

Hydrogen Bonding of Polystyrene Latex Nanospheres to Sidewall Carbon Nanotubes

Carlos Velasco-Santos,^{†,‡,§} Ana L. Martínez-Hernández,^{†,‡,§} and Victor M. Castaño*,[†]

Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México A.P. 1-1010 Santiago de Querétaro, Querétaro 76000, México, Department of Materials Science, University of North Texas, Denton, Texas 76203-5310, and Departamento de Materiales, Departamento de Mecatrónica, Instituto Tecnológico de Querétaro, Av. Tecnológico, Col. Centro, Santiago de Querétaro, Querétaro 76000, México

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Carbon nanotubes and monodispersed nanoparticles are two of the most important building blocks proposed to create nanodevices. Also, the tendency to produce nanomachines with biomolecules has increased in the past few years. Because hydrogen bonding plays an important role in structuring many natural molecules, it is necessary to mimic the same “links” used by nature to form biomolecules such as DNA or proteins. In this paper, we show hydrogen bonding between open-tip and sidewall carbon nanotubes and polystyrene nanoparticles, produced at a pH adequate to create the same bond between natural systems and interesting nanoforms.

Introduction

Nanotechnology quite certainly will become an important field in the science and technology of the next decades, allowing one to manipulate matter at the nanometer scale and to incorporate nanostructures and nanoprocesses into working technological innovations. Materials, such as carbon nanotubes, with outstanding mechanical and electrical properties represent ideal building blocks for nanoengineering through their integration into working devices.^{1,2} Recently, both single-walled carbon nanotubes (SWNT) and multiwalled carbon nanotubes (MWNT) have been proposed as substrates for biological devices.^{3,4} The most common technique of incorporating different groups into carbon nanotubes has been by oxidation. In this regard, the most popular methods are based on liquid-phase approaches, by using HNO₃,^{5,6} KMnO₄/H₂SO₄,⁷ or H₂O₂/H₂SO₄,⁸ among other chemicals. These approaches offer a higher yield than the purified functionalized arc products. The oxidation of carbon nanotubes yields carboxyl groups over the open end cap and on the sidewall of the nanotubes, and these functionalized carbon nanotubes are used to attach different moieties aimed at improving the interaction with biological,^{3,4} inorganic,⁹ and polymeric materials.¹⁰ Other nanoforms which have been proposed as building blocks in nanotechnology are monodispersed spherical nanoparticles,^{11–13} and a number of chemical methods have been developed for producing them in a variety of sizes and shapes and with charges chemically fixed on their surface. In fact, there exist already commercial monodispersed latex particles which contain carboxyl-terminated surfaces, similar to oxidized functionalized carbon nanotubes. The carboxylic acid groups in carbon nanotubes have been proposed to couple amines by covalent functionalization,^{14,15} and it is known that these groups (COOH) form rather stable hydrogen-bonded dimers,^{16,17} which can be used to attach other noncovalent bonds in nanoparticles or carbon nanotubes, in turn required for the incorporation of carbon nanotubes in nanodevices.^{18,19} Recently,

the literature shows a tendency to mimic and assemble natural systems,²⁰ which are constituted by micro- and nanoassembled structures,²¹ giving as a result highly organized subcomponents.^{22–25} The natural systems are characterized by the presence of hydrogen bonds, and their contribution to stabilize these structures is of fundamental importance.²⁶ So, to mimic and assemble natural molecules, it is necessary to replicate the “links” through which they can bond to the proposed building blocks (i.e., nanoparticles and carbon nanotubes). According to the above, it could allow carbon nanotubes and other synthetic nanomaterials to be used in nanodevices such as biological sensors or to form novel self-assembled nanometric arrangements. In addition, it would help to understand the behavior of interactions of nanoforms through hydrogen bonds, which will induce some sort of self-assembly of synthetic nanoforms, similarly to biological systems. Accordingly, in this paper, we have attached hydrogen links to the sidewall of carbon nanotubes with polystyrene latex nanoparticles-terminated COOH. The results show the possibility of forming hydrogen bonds in the majority of the surface of carbon nanotubes and of linking them to other molecules such as DNA or proteins.

