Ultrasonic Dispersions of Single-Walled Carbon Nanotubes

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The nature of single-walled carbon nanotube (SWNT)−solvent interaction that is responsible for the stabilization of ultrasonicated dispersions was investigated using various techniques. It was found that the sonochemical decomposition and polymerization of *o*-dichlorobenzene (ODCB) is necessary for the stabilization of SWNTs in ODCB. The rate of decomposition of ODCB was shown to be dependent on the shape of the sonication vessel. The decomposition products of sonicated ODCB interact irreversibly with SWNTs. Under similar sonication conditions, *N,N*-dimethylformamide (DMF) did not induce discernible modification of the near-infrared spectrum of the dispersed SWNTs.

Introduction

The dispersion and dissolution of single-walled carbon nanotubes (SWNTs) is recognized to be an important step in many of the applications that are contemplated for this unique material. Basically, two separate routes have been followed to stabilize SWNTs in solvents. Covalent[1−4] and noncovalent[5,6] functionalization of SWNTs has been shown to be effective in obtaining dispersions and solutions. However, it is also possible to disperse the (unfunctionalized) as-prepared single-walled carbon nanotubes (AP-SWNTs) by ultrasonication in a suitable organic solvent or in water using a surface-active reagent.[7,8] We include in this classification purified single-walled carbon nanotubes (P-SWNTs), in which functionality is incidentally introduced as part of the purification process—typically, this will include SWNTs that contain carboxylic acid groups that result from oxidative processes. In this paper, we address the dispersion of nonfunctionalized SWNTs, together with the process that often accompanies the formation of such dispersions: ultrasonication.

Organic dispersions of unfunctionalized SWNTs have been established as a useful state for performing chemical modifications of the surface.[6,9−11] Organic dispersions are also employed for investigating bulk samples, using atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and near-infrared (NIR) spectroscopy. SWNTs generated by the arc and laser processes are associated with a large proportion of non-nanotube carbonaceous and catalyst-related impurities. The high-pressure CO disproportionation (HiPco) produces relatively high-purity SWNTs.[12] In fact, dispersions of AP-HiPco SWNTs were observed to be stable in *o*-dichlorobenzene (ODCB),[13] to a greater extent than arc- and laser-produced SWNTs.[14] These dispersions have been used to fabricate the first SWNT crossbars.[10]

While imaging ODCB dispersions of HiPco SWNTs, we observed a coating of uneven thickness on the nanotube surfaces, when viewed at high AFM magnifications. In Figure 1, we show AFM images of the nanotube dispersions, as a function of sonication. A foreign coating of the nanotube bundle surfaces is evident (as previously observed by TEM),[9] after 3 min of sonication, whereas 10−20 min of sonication is the standard protocol for dispersing HIPco SWNTs.[10,11] The uneven nature of the coating suggested the presence of an extraneous material that was adhering to the nanotube surface and that the observed effect is not due to differences in bundle thickness.

Our efforts to obtain clean AFM images of HiPco tubes from ODCB led us to investigate the pure solvent under the ultrasonication conditions that are typically used to disperse SWNTs. We discovered that ODCB decomposes and polymerizes under these conditions, and the formation of this polymer (Figure 2) is responsible for stabilizing the SWNT dispersions. Here, we report the experimental observations that led to these conclusions, and we also discuss their implications on the study of SWNT dispersions.

Materials and Methods

We used high-pressure liquid chromatography (HPLC) grade ODCB and *N,N*-dimethylformamide (DMF) (Aldrich) for our experiments. The other available pure solvents (of anhydrous spectrophotometric grade) showed a greater amount of residue than the HPLC grade, under AFM conditions. Sonication was conducted in a 40.5-kHz bath sonicator (VWR Aquasonics).

