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Nanotube Functionalization and Polymer Grafting: An ab Initio Study

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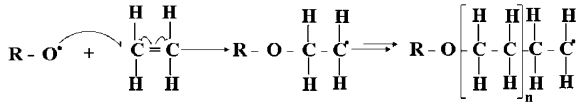
Functionalization of carbon nanotubes (CNTs) is important to increase their solubility and reactivity. This paper investigates possible ways of functionalizing CNTs using the methoxy radical and the secondary butyl anion as initiators and their reactions with ethylene and epoxide, leading to polyethylene- and polyepoxide-grafted nanotubes, with the aid of the density functional theory. The nanotubes were modeled by nanotube segments with H atoms added to the dangling bonds of the perimeter carbons. The study predicts that both free-radical and anionic functionalization methods are energetically favorable; that the resulting CNT radical and the CNT anion can react with ethylene and epoxide, respectively; and that the resulting products have free electrons and negative charges on the carbon and oxygen atoms at the free ends of ethylene and epoxide, respectively. Hence, the in situ free-radical and anionic polymerizations can propagate to produce polymer-grafted CNT. The cationic functionalization of CNTs using BF_3 as an initiator was found to be infeasible.

1. Introduction

The outstanding mechanical and electronic properties of single-walled nanotubes (SWNTs) make them attractive candidates for reinforcing polymers. However, their poor solubility and their tendency to aggregate together as bundles hinder their applications. Earlier, carbon nanotube (CNT)−polymer composites were prepared by mechanical dispersion. Although these composites showed an increase in tensile strength and Young's modulus, the change was not remarkable, because the reinforcement was achieved through adhesion and weak van der Waals forces, which give rise to lower stress transfer ability. To have a high stress transfer,[1] strong bonding between the CNTs and polymer chains is necessary. This can be achieved via chemical functionalization of the nanotubes. On the other hand, excessive functionalization of the CNTs can ruin the tubular framework and thereby reduce its mechanical strength. It has been reported that an acid treatment of CNTs could improve the processability and performance of nanocomposites by introducing carboxylic acid groups on the surface of CNTs, which leads to stabilization in polar solvents and helps to covalently link polymers.[2,3] However, the acids attack defect sites of the CNTs and cut them into many short nanotubes, thereby decreasing their aspect ratios.

Radicals and negative charges can be generated on fullerene C_{60}, and they can serve as radical and anionic initiators for further reactions with alkenes or epoxides, leading to the formation of polymer-grafted fullerene.[4,5] On this basis, a few recent papers have discussed chemically functionalizing nanotubes via the introduction of radicals or anions that can serve as initiators for the in situ polymerization process that can further lead to polymer-grafted CNT composites.[6−9] Each of these functionalization methods has its own merits. In synthesizing different polymers, different initiators that follow different mechanisms are used. For example, polyethylene is prepared by free-radical addition polymerization as described in Scheme 1, whereas polystyrene and polyepoxide are prepared by anionic polymerization as described in Scheme 2. In their work on polystyrene−nanotube composites, Viswanathan et al.[7] used *sec*-butyllithium to introduce carbanions onto the SWNT surface. They also reported that the introduction of negative charges on the nanotube surface helps to exfoliate the nanotube bundle through mutual electrostatic repulsion between tubes and provides initiating sites for the polymerization of styrene. They found that a 0.05 wt % nanotube loading in the polystyrene-grafted composite increased the glass transition temperature, T_g, of the matrix by 15 °C, whereas simple mixing of SWNTs and polystyrene led to little change in T_g. The increase in T_g is attributed to the decrease in chain mobility due to the attachment of polymer chains to the nanotubes. Recently, Qin et al.[9] functionalized SWNTs with polystyrene by the grafting-to and grafting-from methods. In the grafting-to method, they first prepared polystyrene bromide and treated this with NaN_3 to obtain polystyrene-N_3, which then adds to the SWNTs via a cycloaddition reaction. In the grafting-from method, 2-bromopropionate was used as an initiator to functionalize the nanotube, and polystyrene was grown onto this by atom-transfer radical polymerization. They found that, in the latter method, the chain length of polystyrene, and hence the solubility of the functionalized CNTs, could be controlled.

