster pipelines, small mass conveyers, nanoswitches, and nanothermometers.^{5–8} The encapsulation of organic or inorganic molecules in CNTs and the relative characterization is an important research topic.9-14 Usually, adsorption or encapsulation of molecules into single walled carbon nanotubes (SWNTs) can alter the properties of the SWNTs or provide the SWNTs new applications. A p-n junction was fabricated using an isolated SWNT^{3, 15} through doping of potassium and amine atoms onto the SWNTs by altering a p-type SWNT to a n-type one. Upon exposure to gaseous molecules such as NO₂/NH₃, the electrical resistance of a semiconducting SWNT is found to dramatically increase/decrease, based on which a chemical

sensor was prepared.¹⁶ Supramolecular assemblages made of the SWNTs filled with fullerenes are proposed that the encapsulated fullerenes may greatly alter the electronic structure of the surrounding SWNTs, leading to either bandgap modulation¹⁷ or unoccupied density of state modification.¹⁸ It is reported that the C₆₀@SWNTs showed enhanced *p*-type characteristics compared with the pristine SWNTs, whereas the C_{59N} @SWNTs showed the *n*-type behavior.19

Recently the SWNTs filled with a single isolated polyacetylene chain was studied experimentally and theoretically, which is expected to be used for molecular electronic devices.^{20, 21} Low molecular weight polymers such as poly(ethylene oxide) and poly(caprolactone) were selectively intercalated into multiwalled carbon nanotubes (MWCNTs) having the diameter between 50 to 100 nm using an open air method,²² also polystyrene (PS) was encapsulated by MWCNTs having the diameter between 40 to 50 nm with the aid of supercritical CO₂.²³ In this paper, we reported a novel SWNT based nanowire PS@SWNTs, where an isolated single straight PS chain was encapsulated by the SWNTs. The interaction of the PS chain with the SWNTs was systematically characterized using transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and Raman spectroscopy.

^{*}Authors to whom correspondence should be addressed.

2. EXPERIMENTAL DETAILS

2.1. Materials and Measurements

SWNTs were prepared in our laboratory using a modified arcing method.²⁴ The as prepared SWNTs were purified using nitric acid and cut using mixed acid as reported in the literature.²⁵ The SWNTs thus purified were heated at 420 °C in air for 40 min for opening the tube tips and removing the amorphous carbon attached on the SWNTs. All the chemical reagents were purchased from Tianjin No. 3 Chemical Reagent Factory. Styrene (AR) was freshly distilled before use. *N*, *N*-dimethyl formamide (DMF, AR) and acetone (AR) were used without further purification.

2.2. Polymerization of the Styrene in the SWNTs

The styrene was thermally polymerized in the SWNTs. 10 mg of the SWNTs and 3 mL of the distilled styrene were mixed and sonicated by a tip sonicator (Cole Parmer,)v High Intensity Ultrasonic Processor/Sonicator) for 2 h at n 20 W. Then the mixture was magnetically stirred for a 4 week. The mixture was then put into a home made high pressure reaction kettle and heated at 180 °C for 2 h in N_2 to carry out the thermal polymerization. The PS@SWNTs was purified by re-dispersing it in DMF, sonication and filtration using a PTFE membrane (0.1 μ m) in order to remove the PS outside of the SWNTs until the PS in the filtration can not be detected by FTIR. The PS@SWNTs were then dispersed in ethanol and acetone to remove the DMF and then vacuum-dried. The PS in filtration was collected by precipitation in methanol and filtration, and further purified by dissolving it in DMF, precipitation in methanol and filtration. The PS was used as the control sample in NMR and FTIR spectra. AMER