Results and Discussion

MWNTs obtained by the arc-discharge method were employed, supplied by MER Corp. (ground core material), and oxidized with the method proposed in ref 7 with slight variations in the quantity of KMnO₄ and reflux time to obtain purified functionalized-multiwalled carbon nanotubes (purified f-MWNTs) with carboxyl groups on both the open tip and the sidewall. Monodispersed polystyrene latex nanoparticles with carboxyl-terminated groups (PSNC) were supplied by Interfacial Dynamics Corp., 200 nm diameter in size and surfactant-free.

The purified f-MWNTs were characterized via transmission electron microscopy (TEM, JEOL-JEM-1010). The images are shown in Figure 1a and b, which correspond to MWNT and purified f-MWNT after oxidation, respectively. The carboxyl-terminated f-MWNT was analyzed by infrared spectroscopy, shown in Figure 2a and b (MWNT and f-MWNT, respectively), in a 510 Nicolet FTIR spectrophotometer at a resolution of 4

* Corresponding author. E-mail: castano@fata.unam.mx.

[†] Universidad Nacional Autónoma de México.

[‡] University of North Texas.

[§] Tecnológico de Querétaro.

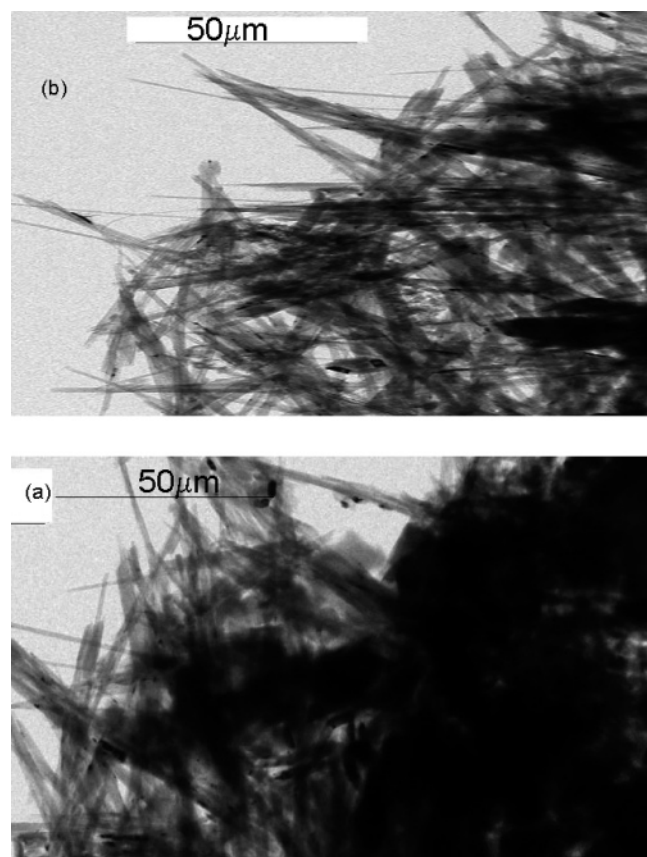


Figure 1. (a) TEM image of multiwalled carbon nanotubes (MWNT). (b) TEM image of purified and functionalized-multiwalled carbon nanotubes (f-MWNT).

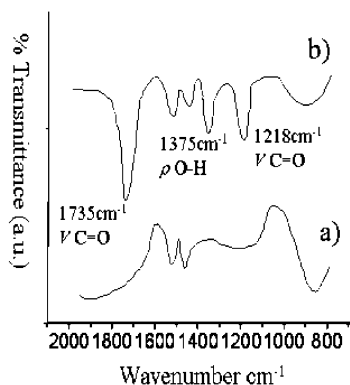


Figure 2. (a) IR spectrum of multiwalled carbon nanotubes (MWNT). (b) IR spectrum of functionalized-multiwalled carbon nanotubes (f-MWNT).

cm^{-1} in KBr tablets. The bands in both spectra at 840 and 1587 cm^{-1} are due to A_{2u} and E_{1u} phonon modes present in carbon nanotubes.^{27,28} The f-MWNT spectrum of Figure 2b shows new bands at 1735 cm^{-1} which correspond to $\nu(\text{C}=\text{O})$ present in carboxylic groups (COOH).^{10,29–31} The bands at 1375 and 1218 cm^{-1} correspond to the $\delta(\text{O}-\text{H})$ and $\nu(\text{C}-\text{O})$ bonds, respectively, found in carboxylic groups.^{10,16,31}