SCHEME 1: Free-Radical Addition Polymerization Scheme



SCHEME 2: Anionic Polymerization Scheme

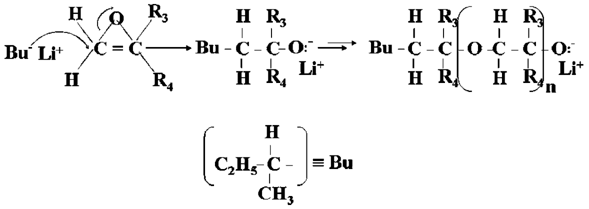


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TABLE 1: Differences in Energy between the Products and Reactants of Various Reactions and the New C−C/C−O Bond Lengths

reactant A	reactant B	difference in energy for the reaction A + B → A−B (kJ/mol)	new C−O/C−C bond length (Å)
$C_{60}H_{10}$	$^{\bullet}OCH_3$	−168.0	1.463
$C_{60}H_{10}$	$CH_3{-}CH^{-}{-}C_2H_5$	−513.6	1.602
$[C_{60}H_{10}{-}OCH_3]^{\bullet}$	$CH_2{=}CH_2$	−130.6	1.566
$[C_{60}H_{10}{-}OCH_3{-}C_2H_4]^{\bullet}$	$CH_2{=}CH_2$	−107.8	1.555
$[C_{60}H_{10}{-}C_4H_9]^{-}$	propylene oxide	+2.0	1.563
$[C_{60}H_{10}{-}C_4H_9]^{-}$	ethylene oxide	−244.7	1.629
$[C_{60}H_{10}{-}C_4H_9]^{-}$	$CH_2{=}CH_2$	−142.2	1.577, 1.571

The above experimental results are quite promising, especially Viswanathan et al.'s work,[7] where the established anionic polymerization scheme is used to grow polystyrene chains on a nanotube. The question is: Can all of the established polymerization schemes be used to prepare nanotube−polymer composites by first functionalizing the nanotubes and then using them as initiators for in situ polymerization? To answer this question, we performed an ab initio quantum chemistry analysis. Bauschlicher[10,11] and Jaffe[12] have used the ab initio quantum chemistry approach to describe the chemical modification of carbon nanotube sidewalls with fluorine and hydrogen, leading to results in agreement with experimental data. We have also performed quantum mechanics calculations and predicted that chemical bonding is feasible in polyethylene−nanotube composites.[13]

This study focuses on functionalizing nanotubes using free-radical, anionic, and cationic initiators and the possible subsequent reactions of ethylene and epoxide monomers with the functionalized CNTs. The feasibility of grafting polymer chains is also demonstrated.

2. Methodology

A (5,0) zigzag nanotube segment containing 60 C atoms (length = 11.36 Å) with hydrogen atoms added to the dangling bonds of the perimeter carbons was selected as the nanotube model. The following reactions were studied by fully optimizing the geometry of the corresponding reactants and products: (i) reaction of a simple oxy radical, $^{\bullet}OCH_3$, with the nanotube model $C_{60}H_{10}$ and the subsequent reaction of the newly formed CNT−oxy radical with a C_2H_4 monomer; (ii) reaction of *sec*-butyl anion with the nanotube model $C_{60}H_{10}$ and the subsequent reaction of the nanotube-butyl anion with an epoxide monomer; and (iii) reaction of BF_3 with the nanotube model $C_{60}H_{10}$. All calculations were performed using density functional theory (DFT) with a hybrid functional B3LYP[14−17] and a 3-21G basis set.[18] The atomic spin densities and charge densities were analyzed by the Mulliken method.[19] For open-shell molecular radicals, the unrestricted formalism was used. The present level of calculation, DFT(UB3LYP)/3-21G, is known to produce reasonable results[20] for bond lengths, bond angles, and bond energies for a wide range of molecules. The computations were carried out on a supercomputer using the ab initio quantum chemistry package, Gaussian 03.[21]

3. Results and Discussion

The calculated differences in energy between the products and reactants of various reactions are reported in Table 1. The nanotube segment considered here is of diameter 3.92 Å and hence has a high curvature. This means that the trigonal carbon atoms of the nanotube segment are quite distorted and the deformation energy required to change the hybridization of the nanotube C atom from sp^2 to sp^3 is low.