2.3. Characterization

The TEM (Philips T20ST) was operated at an acceleration voltage of 200 kV. For TEM characterization, droplets of dilute methanol suspensions containing the SWNTs or the PS@SWNTs were dropped onto carbon-coated copper grids (400 mesh). The solvent was evaporated in air for 1 h. The ¹H NMR spectra were carried out by Varian Unity Inova 400 NMR spectrometer (Varian Inc., Palo Alto, CA) operated at 400 MHz (14.1 T). For NMR determination, 0.5 mg of the PS samples were dissolved in 0.5 mL of CD_3COCD_3 and scanned for 64 times, 5 mg of PS sample were dissolved in 0.5 mL of CDCl₃ and scanned for 8 times, and 5 mg of the PS@SWNT sample was dispersed in 0.5 mL of CD₃COCD₃ and scanned for 1024 times. The FTIR measurements were performed on a Tensor 27 Bruker FTIR spectrophotometer. The samples were prepared as KBr pellets. Fifteen scans were coadded for each spectrum with a spectral resolution of 2 cm^{-1} . Raman spectra were recorded on a RENISHAW inVia spectrometer with a 40 mW argon-ion laser excited at 715 nm.

The abscissa was calibrated with the 520.7 cm^{-1} peak of a silicon standard, and the sharp Raman shifts are accurate within the limits of the resolution.

3. RESULTS AND DISCUSSION

3.1. Synthesis Strategy of the PS@SWNTs

It has been reported that the CNTs can act as nanoscale reactors to synthesize robust metal clusters and nanowires.^{26, 27} Research has shown that organic solution and fusible metal oxide with low surface tension can wet the graphite shell. As a result, the cavities of CNTs can be filled by foreign materials with the aid of a spontaneous capillary driving force.²⁷ Because most common organic liquids have smaller surface tension (<200 mN/m) than SWNTs, insertion will be favorable for most liquid molecular compounds as long as the molecular size is smaller than the SWNTs' diameter.²⁸ Styrene has a surface tension of about 32 mN/cm at room temperature²⁹ and relatively small size; therefore it can be easily encapsulated by SWNTs via a capillary filling method. More importantly, styrene can be thermally polymerized easily without the aid of an initiator.³⁰ In this work the polymerization was carried out at 180 °C for 2 h in order to ensure the polymerization of styrene monomer in SWNTs, as shown in Scheme 1.

3.2. TEM of the PS@SWNTs

SCIEN

PUBLIS

With the constrain of the SWNTs, styrene polymerizes and tends to form an extended line because there is no enough space for the PS chain to self-curl and exist in a random coil formed inside the SWNTs. Using TEM we can clearly observe the extended PS chain in the SWNTs, as shown in Figure 1. Figures 1(a and b) show two empty tubes, and Figures 1(c to m) show the PS@SWNTs. The black arrow denotes the SWNTs' wall, and the white arrow denotes the PS chain. It can be clearly seen that there is almost nothing in the empty SWNTs except for a few amorphous carbon particles formed during the synthesis of SWNTs (e.g., the black dot inside the SWNT in Fig. 1(b)), whereas there are one or two black lines between the tube walls in the PS@SWNTs. Obviously the black line is formed after polymerization of the styrene in the SWNTs. In Figures 1(c and d), there is a distinct PS chain in each



Scheme 1. The schematic representation of the polymerization of the styrene in SWNTs. The polymerization of the styrene in SWNTs includes two steps: (1) the styrene molecules were encapsulated by the open ended SWNTs via a capillary filling method; (2) the styrene was thermally polymerized in the absence of initiators at a temperature of 180 °C for 2 h.

By calculating 102 tubes after polymerization of styrene in SWNTs, there are 90 tubes containing PS chain in the tube, 5 tubes empty, and 7 tubes containing PS chain both in and outside of the tube, showing high reaction efficiency.