Figure 3a and b shows the MWNT and f-MWNT Raman spectra obtained in a Micro-Raman Dilor with a 632 nm laser and spectral resolution of 3 cm^{-1} . In both cases, two bands at 1576 cm^{-1} (G line) and 1328 cm^{-1} (D line) appear. The first peak corresponds to the E_{2g} modes, assigned to the movement of two neighboring carbon atoms in opposite directions, characteristic of highly oriented pyrolytic graphite (HOPG). The second signal is due to the disorder present in the MWNT, a

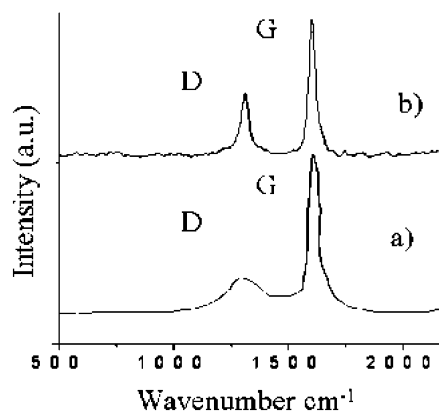


Figure 3. (a) Raman spectrum of multiwalled carbon nanotubes (MWNT). (b) Raman spectrum of functionalized-multiwalled carbon nanotubes (f-MWNT).

feature related to the region near the K-point phonon of the graphite's Brillouin zone.^{28,32,33} As we can see there, the ratio of intensities between the D and G peaks changes in the f-MWNT spectrum (Figure 3b) with respect to the MWNT spectrum (Figure 3a), due to the formation of sp^3 hybridized carbon "defect" sites on the carbon nanotubes walls due to the addition of the functional groups (COOH), which support the results obtained by FTIR analysis.¹⁰

Next, the polystyrene latex nanoparticles (PSNC) were activated by functionalization in aqueous solution: 1.25 mL of latex particles was sonicated for 20 min with 5 mL of buffer solution at a pH of 8.5 for 10 min , and then the supernatant present was removed and redispersed in 5 mL of buffer solution. The new solution was sonicated again for 5 min and freed of the light supernatant formed. On the other hand, 12.5 mg of purified f-MWNTs was washed with deionized water to remove the HCl excess until neutral pH, and then the f-MWNTs were dried. The dry powder was dissolved with 3 mL of buffer solution and sonicated for 5 min , and the f-MWNTs were added to a PSNC-activated solution; this buffer solution was used because the PSNC is not suitable for working in acidic media (a successful good interaction at this pH (up to 8) has been obtained too, when amines were joined to SWNT¹⁵). The solution PSNC/f-MWNT was sonicated for 5 min and then stirred slowly for 10 min . After 30 min , a grayish liquid was obtained with a light precipitate.

A new PSNC solution was prepared, and both samples PSNC and PSNC-f-MWNT were analyzed by IR and Raman spectroscopies. Figure 4a and b shows the IR results, whereas Figure 5a and b corresponds to the Raman spectra. The IR spectra are divided into two zones. The first is from 500 to 2000 cm^{-1} , where the bands in both spectra at 700 and 750 cm^{-1} correspond to $\delta(\text{C}-\text{C})$ and $\delta(\text{C}-\text{H})$, respectively. These groups are due to the polystyrene chain.³⁴ The band at 1066 cm^{-1} corresponds to $\text{C}-\text{O}$ vibration and increases in the PSNC-f-MWNT spectrum (Figure 4b), because a dimer carboxyl is formed.³⁴ The band at 1375 cm^{-1} is due to $\delta(\text{O}-\text{H})$, which decreases in Figure 4b with respect to Figure 4a. Also, this band shifts to higher wavenumbers in part b (1400 cm^{-1}), indicating that there exist dimers.¹⁷ In the band at 1375 cm^{-1} (part a), a little shoulder is formed (1452 cm^{-1}) corresponding to $\delta(\text{C}-\text{H}_2)$. The band at 1568 cm^{-1} (part a) corresponds to a combination of CH out-of-plane wagging modes of polystyrene and is hidden in (b) by the broad band at 1400 cm^{-1} . The band between 1600 and 1700 cm^{-1} corresponds to $\nu(\text{C}=\text{O})$. This band is characterized by a shift to lower wavenumbers when a dimer carboxyl is formed,^{32,35–37} as in the PSNC-f-MWNT spectrum (b), where