The purpose of our investigation was to understand the effects of sonication, as is most commonly used in the processing of SWNTs. Therefore, all sonication experiments were conducted under ambient conditions with no effort to regulate the temperature of the water in the bath or the gas atmosphere inside the sonication vessel. It is not possible to control the amount of energy (given in units of W/cm^2) imparted to the liquid in this configuration. We observe differences in the intensity of the mechanical agitation of the liquid in different regions of the bath. Our experiments were, therefore, performed by immersing and positioning the sonication vessels in the region of the highest visual agitation. From sonoluminescence experiments, sonochemical reactions are known to occur only at certain locations and not necessarily at the regions of highest-intensity sonication.[15] Therefore, although it is possible to reproduce the

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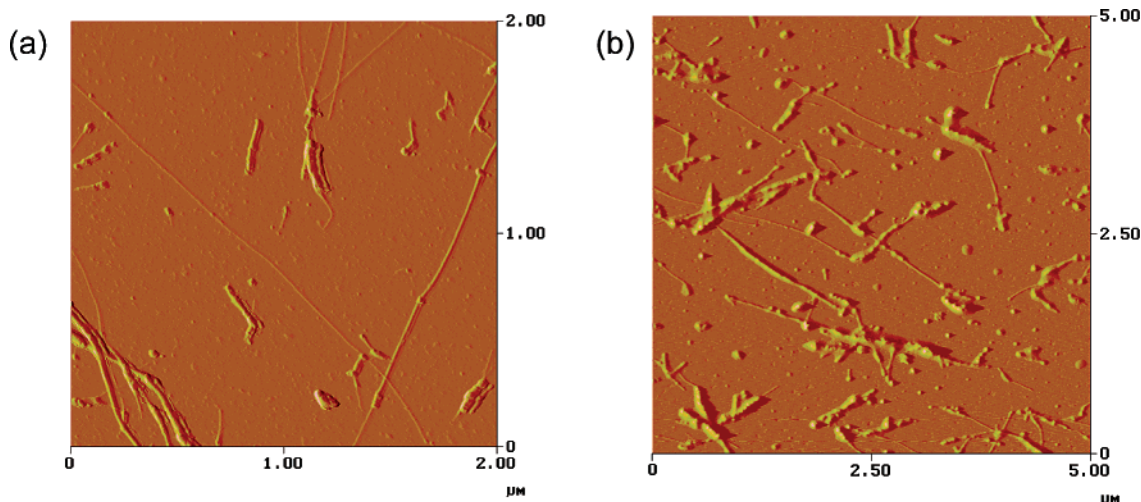
Figure 1. AFM images of HiPco SWNTs sonicated (under M-sonication conditions) in ODCB for (a) 3 min and (b) 60 min.
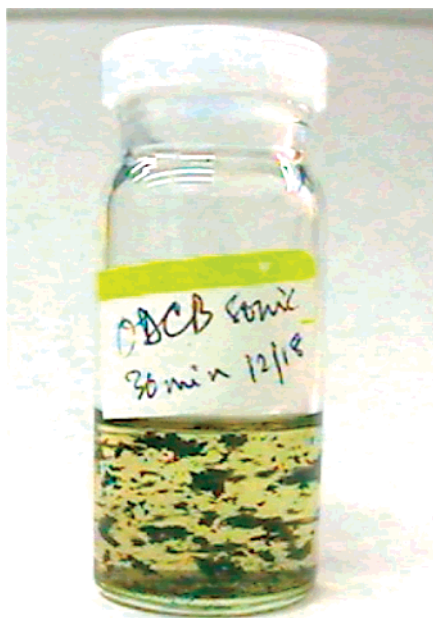

Figure 2. ODCB sonicated in a test tube for 30 min after aggregation on standing.

chemical events, a quantitative estimation of the extent of sonication is not possible.

In preliminary experiments, we established that the shape of the experimental vessel exerts a profound effect on the intensity of the sonication.[15] We, therefore, investigated sonication under two sets of experimental conditions, hereafter referenced as mild (M) and strong (S) sonication. Sonication in a flat-bottom vial generated a random effect on the contents of the vessel, and, in this situation, we sonicated the experimental container together with a blank identical container that contained only the solvent (M-sonication). However, when a 50-mL Pyrex culture tube (round-bottom) was used as the sonication vessel, the effects of sonication were considerably more consistent (S-sonication). The polymer−SWNT state was characterized in both cases. Under the M-sonication conditions, dispersing SWNTs in any solvent requires a longer time period than under the S-sonication conditions. The effects of sonication that we report here were the same under the mild and strong conditions if scaled by the time factor. A Varian model Cary500 spectrophotometer was used for the UV−vis−NIR analyses of the solutions. IR spectroscopy was conducted on ZnSe substrates, using a Nicolet

model Nexus 670 spectrometer. The AP-SWNTs used in this work were obtained from Carbon Solutions, Inc., and Carbon Nanotechnologies, Inc.

