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Organization of Polymers onto Carbon Nanotubes: A Route to Nanoscale Assembly

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ABSTRACT

Atomic scale imaging using scanning tunneling microscopy has been used to investigate the morphology and structure of high molecular weight polymers attached to carbon nanotubes. A surprising degree of regularity is observed in the attached polymers, suggesting a "nanotube-driven" crystallization process is present. The symmetries of this crystalline state of the polymer are directly determined by the underlying nanotube's chirality. Tunneling spectroscopy further demonstrates that the crystallization of the polymer onto the nanotube results in modifications to the nanotube's electronic structure, as would be expected from a strong polymer–tube interaction. The assembly of nanoscale organics into objects with such perfect order clearly foreshadows the construction of large-scale nanoarchitectures with order over many lengths scales.

Since their discovery in 1991, carbon nanotubes have held the promise of nanoscale electronics, nanomachines, and a myriad of other exotic applications at the nanoscale.[1] Utilization of the unique properties of such nanomaterials and realization of next generation miniaturization centers on the development of two fundamental capabilities. The first is spatial control and dispersion of individual nanobuilding blocks including the manipulation of individual molecules into hierarchal architectures. Placing such small objects where they are needed is a Sdaunting task in two dimensions. Schemes for three-dimensional positioning seem impossibly complex. The second is chemical modification and the construction of complex new structures from carbon nanotubes is essential in that it will allow a much broader applicability of these materials. Their properties are amazingly varied, ranging from a rather good metal to semiconducting depending on the macromolecular symmetry called "chirality". Through chemical modification, individual tube-to-tube construction suggests the possibility of many different types of nanomachinery. For this we must learn to use chemistry as our building mortar.[2]

In this article we describe a significantly different approach to these difficult issues; the use of carbon nanotubes to pattern a high molecular weight polymer. The resulting order of the attached polymer across the tube is surprising and seems to reflect the structural perfection of the tube itself. This templating of crystalline polymer order from the nanotube suggests the possibility of constructing uniquely ordered, chemically tailored, nanostructured materials in bulk from carbon nanotubes. The possibilities for such materials are manyfold, from simple attachment to a polymer matrix material for enhanced yield strength to the construction of larger polymeric architectures with order over many different length scales such as artificial bone with the ultimate in toughness.

In these studies, arc-grown multiwalled (MWNT) and single-walled (SWNT) nanotubes are used as the beginning or templating nanomaterial.[3] An initial filtering step was used to reduce impurities in the raw materials as much as possible using micron-sized porous filters. This tends to reduce catalyst content and removes a large portion of the amorphous carbon. Tube lengths were controlled by using acid-cutting techniques reported elsewhere for MWNTs and SWNTs.[4] STM (scanning tunneling microscopy) and TEM (transmission electron microscopy) were used to characterize any damage that may result from the cutting step. Quite generally, the initial filtering coupled with the acid cutting provides an extremely pure starting material, as determined by microscopy techniques.

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To fully recover the carboxylic acid groups on the nanotube surface after initial cutting, an HCl solution was used. This was followed by reflux in neat $SOCl_2$ for 24 h to convert the carboxyl acids into acyl chlorides. After the reflux, these "functionalized" tubes were mixed with poly(propionylethylenimine-*co*-ethylenimine) (PPEI−EI, $M_w \sim$ 200 000, EI mole fraction ~ 15%) and reacted at 165 °C for 20 min so that the tubes would attach to the PPEI−EI via amidation to form nanotube−PPEI−EI polymers. The reaction mixtures were repeatedly extracted with chloroform to obtain the soluble fractions, which were then purified through repeated precipitations. The same reaction conditions were also used to attach shortened SWNTs to poly(vinyl acetate-*co*-vinyl alcohol) (PVA−VA, $M_w \sim$ 110 000 alcohol mole fraction ~ 40%) via ester linkages, though in this paper we will focus on results of PPEI−EI attached tubes. For more complete details of the chemical routes used, see ref 2.

These polymer-bound nanotubes are soluble in both organic solvents and water. The solutions appear colored and homogeneous. Solutions of the MWNT−PPEI−EI polymer samples in chloroform are quite clear, as shown in Figure 1a. When observed under TEM (not shown) as well as STM (below), it is clear that the solution contains large amounts of carbon nanotubes. Figure 1b shows an idealized cartoon for the polymer-attached nanotube species. The optical absorption spectra of these solutions, in general, show very little Rayleigh scattering, indicating almost complete mitigation of aggregation of the nanotubes with an estimated aggregate size of less than 200 nm. Shown in Figure 2, the UV−vis absorption spectra at different concentrations of the SWNT−PPEI−EI polymer, demonstrates that absorption phenomena are linearly dependent on the solution concentrations (Beer's law). This indicates the suppression of any optical behaviors that are typically associated with aggregation or absorption of any bi- and multimolecular species. This is in contrast to ultrasonically dispersed materials, where the absorption behavior depends on the length of time of ultrasonic agitation, settling time, etc.