3.1. CNT Functionalization with Radical Initiator and Subsequent Reaction with Ethylene.

Organic peroxides are generally used as initiators in free-radical addition polymerization reactions. They decompose to form oxy radicals and initiate the polymerization process. Here, we examine the use of an oxy radical to functionalize the CNT. In this study, to reduce the computational cost, we use the simple oxy radical $^{\bullet}OCH_3$.

The optimized geometry of the $C_{60}H_{10}{-}OCH_3$ radical is presented in Figure 1, showing the newly formed C−O covalent bond having a bond length of 1.463 Å. The three C−C bonds radiating from the substituted sp^3 carbon of the nanotube are lengthened to ∼1.5 Å. The newly formed radical is found to be stable by ∼168 kJ/mol. This value is likely to increase with the addition of polarization functions to carbon atoms.[12] This shows that it is possible to functionalize a CNT with a radical initiator. A Mulliken spin density analysis showed that the free electron is delocalized on several nanotube carbon atoms. The nanotube carbon atom with the highest electron density was selected for reaction with ethylene monomer. The optimized geometry of the new radical (i.e., $C_{60}H_{10}{-}OCH_3{-}C_2H_4$ radical) is shown in Figure 2. We found that the new $C_{60}H_{10}{-}OCH_3{-}C_2H_4$ radical is ∼131 kJ/mol lower in energy than the reactants $C_{60}H_{10}{-}OCH_3$ radical and C_2H_4. In this case, the Mulliken spin density analysis showed that the free electron is mainly localized

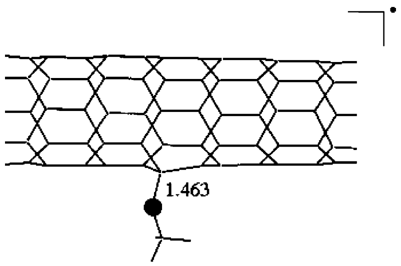

Figure 1. DFT(B3LYP)/3-21G-optimized geometry of $C_{60}H_{10}{-}OCH_3$ radical. Note that the solid sphere within the molecular framework represents an oxygen atom.

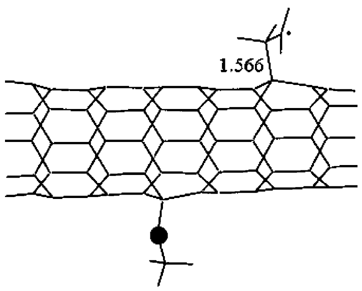

Figure 2. DFT(B3LYP)/3-21G-optimized geometry of $C_{60}H_{10}{-}OCH_3{-}C_2H_4$ radical. Note that the solid sphere within the molecular framework represents an oxygen atom.

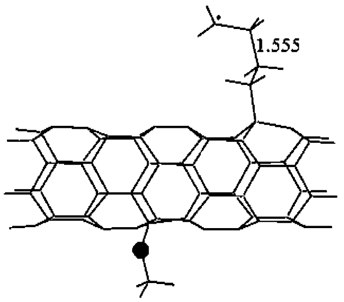

Figure 3. DFT(B3LYP)/3-21G-optimized geometry of $C_{60}H_{10}$−OCH_3−C_2H_4−C_2H_4 radical. Note that the solid sphere within the molecular framework represents an oxygen atom.