Results and Discussion

Sonolysis of the Dispersing Medium. The decomposition of organic solvents and water under ultrasonication is well documented in the literature.[16] The decomposition products of certain haloaromatic solvents are also known to polymerize when subjected to ultrasonication.[17,18] DMF, which is the standard solvent for dispersing electric arc (EA) and laser SWNTs,[8] did not show any modification of its spectrum in the NIR region for sonication times up to 30 min. Therefore, the following discussion relates only to ODCB.

We visually observed that ODCB changed from colorless to yellow[18] after 2 min of S-sonication. Organic solvent decomposition is dependent on the frequency of the ultrasound used, and 55-kHz instruments are often used to make SWNT dispersions. The shape of the ultrasonication vessel has a pronounced effect on the structure of the sonic field.[19] We observed that a round-bottom tube is more effective in dispersing SWNTs and also in decomposing ODCB. The sonolytic decomposition of ODCB was followed by NIR−vis spectroscopy (see Figure 3a). The gradual increase of the absorbance in the visible region with sonication time (Figure 3b) indicates the formation of a highly conjugated species. The absorbances of pure ODCB and the sonopolymer in the region of 6400−7600 cm^{-1} are compared in Figure 3c and d. The structured band in this region can be assigned to the overtones of the fundamental aromatic C−H vibrations (3068 cm^{-1}; see Figure 4a). After sonication, this band is replaced by a strong sharp peak.

After 30 min of S-sonication, ODCB becomes dark brown in color but remains a solution. The polymeric products coagulate after standing overnight at room temperature (Figure 2). This sonopolymer is insoluble in pure ODCB. Koshio et al.[9] sonicated SWNTs in monochlorobenzene for 5 h and then rinsed the SWNTs with the parent solvent in an attempt to remove polymerized residues. On the basis of mid-IR analysis of their products, they inferred a sonochemical reaction of nanotubes with the solvent. Oxidative heating at 400 °C removed the observed bands.

In Figure 4a and b, we compare the mid-IR spectra of pure ODCB (Figure 4a) to that of the sonopolymer that has been derived from ODCB (Figure 4b). In Figure 4a, the two bands
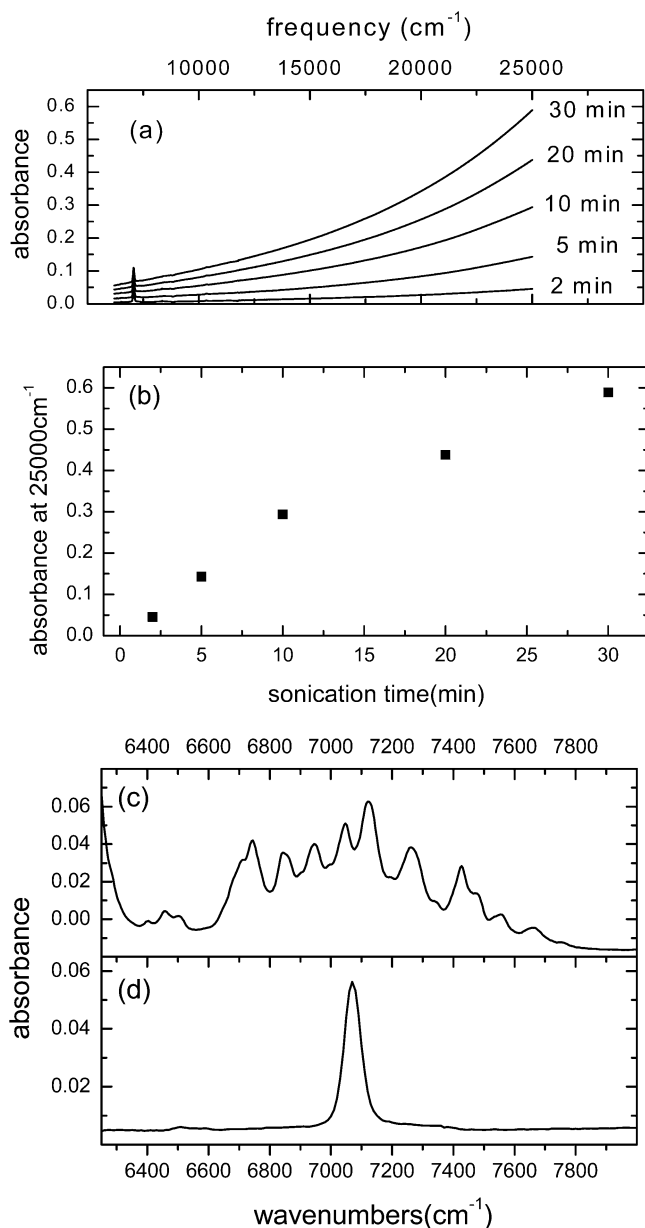
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Figure 3. (a) NIR spectra of ODCB as a function of sonication (under S-sonication conditions); (b) plot of absorption versus sonication time for pure ODCB; (c) overtones of the aromatic C−H vibration spectral region for pristine ODCB; and (d) the same region of the ODCB spectrum after sonication.