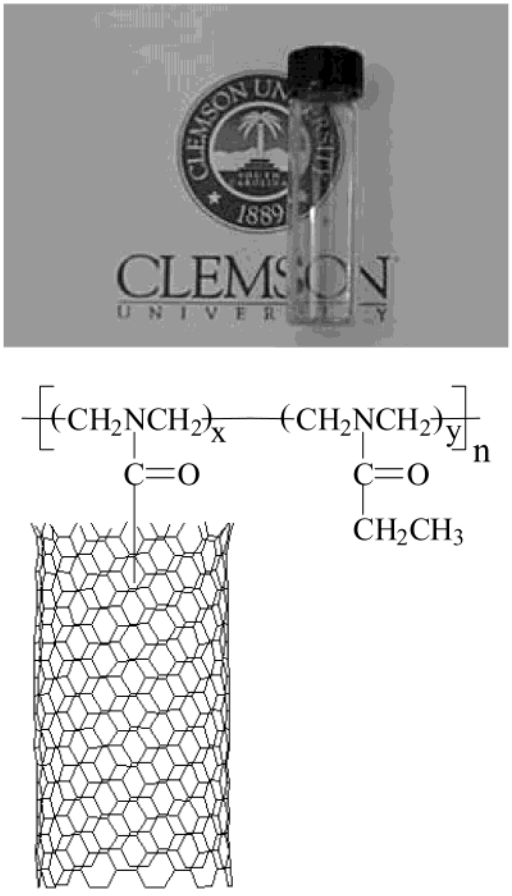

Figure 1. (a) Suspension of functionalized nanotubes with ~0.5 wt % of SWNTs. (b) Idealized cartoon of the PPEI-EI attachment.

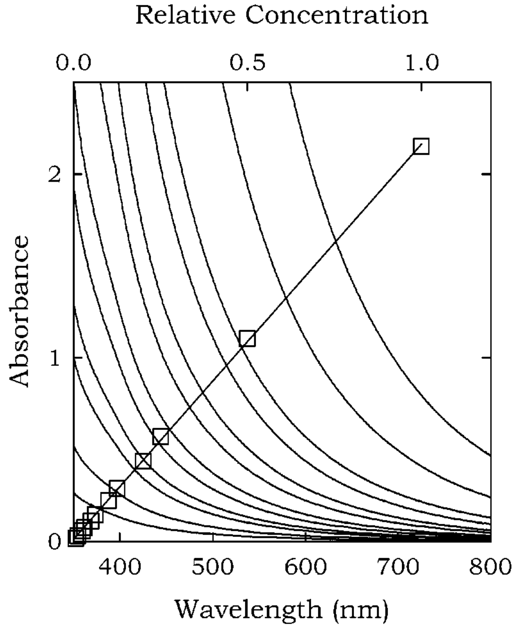

Figure 2. UV−vis absorption spectra as a function of concentration. The straight line shows a linear absorption dependence on concentration (scale on top).

While the optical properties of these suspended tubes provide compelling evidence that polymer functionalization has occurred, they can give only limited information as to the structure of the attached species relative to the nanotubes. However, scanning tunneling microscopy can supply a direct, visual, account of the structure of the functionalizing polymer as well as spatially resolved electronic information. Figure 3, below, shows several images of the film of the SWNT−PPEI−EI as cast on highly oriented pyrolytic graphite (HOPG). Notice that in "far-view", the film appears to be disordered clumps of polymer with nanotube "sticks" protruding all around. In higher magnifications of a single set of nanotubes, it is clear that this particular film has been made with shortened SWNTs, as most of the tubes are around 30 nm in length. Under still greater magnification it can be clearly seen that the tubes are separated from their bundles with the tips of the tubes slightly greater in diameter than the tube body. Figure 4 shows several of these functionalized nanotube−polymers at "atomic" scale. The organization of the polymer at the tube tip and in many cases along the tube body is stunning and suggests that the interaction along the tube body is far from random. Notice that there exist several different patterns that occur.