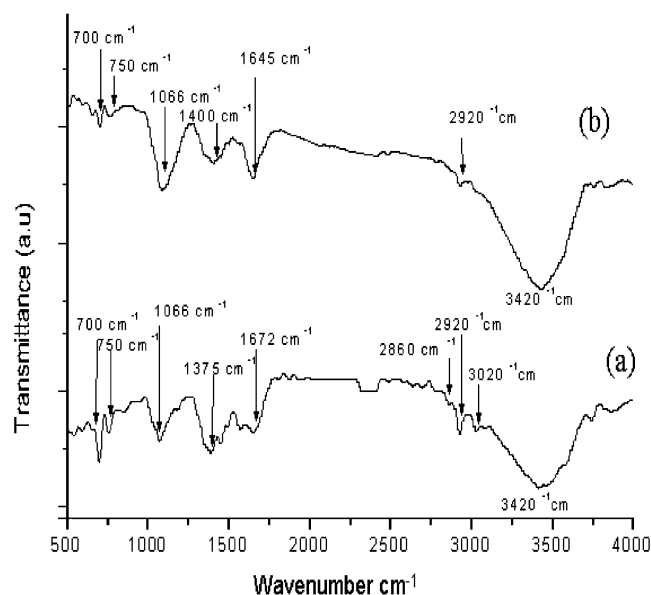


Figure 4. (a) IR spectrum of polystyrene nanoparticles carboxyl-terminated solution (PSNC). (b) IR spectrum of polystyrene nanoparticles carboxyl-terminated and functionalized-multiwalled carbon nanotubes solution (PSNC-f-MWNT).

the band is found at 1650 cm^{-1} and the PSNC shows the band nearer to 1700 cm^{-1} . The peak of $\nu(\text{C}=\text{O})$ in Figure 2b corresponds to f-MWNT at 1735 cm^{-1} ; the band does not appear in Figure 4b until 1650 cm^{-1} , which indicated that there indeed exists a shift due to the COOH groups in carbon nanotubes forming dimers, bonded by hydrogen “links”.

The IR spectra of Figure 4a and b show bands from 2500 to 4000 cm^{-1} and, additionally, in PSNC (a) four bands at 2860 , 2920 , 3020 , and 3450 cm^{-1} . The three first bands belong to polystyrene and correspond to $\nu(\text{CH}_2)$, $\nu(\text{C}-\text{H})$, and aromatic $\nu(\text{C}-\text{H})$, respectively.³⁸ The last band at 3450 cm^{-1} is characteristic of $\nu(\text{OH})$; this signal increases and broadens when the OH moieties form hydrogen bonding,^{16,39,40} as in Figure 4b, showing that the COOH carboxyl of MWNT and PSNC are linked by hydrogen bonds. The broadening is due to new bands formed between 2985 and 3130 cm^{-1} .^{40,41} Thus, we can conclude that COOH dimers produced between two solids materials in liquid medium produce interaction and IR activity similar to those produced in the other state (i.e., between liquid molecules).

In Figure 5 a and b, the Raman spectra of PSNC and PSNC-f-MWNT are displayed. The D-band is increased with respect to the G-band, as it is known that this band is sensitive to the disorder induced on the open tip and on the side wall, so it is possible that the peak increases due to the interaction of hydrogen bonds with the defects introduced by the oxidation. In addition, Figure 5b shows shifts of the D-band at 1300 cm^{-1} and its second-order band of higher intensity around 2580 cm^{-1} . These peaks are commonly found between 1328 and 1350 cm^{-1} for the first-order and 2650 and 2680 cm^{-1} in the case of second-order, for this type of nanotube.^{10,28,42} Therefore, the Raman shift could be influenced by interactions of organic groups in the carbon nanotube surface through hydrogen bonds. Both Raman spectra, PSNC and PSNC-f-MWNT, show an intense and broad band around 3260 cm^{-1} , which corresponds to $\nu(\text{OH})$ as usual in PSNC; however, the band in Figure 3b is stronger and shows a broadening as compared to the Figure 3a spectrum, which presents the same behavior as in the IR spectrum, characteristic of OH moieties forming hydrogen bonding.^{16,39,40}