3.3. FTIR of the PS@SWNTs

FTIR is one of the powerful spectroscopic tools investigating the functional groups of molecules. Figure 2 shows the FTIR spectra of the PS and the PS@SWNTs in the range 500+3500 cm⁻¹. The solid line is the spectrum of the PS and the dashed line is that of the PS@SWNTs. PS shows typical absorption bands at 3082, 3060, and 3026 cm⁻¹ (aromatic C-H stretching); 2922 and 2849 cm⁻¹ (aliphatic C-H stretching); 1601, 1493, and 1452 cm⁻¹ (C-C skeletal in-plane vibration of the phenyl ring); and 756 and 698 cm⁻¹ (C–H out of plane deformation of the phenyl ring).³¹ The PS chain in the PS@SWNT shows different spectral feature compared with the bulk one. The peaks of the PS@SWNTs at $\sim 3000 \text{ cm}^{-1}$ (2961, 2924, and 2853 cm⁻¹) and \sim 700 cm⁻¹ (757 and 698 cm⁻¹), corresponding to the C-H stretching modes of the PS, are almost disappeared. While the peaks of the PS@SWNTs in the region between ~ 1400 to ~ 1600 cm⁻¹ (1601, 1481, and 1466 cm⁻¹), corresponding to the C-C skeletal vibration modes of the phenyl ring, have comparable intensity as the ones of the bullk PS except for a little broadened. The possible reason might be that for the PS chain in the

PS 1601 Transmittance PS@SWCNTs 757 3082 2853 698 3060 2924 1601 а 466 b 1481 3026 756 1493 2922 1452 698 3000 2500 2000 1500 1000 500 3500

Wave number (cm⁻¹)

Fig. 2. FTIR spectra of the PS (solid line) and the PS@SWNTs (dashed line) in the wave length region.

Fig. 1. TEM pictures of the empty SWNTs (a and b), the PS@SWNTs (c-h), and the same PS@SWNT at different time with the time interval of 3 s (i-m). The scale bar denotes 10 nm. The white arrows point out the PS chains in or outside of the SWNTs, and the black arrows point out the SWNT's wall.

SWNT. Although the PS chain is slightly bent, it straightens when approaching the SWNT's wall, existing in a quasi-straight line.

If the PS chain exists outside of the SWNTs, it is difficult to arrange itself along the tube axis because there is no restriction forcing the chain to exist as an extended line. On the contrary, the PS chain tends to wind or gets apart from the SWNT to achieve a high entropy and more stable state. Therefore there should be cross-points between the PS chain and the SWNT's wall. Figure 1(e) is another view of Figure 1(d) with different focus in electron beam of TEM. The white arrow points out a typical PS chain outside of the tube, which winds around the SWNT rather than extend along the SWNT's axis. Because of the different focus in the electron beam, this PS chain can not be clearly seen in Figure 1(d), while the PS chain in Figure 1(d) is also a little blurry in Figure 1(e).

In Figure 1(f), there are two parallel PS chains in the SWNT. They are parallel to each other in the right site of the SWNT and wind each other to form a double-stranded-helix configuration in the left site of the SWNT. They get out of the SWNT's tip and bent back outside of the SWNT, as pointed by the white arrow below the SWNT. Figure 1(g) shows one SWNT and Figure 1(h) shows two SWNTs. We can find PS chains in the SWNTs as pointed by the white arrows. Figures 1(i to m) show the TEM pictures of the same PS@SWNTs at different time with the time interval of 3 s. There is a single stranded PS chain in the left of the SWNT. It moves in the SWNT under the irradiation of the electron beam and



PS@SWNTs, the C-H bonds exist in the exterior region of the PS chain. They can feel the pressure from the tube wall, and then the C-H stretching modes are inhibited. The C-C bonds exist in the interior region of the PS chain and are less influenced by the constraint of the SWNTs, and then the C-C skeletal vibration modes of the PS are not greatly inhibited.