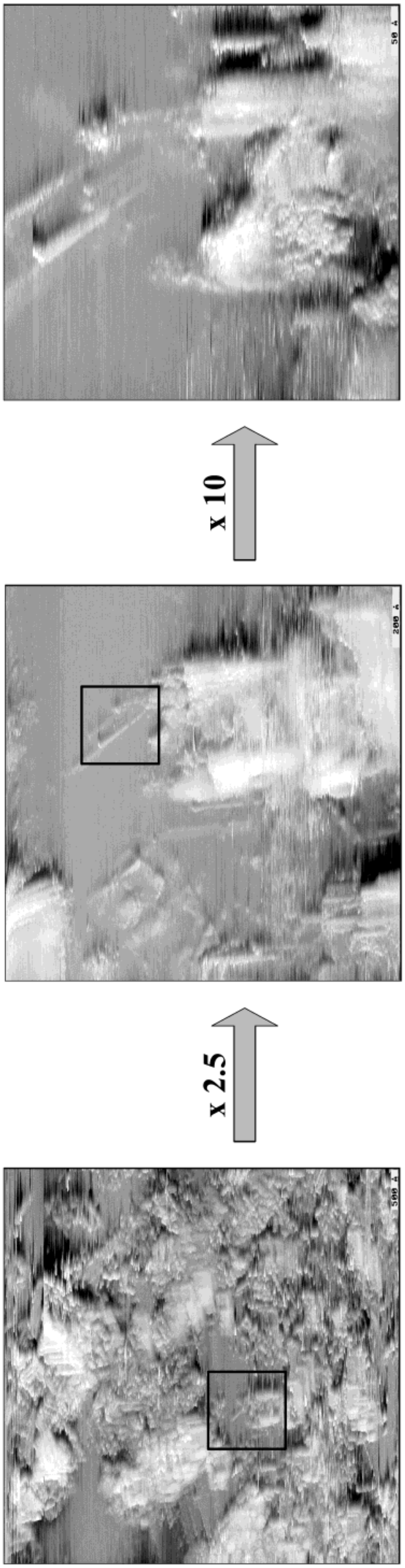

Figure 3. STM images of cast NT-PPEI-EI films show an abundance of nanotubes throughout. At low magnifications the cast PPEI−EI film appears as nonwetting domains across the HOPG surface (left). At higher magnifications it becomes evident that the film is actually composed of many sticklike structures surrounded by an "amorphous" material (middle). At yet higher magnifications, the nanostructures (carbon nanotubes) are seen to be well-separated from their bundles (right).

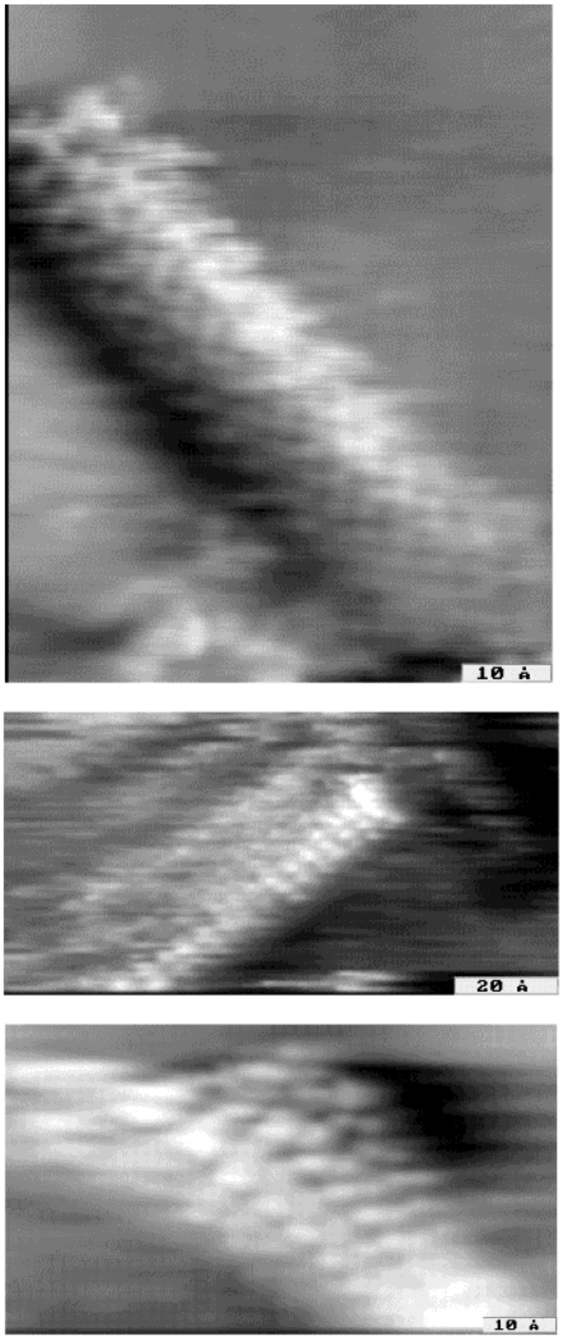

Figure 4. Several patterns of the polymer−nanotube system are observed in STM imaging.