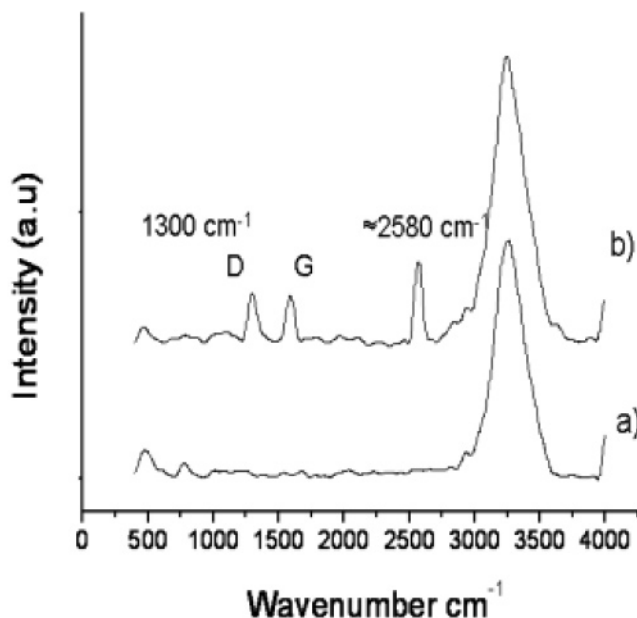


Figure 5. (a) Raman spectrum of polystyrene nanoparticles carboxyl-terminated solution (PSNC). (b) Raman spectrum of polystyrene nanoparticles carboxyl-terminated and functionalized-multiwalled carbon nanotubes solution (PSNC-f-MWNT).

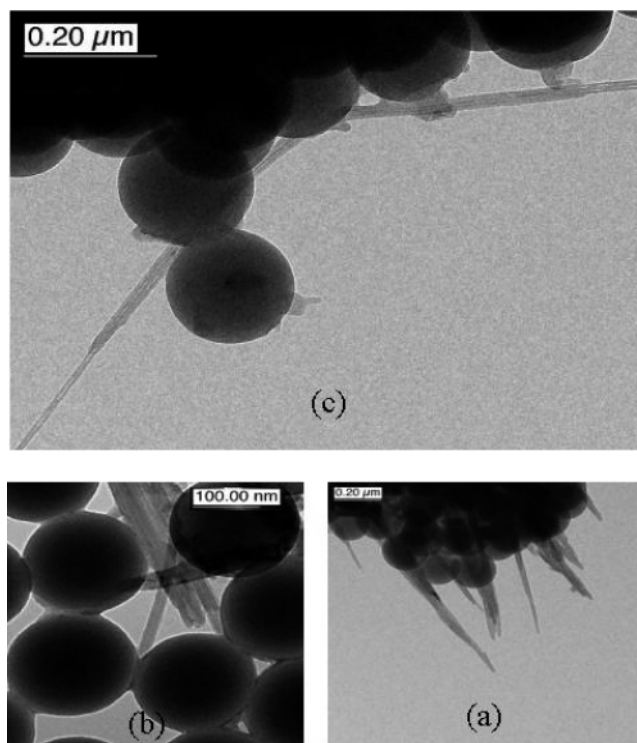


Figure 6. (a) TEM image of polystyrene nanoparticles carboxyl-terminated and functionalized-multiwalled carbon nanotubes group. (b) TEM image of carbon nanotubes adhered to polystyrene nanoparticles carboxyl-terminated by dimers of carboxyl. (c) TEM image of sidewall carbon nanotubes adhered to some polystyrene nanoparticles carboxyl-terminated by dimers of carboxyl.