Figure 4. Mid-IR spectra of (a) pure ODCB film on ZnSe and (b) the sonopolymer formed from ODCB.

revealed M^+ peaks at 538 and 652(m/z) in one batch of the sonopolymer, whereas in another batch, we obtained M^+ peaks at 174 and 429(m/z). This variation in the molecular weight of the product may be expected, on the basis of the extreme conditions in the sonochemical process. We did not observe any higher mass fractions.

Chemical Inhibition of the Polymer Formation. For practical purposes, we considered it important to prevent the formation of the ODCB sonopolymer and to obviate its interaction with SWNTs. Alcohols and acetone are known to retard decomposition and polymer formation in certain organic solvents and, at certain concentrations, can inhibit the polymer formation completely.[20] To study whether it was possible to use this technique to prevent polymer formation, we studied the effect of ethanol on ODCB sonication. ODCB was M-sonicated with 1 vol % ethanol, and the evolution of the electronic spectrum was followed in the visible region. In Figure 5a, the absorbance at 325 nm of sonicated ODCB with and without 1 vol % of ethanol is plotted with respect to time. In the presence of ethanol, we observe a significant reduction of the absorption intensity in the visible region. Furthermore, at short times (<5 min), the polymer formation in the presence of 1 vol % of ethanol is appreciably inhibited.

In the widely accepted "hot-spot" theory, the decomposition of organic solvents is believed to occur through a radical pathway.[15] Ethanol, therefore, may act as a radical quencher in inhibiting the polymerization of ODCB. This provides a tool to study the role of the sonopolymer in stabilizing the dispersions of HiPco tubes. In Figure 5b, we show three samples (after standing for 6 months) of AP-HiPco SWNTs at similar concentrations, sonicated (under M-sonication conditions) in ODCB for increasing periods of time, both with and without 1 vol % of ethanol. The SWNTs, in the presence of ethanol, coagulate overnight; however, we see that the polymerized ODCB can keep HiPco tubes solvated for rather long periods of time. Polymer wrapping can render SWNTs soluble in organic solvents.[21−24] The following experiments establish that chemical interactions that are stronger than physical wrapping are achieved by sonicating SWNTs in ODCB.

Polymer−SWNT Interaction. We have recently reported a procedure that was based on solution-phase NIR analyses, for evaluating the relative concentration of SWNTs in a given sample.[25] Spectroscopically observed electronic transitions in