3.4. ¹H NMR of the PS@SWNTs

Because the PS in this paper has a relatively small solubility in CD₃COCD₃, the concentration (1 mg/mL) is only $\sim 1/10$ of the typical concentration used in NMR determination (10 mg/mL), therefore it is scanned for 64 times. The PS content in the PS@SWNTs/CD₃COCD₃ dispersion is also very low and it is scanned for 1024 times. As a comparison, we determined the NMR spectra of the PS in CDCl₃, in which the PS has a good solubility and scanned for 8 times. Because of the rel-by Ingenta to: atively more scan times for the PS@SWNTs, there are all many impurity peaks in the ¹H NMR spectrum, especially 4 in the high field region. Therefore, we only investigate the ¹H NMR signals in the low field region 5.8 ppm $< \delta <$ 7.25 ppm, as shown in Figure 3. In the ¹H NMR spectrum of the PS in CDCl₃, there are two peaks at 7.084 ppm (protons b and c) and 6.578 ppm (proton a), which is in consistent with the literature.³² They are a little broad and irregular, showing a typical feature of the macromolecule's



Fig. 3. The NMR spectra in the low field region of the PS@SWNTs in CD₃COCD₃, the PS in CD₃COCD₃, and the PS in CDCl₃. The PS in $CDCl_3$ shows two peaks at 7.084 ppm (protons b and c) and 6.578 ppm (proton a), the PS in CD_3COCD_3 shows two peaks at 7.082 ppm (protons b and c) and 6.678 ppm (proton a), and the PS@SWNT in CD_3COCD_3 shows two peaks at 6.750 ppm (protons b and c) and 6.047 ppm (proton a). The peak shift can be attributed to the electromagnetic shielding effect of the SWNTs.

NMR spectrum. In the ¹H NMR spectrum of the PS in CD_3COCD_3 , the positions of the two peaks are at 7.082 ppm (protons b and c) and 6.678 ppm (proton a), which also have board and irregular shapes, very similar to those in CDCl₃. In the ¹H NMR spectrum of the PS@SWNTs in CD₃COCD₃, two peaks can be observed in new positions at 6.750 and 6.047 ppm and the peak shape gets regular. Obviously the peak of the protons of the phenyl ring shifts from 7.082 to 6.750 ppm (protons band c) and from 6.678 to 6.047 ppm (proton a). The peak shift can be attributed to the electromagnetic shielding effect of the SWNTs. The H NMR data of the PS show a diamagnetic shift of 0.3-0.5 ppm since the encapsulated PS chain experiences a higher magnetic shielding caused by the surrounding π -electron system of the nanotubes, as predicted by the recent ab initio NMR calculations³³ and also in consistent with the experimental results in the literature.34

3.5. Raman Spectra of the PS@SWNTs

As is known Raman spectrometry is proved to be the most informative tool for the characterization of the SWNTs by allowing determining structural and electronic properties of the SWNTs.³⁵ To investigate the interaction between the encapsulated PS chain and the SWNTs, we recorded the Raman spectra in the radial breath modes (RBMs) region, as shown in Figure 4.



Fig. 4. RBM region of the Raman spectra of the SWNTs and the PS@SWNTs excited at 785 nm (the solid lines). The RBM peaks of the two samples are separated into two Lorentzian components with the same peak positions at 157.2 and 167.3 cm⁻¹ (the dashed lines) using Lorentzian lines. The SWNT with the RBM peak at 157.2 cm⁻¹ is calculated to have the diameter of 1.59 nm and the chirality of (13, 10), and the one with the RBM peak at 167.3 cm⁻¹ is calculated to have the diameter of 1.49 nm and the chirality of (15, 6) according to the equation $\omega = 234/d + 10$ and the revised Kataura plot. The relative peak intensity at 167.3 cm⁻¹ compared with that at 157.2 cm⁻¹ decreases greatly after filling, indicating that there is strong electron interaction between the intercalated PS and the SWNTs.