In fact, these patterns seem to follow (where it can be determined) the macromolecular twist, or chirality, of the tube that is templating (or crystallizing) the polymer. We note that changes in the scan direction do not change the overall pattern observed and generally atomic resolution of the substrate is seen on both sides of the object as we image. This fact is important in that it is well-known that moiré patterns, due to sliding instabilities, can occur in imaging at nanotube tips, making it appear as though ordered adsorbates are present.[5] Further evidence of this can be seen in cases where a tube has been pinned on both ends by the polymer film. Again, the same repeat patterns and length scales typical of these objects are observed. Clearly, the images of Figure

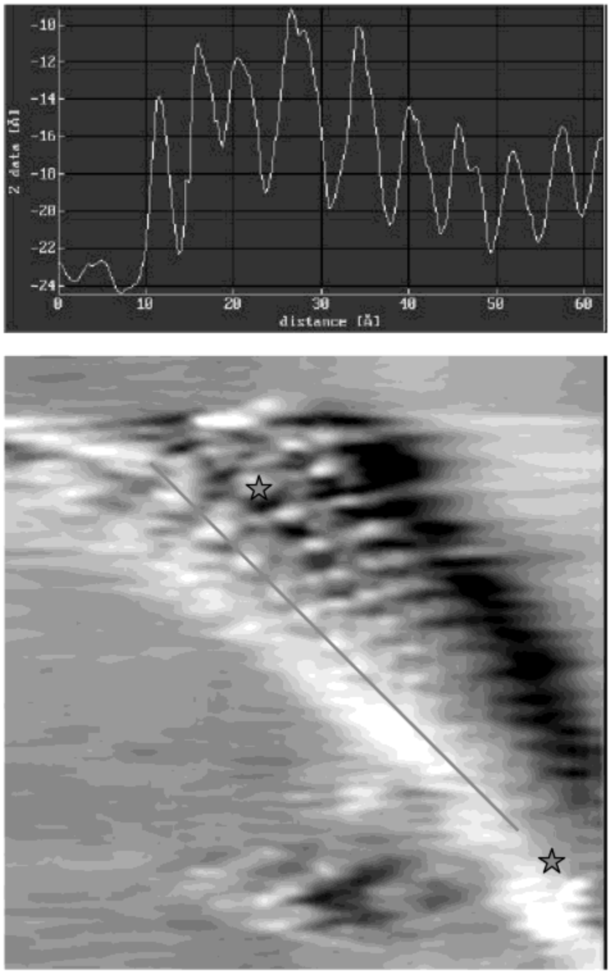

Figure 5. Cross-section along the tube showing the regularity of the polymer structures. The stars mark the positions of tunneling spectra as shown below.

4 imply that the polymer is interacting with the length of the tube and not just at the tip, as we had supposed given the reaction chemistry used. It is generally true of all images of these objects that the polymer can be found quite far down the length of the tube from the tip and sometimes covering the entire tube. We do note that the tubes are surrounded in the image with PPEI−EI polymer. The HOPG surface does not seem to induce the same ordering as that seen on the nanotubes.

In Figure 5 a cross section of the structure reveals its amazing regularity. The repeat unit along the tube axis is around 0.6 nm. The heights of these objects (for SWNTs) are between 2 and 4 nm. Again, we note that the hexagonal structure of the tube is recovered on the tube body for longer tubes. This tube happened to be chiral and the polymer structure appears to mimic the chirality. Calculations are currently underway to determine the lowest energy configuration for the polymer on the hexagons of the nanotube.