Figure 6a–c shows the TEM images of PSNC-f-MWNT. Figure 6a shows a group of PSNC and f-MWNT; however, Figure 6b shows the interaction of f-MWNT and latex particles, and Figure 6c shows a f-MWNT adhered to the sidewall of PSNC through hydrogen bonds. The TEM images show graphically the interaction between carboxyl-

terminated nanoparticles and functionalized-multiwalled carbon nanotubes, as IR and Raman spectroscopies had indicated indirectly.

Conclusions

The results showed that the quantity of COOH moieties on the sidewalls of f-MWNT and PSNC is enough to achieve the hydrogen links, due to the concentration of these groups.⁴³ The pH is key in producing the same interaction as in activated natural biomolecules, inasmuch as these molecules are degraded in acidic conditions.⁴⁴ The approach of this present work allows one to control the interaction between carbon nanotubes and latex particles utilizing functionalized polymers, and the same technique can be applied to natural chemical structures to form biological nanodevices and novel hybrid materials with movable bonds. This work is currently underway in our group.

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References and Notes

- (1) Liu, X.; Pichler, T.; Knupfer, M.; Golden, M. S.; Finj, J.; Walters, D. A.; Casavant, M. J.; Schmidt, J.; Smalley, R. E. *Synth. Met.* **2001**, *121*, 1183.
- (2) Pichler, T.; Sing, M.; Knupfer, M.; Golden, M. S.; Fink, J. *Solid State Commun.* **1999**, *109*, 721.
- (3) Shim, M.; Shikum, N. W.; Chen, R. J.; Li, Y.; Dai, H. *Nano Lett.* **2002**, *2*, 285.
- (4) Huang, W.; Taylor, S.; Fu, K.; Lin, Y.; Zhang, D.; Hanks, T. W.; Rao, A. M.; Sun, Y.-P. *Nano Lett.* **2002**, *2*, 311.
- (5) Lin, Y.; Rao, A. M.; Sadaradan, B.; Kenik, E. A.; Sun, Y.-P. *J. Phys. Chem. B* **2002**, *106*, 1294.
- (6) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, A. M.; It, H.; Cohn, R. W.; Eklund, P. C.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C.; *J. Phys. Chem. B* **2001**, *105*, 2575.
- (7) Hiura, H.; Ebbesen, T. W.; Tanigaki, K. *Adv. Mater.* **1995**, *7*, 275.
- (8) Tu, Z.; Brus, L. E. *J. Phys. Chem. A* **2000**, *104*, 10995.
- (9) Wu, G. T.; Wang, C. S.; Zhang, X. B.; Yang, H. S.; Oi, Z. F.; Li, W. Z. *J. Power Sources* **1998**, *75*, 175.
- (10) Velasco-Santos, C.; Martínez-Hernández, A. L.; Lozada-Cassou, M.; Alvarez, A.; Castaño, V. M. *Nanotechnology* **2002**, *13*, 495.
- (11) Yin, Y.; Xia, Y. *Adv. Mater.* **2001**, *13*, 267.
- (12) Zhenan, B.; Chen, L.; Weldon, M.; Chandross, E.; Cherniavskaya, O.; Dai, Y.; Jeffery, B.-H. T. *Chem. Mater.* **2002**, *14*, 24.
- (13) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater.* **2000**, *12*, 693.
- (14) Stanislaus, S. W.; Joselevich, E.; Wooley, A. T.; Cheung, C. L.; Lieber, C. M. *Nature* **1998**, *394*, 52.
- (15) Stanislaus, S. W.; Joselevich, E.; Wooley, A. T.; Lieber, C. M. *J. Am. Chem. Soc.* **1998**, *120*, 8557.
- (16) Seifert, G.; Patzlaff, T.; Graener, H. *Chem. Phys. Lett.* **2001**, *248*, 248.
- (17) Palacios, E. G.; Monhemius, A. J. *Hydrometallurgy* **2001**, *62*, 135.