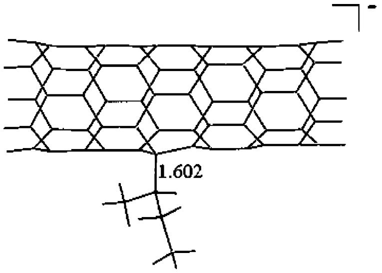

Figure 4. DFT(B3LYP)/3-21G-optimized geometry of $C_{60}H_{10}$−C_4H_9 anion.

on the carbon at the free end of C_2H_4, indicating that the resulting radical is ready to undergo a propagation reaction with another C_2H_4 monomer. Addition of a second C_2H_4 molecule formed a bond with the C atom where the free electron was localized, showing the typical propagation step in polymerization. The optimized geometry is shown in Figure 3. The new radical is 107.8 kJ/mol lower in energy than the reactants. Thus, once the nanotube is fuctionalized with a peroxide initiator, a polyethylene chain could be grafted onto the nanotube via in situ polymerization.

3.2. CNT Functionalization with Anionic Initiator and Subsequent Reaction with Epoxide. In anionic polymerization reactions, butyllithium is used as an initiator. Here, we use *sec*-butyllithium as an initiator to study the in situ composite preparation of CNT−poly(propylene oxide). The optimized geometry of the $C_{60}H_{10}$−C_4H_9 anion is presented in Figure 4. This anion is lower in energy than its corresponding reactants by ∼514 kJ/mol. This shows that the CNT can be functionalized with the anionic initiator *sec*-butyllithium and that the resulting CNT anion is very stable, as observed in an experiment by Viswanathan et al.[7] A Mulliken charge density analysis showed that the negative charge on the CNT is not concentrated on one carbon atom, but distributed over several carbon atoms. The nanotube carbon atom with the highest charge density was selected for reaction with propylene oxide. The optimized geometry of the new $C_{60}H_{10}$−C_4H_9−propylene oxide anion is displayed in Figure 5. This shows that the new C−C bond length is 1.563 Å and, as indicated in Scheme 2, the CNT anion attacks the methylene carbon of the propylene oxide. Here, the reactants and products have almost the same energy. A Mulliken charge density analysis showed that a portion of the negative charge is on the oxygen atom, indicating that the resulting anion can react with another propylene oxide monomer as in Scheme 2 so that the reaction can propagate.

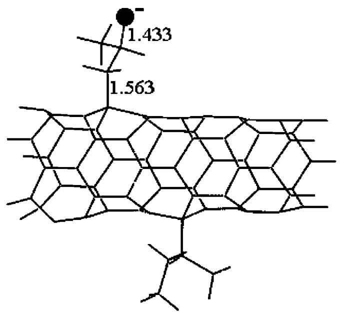

Figure 5. DFT(B3LYP)/3-21G-optimized geometry of $C_{60}H_{10}$−C_4H_9−C_3H_6O anion. Note that the solid sphere within the molecular framework represents an oxygen atom.

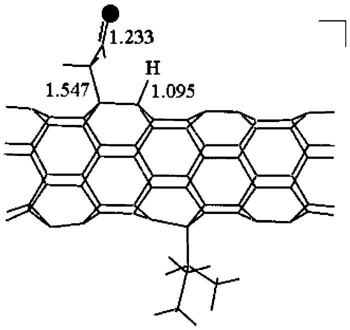

Figure 6. DFT(B3LYP)/3-21G-optimized geometry of $C_{60}H_{10}$−C_4H_9−C_2H_4O anion. Note that the solid sphere within the molecular framework represents an oxygen atom.

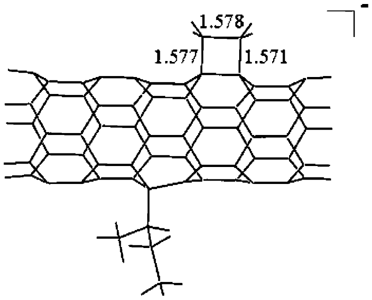

Figure 7. DFT(B3LYP)/3-21G-optimized geometry of $C_{60}H_{10}$−C_4H_9−C_2H_4.

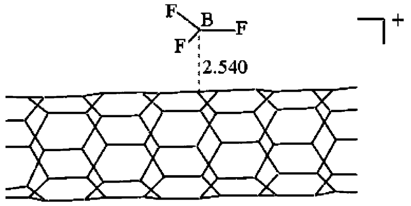

Figure 8. DFT(B3LYP)/3-21G-optimized geometry of $C_{60}H_{10}$−BF_3 cation.