at 659 and 748 cm^{-1} are assigned to the C−Cl in-plane bending modes of an ortho-disubstituted benzene; the band at 1035 cm^{-1} is assigned to the substituent sensitive mode in the phenyl ring; the bands between 1430 and 1450 cm^{-1} are due to the aromatic ring; and the bands at 3068 cm^{-1} are due to the aromatic C−H stretching vibrations. The removal or broadening of the key vibrations of ODCB on formation of the sonopolymer is evident. It may be noted that the vibrational structure resembles a cross-linked polystyrene, similar to that which is observed after toluene undergoes sonication.[18] However, Koshio et al. did not observe any IR bands after sonicating SWNTs in toluene. Koshio et al. observed the band at 1730 cm^{-1}, along with the alkyl C−H stretching bands at ∼2800−2900 cm^{-1}. Their observation of a much weaker IR signature may be explained by the fact that they analyzed SWNT samples, whereas we analyzed the isolated polymer. The matrix-assisted laser desorption ionization time-of-flight (MALDI TOF) mass spectrum of the sonopolymer
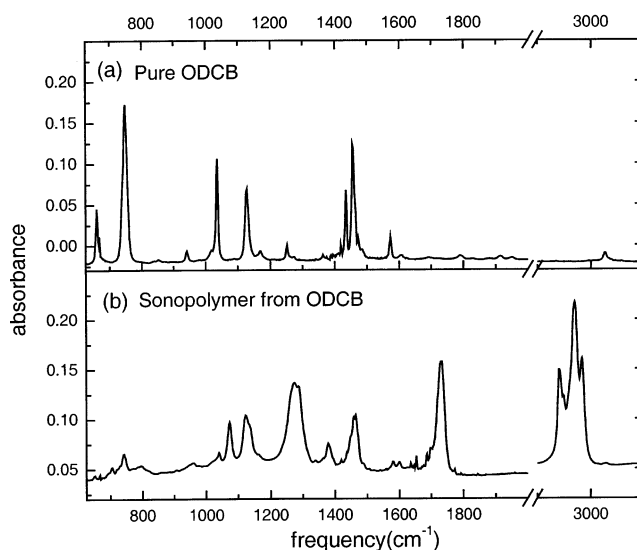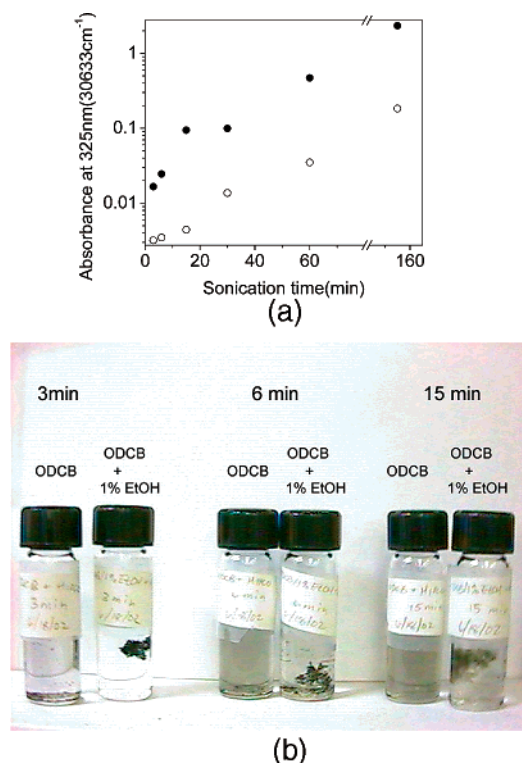
Figure 5. (a) Growth of the conjugated polymer with sonication time (under M-sonication conditions) in (●) pure ODCB and (○) ODCB with 1 vol % ethanol; (b) the behavior of HiPco AP-SWNTs in pure ODCB and in the presence of 1 vol % of ethanol, as a function of sonication time.

SWNTs have been interpreted in terms of the aggregation state of SWNTs.[26,27] We now use NIR spectroscopy to understand the polymer−SWNT interaction.[28−30]

To investigate the nature of the interaction of the sonochemical polymer and solvent decomposition products with SWNTs, EA and HiPco AP-SWNT samples were sonicated both in ODCB and DMF. As controls, samples of the pure solvents were sonicated at the same position and time intervals. This allowed us to follow the time dependence of the NIR spectrum of SWNTs in pure and sonicated solvents. Similar results were obtained under the M- and S-sonication conditions. We shall discuss the results from the S-sonication experiments, for the reasons outlined previously.

(a) o-Dichlorobenzene (ODCB). In Figure 6a, we show the NIR spectrum of EA SWNTs in ODCB, as a function of the sonication time, with pure ODCB as the background. With increasing sonication time, the baseline of the spectra grows, similar to that observed in Figure 3a for pure ODCB. The diminution of the NIR fine structure (Figure 6b) is obvious. By subtracting a linear baseline [25] from the S_{22} transition band of SWNTs, we observe a loss of fine structure and intensity, as well as a shift of spectral weight toward higher frequency.