Remarkable difference in RBM region of the Raman spectra in the range 120 cm⁻¹ $< \omega < 200$ cm⁻¹ can be observed for the SWNTs and the PS@SWNTs, which is in consistent with the literature about encapsulation of the SWNTs with foreign materials.¹⁹ In the empty SWNTs and the PS@SWNTs, a broad RBM band can be observed. which is actually represented by a superposition of a few Lorentzian components. We then carry out the peak separation of the RBM bands using Lorentzian lines, shown in Figure 4 as the dashed lines. The Lorentzian components for the two samples are at the same peak positions: 157.2 cm⁻¹ (1.59 nm) and 167.3 cm⁻¹ (1.49 nm), where the tube diameter in brackets (d) is calculated using the relation $\omega = 234/d + 10^{36}$ (ω : RBM frequency). After encapsulating the PS chain into the SWNTs, there is no shift in the RBM frequency of the Raman spectra. while the relative peak intensity at 167.3 cm⁻¹ compared with that at 157.2 cm⁻¹ decreases greatly after filling. Large RBM intensities result from nanotubes with diam-by eters close to the peak of the diameter distribution and na with optical transition energy E_{ii} values of the transitions 4 between pairs of van Hove singularities (vHS) that fall in 20 the Raman resonance window (full width at half-maximum (fwhm) of about 120 meV for bundled nanotubes³⁷ at a given excitation energy.³⁸ The excitation energy of laser with the wavelength 785 nm is 1.58 eV. According to the revised Kataura plot,³⁹ it is suggested that the metallic SWNTs are predominantly resonant in the Raman spectra in Figure 4. From the relationship between the diameter and the chirality of the isolated SWNTs, the SWNTs having the diameter of 1.49 nm corresponds to the chirality of (15, 6), whose E_{11}^M values are 1.72 and 1.62 eV. The SWNT having the diameter of 1.59 nm corresponds to two chiralities of (13, 10) and (17, 5). The SWNTs having the chirality of (13, 10) has the E_{11}^M values of 1.58 and 1.55 eV, and the one having the chiality of (17, 5) has the E_{11}^{M} values of 1.62 and 1.51 eV.40 By considering that the bundled SWNTs have E_{ii} resonances a few tens of millielectronvolts smaller than the SWNTs dispersed individually,37,38 the difference between the exitation energy (1.58 eV) and the E_{11}^M value (1.62 eV) of the SWNT having the chirality of (15, 6) will be very close to the exitation energy.³⁷ From the fact that the intensity of the peak at 167.3 cm^{-1} of the empty SWNT in Figure 4 is greater than that of the peak at 157.2 cm⁻¹, the SWNT having a RBM peak at 157.2 cm⁻¹ should be assigned to the chirality of (13, 10), whose E_{11}^M value is a little away from the exitation energy compared with that of the SWNT having the chirality of (15, 6), and is also in the half of the fwhm of the Raman resonance window for bundled nanotubes (about 60 meV).37 After filling of the PS, the relative intensity of the RBM peak at 167.3 cm⁻¹ decreases but still high compared with that of the RBM peak at 157.2 cm⁻¹, indicating that the E_{11}^{M} value of the SWNT having the chirality of (15, 6) gets away from laser exitation energy (1.58 eV) and that the E_{11}^{M}

value of the SWNT having the chirality of (13, 10) is further away from the excitation energy (1.58 eV) compared with that of the SWNT having the chirality of (15, 6). Therefore, it can be deduced that the encapsulation of the PS chain by the SWNT decreases the E_{11}^M value of the SWNTs.