- (18) Ausman, K. D.; Rohrs, H. W.; Yu, M. F.; Ruoff, R. S. *Nanotechnology* **1999**, *10*, 258.
- (19) Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. *J. Am. Chem. Soc.* **2001**, *123*, 3838.
- (20) Balavoine, F.; Schultz, P.; Richard, C.; Mallouh, V.; Ebbesen, T. W.; Mioskowski, C. *Angew. Chem., Int. Ed.* **1999**, *38*, 1912.
- (21) Bashir, R. *Superlattices Microstruct.* **2001**, *29*, 1.
- (22) Martínez Hernández, A. L.; Velasco-Santos, C.; de Icaza, M.; Castaño, V. M. *Int. J. Environ. Pollut.* **2004**, in press.
- (23) Puthanarat, S.; Stribeck, N.; Fossey, S. A.; Eby, R. K.; Adams, W. W. *Polymer* **2000**, *41*, 7735.
- (24) Fratzl, P.; Misof, K.; Zizak, I. *J. Struct. Biol.* **1997**, *122*, 119.
- (25) Prockop, J. D.; Fertala, A. *J. Struct. Biol.* **1998**, *122*, 111.
- (26) Kovács, A.; Keresztury, G.; Izvekov, V. *Chem. Phys.* **2000**, *253*, 193.
- (27) Kastner, J.; Pichler, T.; Kuzmany, H.; Curran, S.; Blau, W.; Woldo, D. N.; Delamesier, M.; Draper, S.; Zandbergen, H. *Chem. Phys. Lett.* **1994**, *221*, 53.
- (28) Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *Physical Properties of Carbon Nanotubes*; Imperial College Press: Boca Raton, FL, 1999.
- (29) Kuznetsova, A.; Douglas, D.; Namneko, V.; Yates, J. T., Jr.; Liu, J.; Smalley, R. E. *Chem. Phys. Lett.* **2000**, *321*, 292.
- (30) Creswell, C. J.; Runquist, O. A.; Campbell, M. M. *Spectral Analysis of Organic Compounds*, 2nd ed.; Burgess Publishing Co.: USA, 1972; Chapter 3.
- (31) Roeges, N. P. G. *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*; John Wiley & Sons: Chichester, 1997.
- (32) Zhao, X.; Ando, Y. *Jpn. J. Appl. Phys.* **1998**, *37*, 4846.
- (33) Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A.; Souza Filho, A. G.; Saito, R. *Carbon* **2002**, *40*, 2343.
- (34) Socrates, G. *Infrared Characteristic Group Frequencies, Tables and Charts*, 2nd ed.; John Wiley & Sons: London, 1994.
- (35) Yohannan, C.; Varghese, H. T.; Annamma, J.; Philip, D.; Istvan, K.; Keresztury, G. *Spectrochim. Acta, Part A* **2002**, *58*, 281.
- (36) Takasuka, M.; Kobayashi, S.; Ino, A.; Iwata, T.; Hayase, Y. *Vib. Spectrosc.* **2000**, *23*, 243.
- (37) Kolbe, A.; Plass, M.; Kresse, H.; Kolbe, A.; Drabowicz, J.; Zurawinski, R. *J. Mol. Struct.* **1997**, *436–437*, 161.
- (38) Matsushita, A.; Ren, Y.; Matsukawa, K.; Inoue, H.; Minami, Y.; Noda, I.; Ozaki, Y. *Vib. Spectrosc.* **2000**, *24*, 171.
- (39) Nakamura, Y.; Taki, M.; Asami, A.; Inokuma, S.; Hiratani, K.; Taguchi, K.; Higuchi, M.; Nishimura, J. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1615.
- (40) Szafran, M.; Dega-Szafran, Z.; Buczak, G.; Katrusiak, A.; Potrzebowski, M. J.; Komasa, A. *J. Mol. Struct.* **1997**, *416*, 145.
- (41) Drichko, N. V.; Kereskaia, G. Y.; Schreiber, V. M. *J. Mol. Struct.* **1999**, *477*, 127.
- (42) Velasco-Santos C. Ph.D. Thesis, Universidad Autónoma de Querétaro - Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Mexico, July, 2003.
- (43) Tanaka, N.; Kitano, H.; Ise, N. *J. Phys. Chem.* **1990**, *94*, 6290.
- (44) Martínez-Hernández, A. L.; Velasco-Santos, C.; de Icaza, M.; Castaño, V. M. *e-Polym.* **2003**, no. 016.