Similar effects are also observed for the HiPco SWNTs (Figure 7). In Figure 7a, the spectra are offset to emphasize the increasing baseline and decreasing band structure of the S_{11} transition. It may be noted that the S_{11} transition of HiPco SWNTs is located at a lower frequency than the S_{11} transition of the EA SWNTs, because of the inverse relation of the energy band gap to the diameter of the nanotubes.

Covalent functionalization on the sidewalls is expected to disrupt the electronic band structure of SWNTs, and the observed loss of spectral intensity and structure after chemical processing has been ascribed to such chemical changes in the
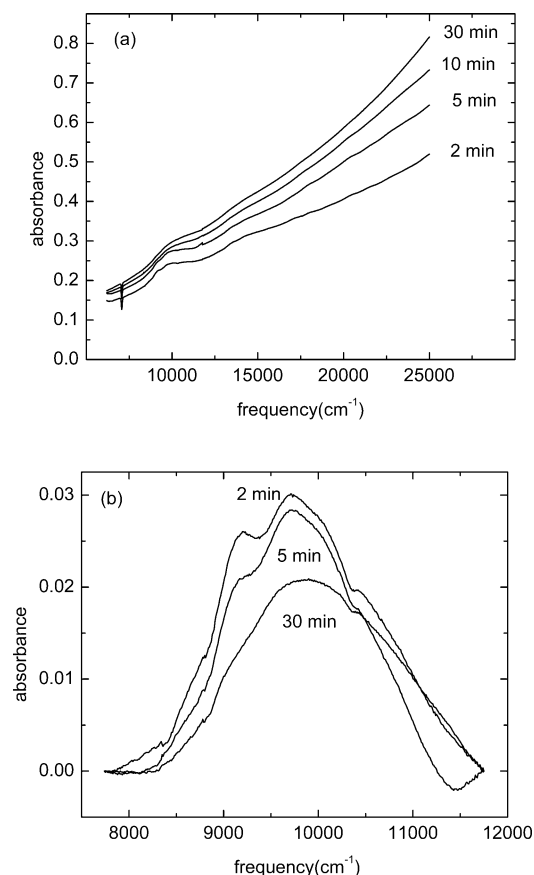

Figure 6. NIR spectra of EA AP-SWNT sonicated (under S-sonication conditions) in ODCB: (a) uncorrected and (b) the S_{22} peak after baseline correction.
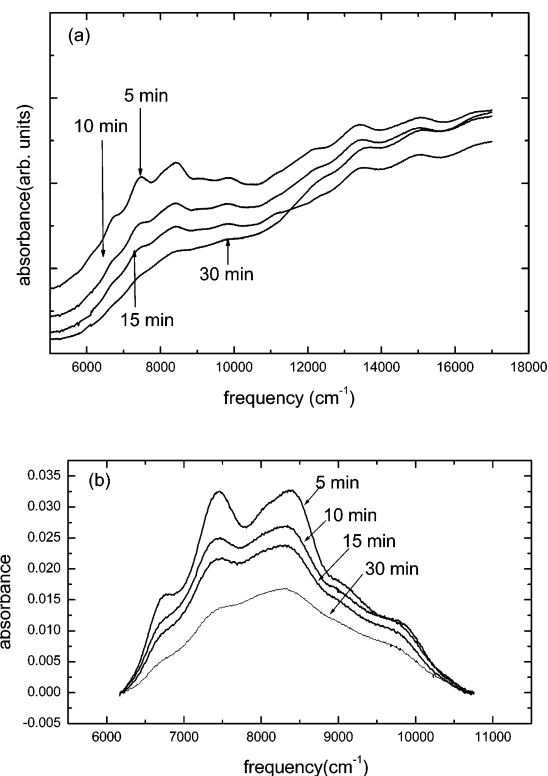

Figure 7. NIR spectra of HiPco AP-SWNTs sonicated (under S-sonication conditions) in ODCB: (a) uncorrected, but offset for clarity, and (b) the S_{11} peak after baseline correction.

structure of SWNTs.[1,11,31,32] The doping of SWNTs has also been shown to alter the spectral intensity of the S_{11} transi-