To better understand nanotube−polymer interactions, the low-energy electronic structure of the nanotube−polymer was investigated by tunneling spectroscopy. Generally, this involves holding the STM tip over some area of interest in the functionalized tube, disabling the feedback, ramping the voltage, and collecting the current. This was done during image acquisition so that tip drift from the areas under investigation would not be an issue. The resulting IV spectra are then differentiated to reflect the differential conductivity and then renormalized to remove the effects of tip height as described by Feenstra.[6] We will take the normalized conductance to be equivalent to the local density of electronic states around the region that the spectrum was collected. It is noted that these spectra were collected at ±1.0 V to maintain the integrity of the tunneling junction. Since these energies are smaller than bonding energies expected in C−C systems (recall that the $\pi-\pi^*$ states occur at ±1.5 V), it is not expected that the tunneling spectra can provide direct information about the polymer−nanotube bond in this system. However, it is useful to compare the modification of the tube's electronic structure near the Fermi level as an indication of the interaction between tube and polymer. Shown in Figure 6, the LDOS (local density of electronic states) is compared between positions along the bare nanotube and on the polymer structure as marked in Figure 5.

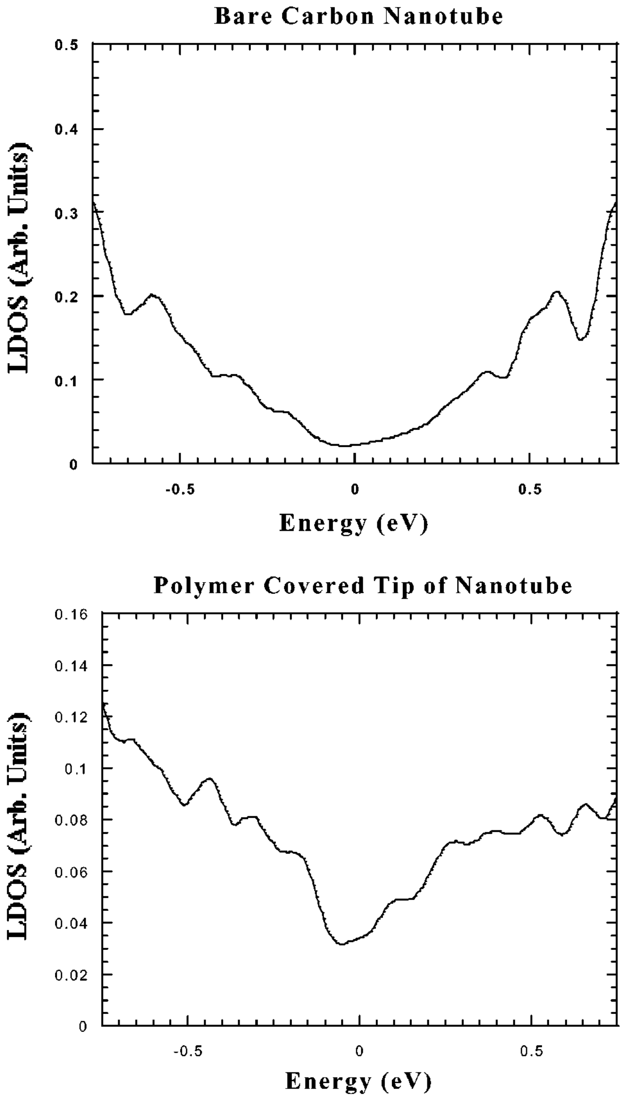

Figure 6. Local density of electronic states (LDOS) plots show a significant polymer−nanotube interaction. Above is the clean tube; below is the polymer covered tube.

Along the bare tube, van Hove singularities are seen, as expected.[7] In the example shown, the nanotube is a chiral tube with a semiconducting band gap of approximately 0.5 eV. The LDOS spectrum over the polymer portion of the tube is quite different however. Clearly, significant modifications to the negative portion of the LDOS have occurred. Since the tip is biased relative to the substrate, this part of the LDOS represents the unfilled states or the valence band states of the object. The addition of low-energy acceptor states to this system suggests that a nonnegligible interaction between the nanotube and the polymer has taken place. Further, it seems plausible that the resulting transfer of charge out of the nanotube onto the polymer structure has an effect on the process of crystallization of the polymer around the tube.

In summary, we have demonstrated chemical control over carbon nanotubes through the attachment of high molecular weight polymers. The attachment results in a highly ordered polymer around the nanotube. This provides us with a first step toward more complex construction using these nanomaterials.

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(3) For the images shown here, arc grown materials were used. However, these processes have been tried with laser grown materials from tubes@rice with the same results.

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(7) Wildöer, W. G.; et al. *Nature (London)* **1998**, *391*, 59. Odom, T.; et al. *Nature (London)* **1998**, *391*, 62. Note, in fact, these are groups of Van Hove singular points. Since the experiment is done at room temperature, individual singularities are not resolved.

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