4. CONCLUSIONS

In this paper, a novel molecular wire comprising an isolated straight polystyrene chain encapsulated by a SWNT was prepared. Such a peapod structure was observed using TEM. The spectroscopic properties of the PS@SWNTs including FTIR, ¹H NMR, and Raman were systematically studied and great differences were observed for the PS@SWNTs compared with the PS and the empty SWNTs. In the FTIR spectra, the intensity of C–H stretching modes of the PS in the PS@SWNTs is very low compared with that of the bulk PS, while the C-C vibration modes of the phenyl ring of the PS in the PS@SWNTs have comparable intensity with the bulk PS. This reflects that the C-H bonds exist in the exterior region of the PS chain and they can feel the pressure from the SWNT's wall, while the C-C bonds exist in the interior region of the PS chain and are therefore less influenced by the constrain of SWNTs. The ¹H NMR analysis shows that the characteristic aromatic proton peaks of the PS in the PS@SWNTs show obvious diamagnetic shift compared with that of the bulk PS, indicating that the PS chain encapsulated by SWNTs experiences a high magnetic shielding caused by the surrounding π -electron system of the SWNTs. In Raman spectroscopy, the RBM peak feature of the PS@SWNTs peapod differs greatly from that of the empty SWNTs. The relative intensity of the separated RBM peaks using Lorentzian lines changes greatly after filling, showing strong electron interaction between the PS chain and the SWNTs.

Acknowledgments: The authors thank the "863" project (# 2003AA302640) of MOST and the NSF of Tianjin (# 043803711) of China for financial support of this work.

References and Notes

- 1. R. F. Service, Science 302, 556 (2003).
- 2. A. Nitzan and R. A. Ratner, Science 300, 1384 (2003).
- 3. C. Zhou, J. Kong, E. Yenilmez, and H. Dai, <u>Science 290, 1552</u> (2000).
- J. A. Misewich, R. Martel, P. Avouris, J. C. Tsang, S. Heinze, and J. Tersoff, *Science* 300, 783 (2003).
- A. L. Elias, J. A. Rodriguez-Manzo, M. R. McCartney, D. Golberg, A. Zamudio, S. E. Baltazar, F. Lopez-Urias, E. Munoz-Sandoval, L. Gu, C. C. Tang, D. J. Smith, Y. Bando, H. Terrones, and M. Terrones, *Nano Lett.* 5, 467 (2005).
- D. Golberg, P. M. F. J. Costa, M. Mitome, S. Hampel, D. Haase, C. Mueller, A. Leonhardt, and Y. Bando, *Adv. Mater.* 19, 1937 (2007).

- P. S. Dorozhkin, S. V. Tovstonog, D. Golberg, J. Zhan, Y. Ishikawa, M. Shiozawa, H. Nakanishi, K. Nakata, and Y. Bando, <u>Small 1, 1088</u> (2005).
- 8. Y. Gao and Y. Bando, *Nature* 415, 599 (2002).
- Z. Liu, K. Yanagi, K. Suenaga, H. Kataura, and S. Iijima, <u>Nat. Nan-otech.</u> 2, 422 (2007).
- S. Banerjee, S. Murad, and I. K. Puri, <u>Chem. Phys. Lett.</u> 434, 292 (2007).
- K. Yanagi, K. Iakoubovskii, H. Matsui, H. Matsuzaki, H. Okamoto, Y. Miyata, Y. Maniwa, S. Kazaoui, N. Minami, and H. Kataura, *J. Am. Chem. Soc.* 129, 4992 (2007).
- H. Shiozawa, T. Pichler, C. Kramberger, M. Rümmeli, D. Batchelor, Z. Liu, K. Suenaga, H. Kataura, and S. R. P. Silva, <u>*Phys. Rev. Lett.*</u> 102, 046804 (2009).
- U. K. Gautam, Y. Bando, L. Bourgeois, X. Fang, P. M. F. J. Costa, J. Zhan, and D. Golberg, *J. Mater. Chem.* 19, 4414 (2009).
- H. A. Zambrano, J. H. Walther, P. Koumoutsakos, and I. F. Sbalzarini, *Nano Lett.* 9, 66 (2009).
- 15. J. Kong and H. Dai, J. Phys. Chem. B 105, 2890 (2001).
- J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, *Science* 287, 622 (2000).
- J. Lee, H. Kim, S. J. Kahng, G. Kim, Y. W. Son, J. Ihm, H. Kato, Z. W. Wang, T. Okazaki, H. Shinohara, and Y. Kuk, *Nature* 415, 1005 (2002).
- D. J. Hornbaker, S. J. Kahng, S. Misra, B. W. Smith, A. T. Johnson, 47
 E. J. Mele, D. E. Luzzi, and A. Yazdani, <u>Science 295, 828 (2002)</u>, 70
- T. Kaneko, Y. Li, S. Nishigaki, and R. Hatakeyama, <u>J. Am. Chem.</u> <u>Soc. 130, 2714 (2008)</u>.
- 20. G. Kim, Y. Kim, and J. Ihm, Chem. Phys. Lett. 415, 279 (2005).
- D. Nishide, T. Wakabayashi, T. Sugai, R. Kitaura, H. Kataura, Y. Achiba, and H. Shinohara, J. Phys. Chem. C 111, 5178 (2007).
- V. A. Bazilevsky, K. Sun, A. L. Yarin, and C. M. Megaridis, <u>Langmuir</u> 23, 7451 (2007).
- 23. Z. M. Liu, X. H. Dai, J. Xu, B. X. Han, J. L. Zhang, Y. Wang, Y. Huang, and G. Y. Yang, <u>Carbon 42, 458 (2004)</u>.