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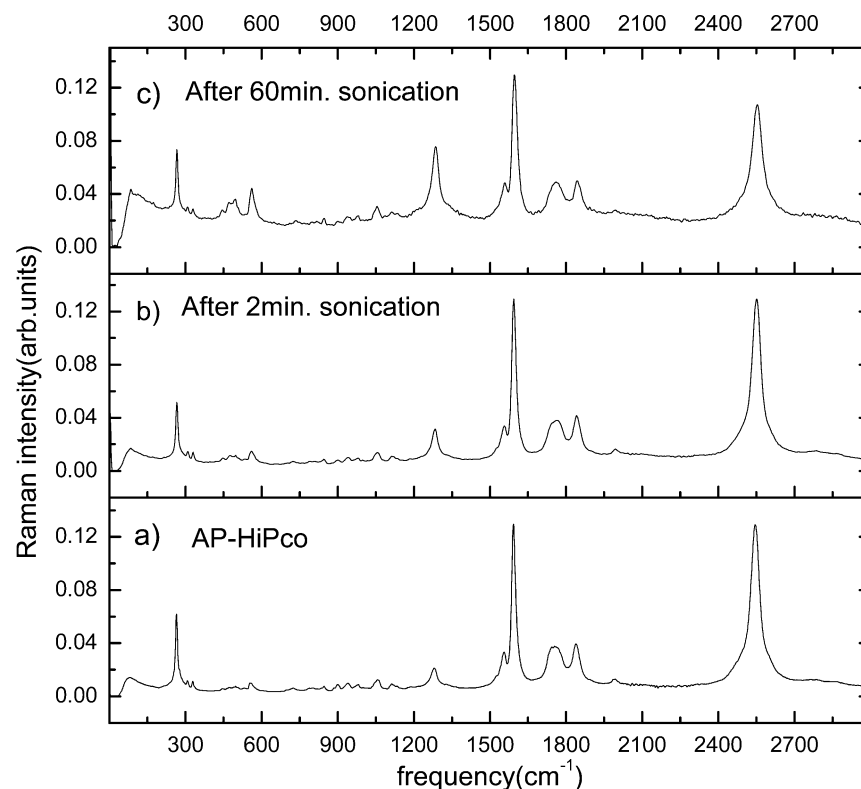*J. Phys. Chem. B, Vol. 107, No. 34, 2003* **8803**

Figure 8. Raman spectra of SWNT films prepared from dispersions in ODCB, showing the effect of sonication on AP-HiPco SWNT. All sonications were conducted under S-sonication conditions. Spectra have been normalized at the tangential-mode band frequency.

tions,[1,33−37] and, in certain circumstances, the S_{22} transition is also affected.[1,38] In some cases, the missing spectral intensity can be partially restored.[31,37−39] Complete restoration of the spectral intensity after covalent modification of the sidewalls has not been achieved.[31,38,40] In our case, films of HiPco SWNTs, prepared by sonication (under S-sonication conditions) in ODCB, when annealed for 90 min at 350 °C at 10^{-6} Torr, did not lead to complete recovery of the fine structure and intensity. Annealing the same film to 500 °C decreased the intensity and structure of the electronic transitions, contrary to previous observations.[31,38,40] These observations lead us to believe that sonication in ODCB irreversibly damages the integrity of the SWNT structure.[41,42]

The Raman spectra of SWNTs is resonantly enhanced if the excitation energy is close to the band-gap transition energies.[43] Thus, Raman spectroscopy can be used to study structural changes in SWNTs that lead to changes in the electronic structure. The Raman spectrum of SWNTs consists of three prominent vibrational groups, which are called the radial breathing mode (RBM) ($\sim$200 cm^{-1}), the tangential mode (TM) ($\sim$1600 cm^{-1}), and the disordered (D) band ($\sim$1300 cm^{-1}). The intensity of the D-band is commonly interpreted in terms of the concentration of sp^3 defects that are present in the nanotube sidewalls,[44] in accord with previous observations on SWNT samples that had undergone covalent wall functionalization.[31] AP-HiPco SWNTs that had been sonicated (under S-sonication conditions) showed a marked increase in the D-band intensity (Figure 8), with respect to the RBM- and the TM-band intensities. Similar effects may be expected for the EA- or laser-produced tubes.