We have also studied the reaction of the CNT anion with ethylene oxide. The optimized geometry of the new $C_{60}H_{10}$−C_4H_9−ethylene oxide anion is shown in Figure 6. The newly formed C−C bond length is 1.629 Å. Unlike the reaction with propylene oxide, when the anion reacts with ethylene oxide, the epoxide ring opens as in Scheme 2 and the −C−O bond shortens to −C═O and loses one hydrogen atom to the nanotube. As a result, the oxygen atom no longer possesses a negative charge for the reaction to propagate. This means that grafting a poly(ethylene oxide) chain onto a nanotube via anionic polymerization might not be feasible. An investigation on the possible reaction of ethylene with the nanotube functionalized by an anionic initiator found that the optimized geometry of the CNT anion−ethylene complex is cyclic, as shown in Figure 7. This indicates that the propagation reaction and its subsequent polymerization reaction might not take place.

3.3. CNT Functionalization with Cationic Initiator. BF_3 is used as an initiator in cationic polymerization reactions. To explore whether this established scheme can be used to prepare CNT composites, here, we study the first step: functionalization of a CNT using BF_3. The optimized geometry of $C_{60}H_{10}-BF_3$ cation is presented in Figure 8. Unlike the free-radical and anionic initiators, the cationic initiator BF_3 did not form a covalent bond with $C_{60}H_{10}$; only a van der Waals complex was formed, as shown in Figure 8, and the complex had a much higher energy than its reactants $C_{60}H_{10} + BF_3$. This indicates that the fuctionalization of a CNT with a cationic initiator BF_3 might be infeasible.

4. Conclusion

This study demonstrated that CNTs can be functionalized either by an oxy radical or by a secondary butyl anion and that the resulting CNT radical and CNT anion can function as initiators for the polymerization of ethylene and propylene oxide (but not for ethylene oxide), respectively. Functionalizing CNTs with the cationic initiator BF_3 is found to be infeasible. Thus, the established free-radical and anionic polymerization schemes can be used to prepare nanotube−polymer composites, but the cationic polymerization scheme using BF_3 as an initiator cannot be used.

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References and Notes

(1) Xiao, K. Q.; Zhang, L. C. *J. Mater. Sci.* **2004**, *39*, 4481.

(2) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95.

(3) Hill, D. E.; Lin, Y.; Rao, A. M.; Allard, L. F.; Sun, Y.-P. *Macromolecules* **2002**, *35*, 9466.

(4) Patil, A. O.; Brois, S. J. *Polymer* **1997**, *38*, 3423.

(5) Ederle, Y.; Mathis, C. *Macromolecules* **1997**, *30*, 4262.

(6) Shaffer, M. S. P.; Koziol, K. *Chem. Commun.* **2002**, *18*, 2074.

(7) Viswanathan, G.; Chakrapani, N.; Yang, H.; Wei, B.; Chung, H.; Cho, K.; Ryu, C. Y.; Ajayan, P. M. *J. Am. Chem. Soc.* **2003**, *125*, 9258.

(8) Kong, H.; Gao, C.; Yan, D. *J. Am. Chem. Soc.* **2004**, *126*, 412.

(9) Qin, S.; Qin, D.; Ford, W. T.; Resasco, D. E.; Herrera, J. E. *Macromolecules* **2004**, *37*, 752.

(10) Bauschlicher, C. W. *Chem. Phys. Lett.* **2000**, *322*, 237.

(11) Bauschlicher, C. W. *Nano Lett.* **2001**, *1*, 223.

(12) Jaffe, R. L. *J. Phys. Chem. B* **2003**, *107*, 10378.

(13) Mylvaganam, K.; Zhang, L. C. *J. Phys. Chem. B* **2004**, *108*, 5217.

(14) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(16) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(18) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(19) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

(20) D'Souza, F.; Zandler, M. E.; Smith, P. M.; Deviprasad, G. R.; Arkady, K.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 649.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 2003.