- 24. X. Lv, F. Du, Y. Ma, Q. Wu, and Y. Chen, Carbon 43, 2020 (2005).
- 25. J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, *Science* 22, 1253 (1998).
- H. Dai, E. W. Wong, S. Fan, and C. M. Lieber, <u>Nature 375, 769</u> (1995).
- 27. L. Cao, H. Z. Chen, H. Y. Li, H. B. Zhou, H. Z. Sun, X. B. Zhang, and M. Wang, <u>Chem. Mater.</u> 15, 3247 (2003).
- 28. D. A. Britz and A. N. Khlobystov, Chem. Soc. Rev. 35, 637 (2006).
- K. Landfester, N. Bechthold, S. Forster, and M. Antonietti, Macromol. Rapid Commun. 20, 81 (1999).
- **30.** J. R. Ebdon, Bri. Polym. J. 3, 9 (1970).
- 31. X. Fu and S. Qutubuddin, Langmuir 18, 5058 (2002).
- **32.** M. Degirmenci, I. Cianga, and Y. Yagci, *Macromol. Chem. Phys.* 203, 1279 (**2002**).
- **33.** M. A. L. Marques, M. d'Avezac, and F. Mauri, *Phys. Rev. B* 73, 125433 (2006).
- 34. J. Steinmetz, S. Kwon, H. J. Lee, E. bou-Hamad, R. Almairac, C. Goze-Bac, H. Kim, and Y. W. Park, <u>*Chem. Phys. Lett.*</u> 431, 139 (2006).
- 35. M. V. Chernysheva, A. A. Eliseev, A. V. Lukashin, Y. Tretyakov,
- 19 S. V. Savilov, N. A. Kiselev, O. M. Zhigalina, A. S. Kumskov, A. V.
- Seoul National Unkrestinin, and J. L. Hutchison, *Physica E* 37, 62 (2007).
 - **36** M. Milnera, J. Kurti, M. Hulman, and H. Kuzmany, *Phys. Rev. Lett.* **84**, 1324 **(2000)**.
 - C. Fantini, A. Jorio, M. Souza, M. S. Strano, M. S. Dresselhaus, and M. A. Pimenta, *Phys. Rev. Lett.* 93, 147406 (2004).
 - **38.** A. Ilie, J. S. Bendall, D. Roy, E. Philp, and M. L. H. Green, *J. Phys. Chem. B* 110, 13848 (**2006**).
 - H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, and Y. Achiba, *Synth. Met.* 103, 2555 (1999).
 - A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. Lett.* 86, 1118 (2001).

Received: 22 June 2009. Accepted: 8 September 2009.

AMERICAN SCIENTIFIC PUBLISHERS