SWNTs have previously been observed to act as chain-terminating surfaces when a polymerization reaction is conducted in their presence.[21,45] We have observed that the formation of the polymer is directly responsible for stabilizing SWNTs in solvents; therefore, it is possible that the polymer undergoes termination and becomes immobilized on the nanotube surface. This would also lead to a gradual exfoliation of the SWNT bundles, exposing the smaller-diameter tubes. The shift of spectral weight to higher frequency in Figure 6b hints at such behavior; however, such a mechanism would also lead to a difference in the rate of polymerization of pure ODCB versus ODCB in the presence of SWNTs. Although our NIR experiments with sonicated ODCB backgrounds indicate a faster saturation of the polymerization in the presence of SWNTs, the nature of the ultrasonic field, as explained previously, prohibits conclusive arguments.

(b) Dimethylformamide (DMF). Under 50-kHz sonication, liquid amides decompose but are not known to polymerize.[46] EA-produced AP-SWNTs that were sonicated in DMF (under S-sonication conditions) did not exhibit obvious changes in the electronic structure of the nanotubes (Figure 9). HiPco SWNTs do not form dispersions in DMF[13] at useful concentrations, although the NIR spectral features of these dilute dispersions were retained when subjected to ultrasonication under S-sonication conditions. Ultrasonication is known to damage SWNT walls;[47] however, the damage is not detectable by NIR spectroscopy under these conditions.

Conclusion

The dispersion of single-walled carbon nanotubes (SWNTs) in *o*-dichlorobenzene (ODCB) leads to the formation of a sonopolymer, which adheres to the nanotube surface. If this polymer is prevented from forming, nanotubes do not form stable dispersions in ODCB. Furthermore, if ODCB is allowed to polymerize sonochemically, SWNTs cannot be dispersed in the decomposed and partially polymerized solvent by vigorous agitation or heating. If a simple polymer-wrapping mechanism was involved in dispersing SWNTs in ODCB, SWNTs would be expected to be dispersed in the preformed polymer relatively
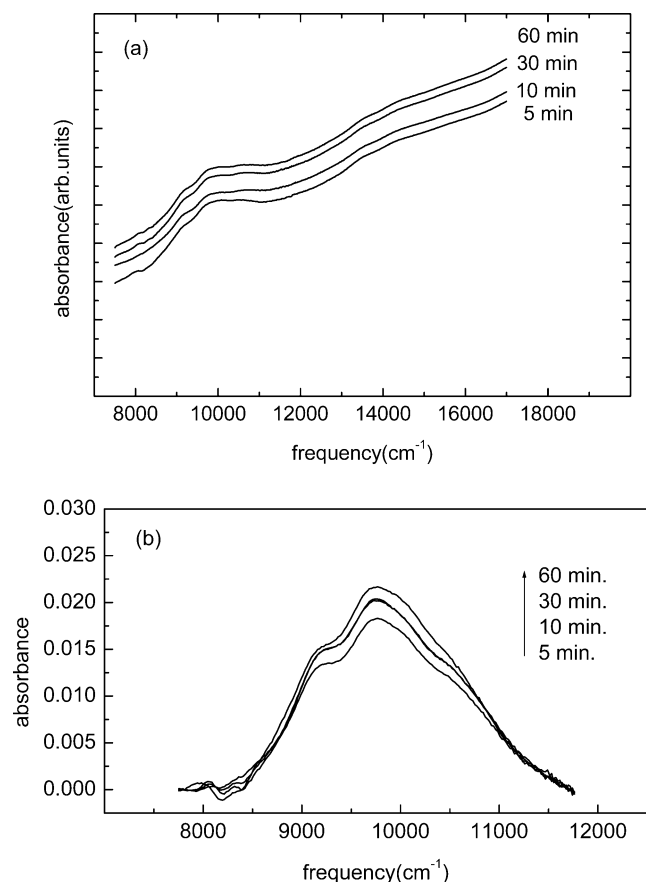
Figure 9. NIR spectra of EA AP-SWNTs sonicated (under S-sonication conditions) in DMF: (a) uncorrected, but offset for clarity, and (b) the S_{22} peak after baseline subtraction.

easily. The chemical interaction of the sonopolymer with the SWNTs was found to be irreversible, and, under conditions that might be expected to remove covalent functionalities, we observe degradation of the SWNTs. The fact that sonication can cause structural damage has been known[47,48] for some time. The present manuscript shows that sonication can irreversibly disrupt the electronic and molecular structure of SWNTs.[22]

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