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Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping

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Abstract

Single-walled carbon nanotubes (SWNTs) have been solubilized in water by non-covalently associating them with linear polymers, most successfully with polyvinyl pyrrolidone (PVP) and polystyrene sulfonate (PSS). This association is characterized by tight, uniform association of the polymers with the sides of the nanotubes. A general thermodynamic drive for this wrapping is discussed, wherein the polymer disrupts both the hydrophobic interface with water and the smooth tube–tube interactions in aggregates. The nanotubes can be unwrapped by changing the solvent system. This solubilization process opens the door to solution chemistry on pristine nanotubes, as well as their introduction into biologically relevant systems. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

For all the promise of single-walled carbon nanotubes (SWNTs) implied by their unique architecture and remarkable mechanical [1] and electrical [2] properties, their poor solubility characteristics [3] have hindered their chemical manipulation, and thus their use in applications. The most successful approaches to SWNT solubilization to date have involved chemical modification of the tubes, significantly altering their desirable properties [4,5]. And the attempts at dissolving the SWNTs in water, the medium required for any eventual interface to biochemistry, have relied on surfactants, an approach severely restricting the concentrations accessible [6] and with the potential to denature biological molecules.

In this study we describe a technique for rendering underivatized SWNTs water soluble in the g/l concentration range. This approach, wrapping water-soluble linear polymers around the tubes, is robust and general, allowing pristine nanotubes for the first time to be manipulated reliably by solution-phase techniques such as chromatography and electrophoresis, and simplifying their use as chemical reagents.

2. Experimental

SWNTs were produced by both the laser-oven [7] (Tubes@Rice, Houston, TX) and HiPco [8]

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methods. As received, laser-oven SWNT material (dispersed in toluene) was filtered (Whatman #41) and washed with methanol and then with water. The SWNTs were then homogenized with a high-shear mixer (Polyscience X-520) and refiltered repeatedly until the filtrate was clear and colorless. HiPco SWNT material was purified by gas-phase oxidation, hydrochloric acid extraction, and high-temperature annealing [9].

SWNT material from both sources was dispersed in 1% sodium dodecyl sulfate (SDS) in water at a concentration of 50 mg/l by a combination of high-shear mixing and sufficient ultrasonication to ensure that primarily individual SWNTs were present, as evaluated by AFM [10]. Enough polyvinyl pyrrolidone (PVP) was added to the mixture to result in a 1% solution by weight, which was then incubated at 50°C for 12 h. The mixture was passed through a 1 μm track-etched polycarbonate filter. Catalyst particles remaining from the SWNT synthesis were then removed by passing the dispersion through a high-gradient magnetic separator (HGMS) [11]. Residual SDS and polymer were removed by at least three cycles of high-speed centrifugation (200 000 g, 2 h), decanting, and redispersion in pure water by mechanical agitation including mild (10 min or less) ultrasonication to produce a stable solution of PVP wrapped SWNTs (PVP–SWNTs) in water, uniformly dispersible up to 1.4 g/l.

3. Results and discussion

3.1. Solubilization by polymer wrapping

AFM images of PVP–SWNT supramolecular aggregates adsorbed onto amine-functionalized substrates show SWNT height and length distributions consistent with the notion that most of the complexes consist of a single SWNT associated with at most a monolayer of polymer, and a
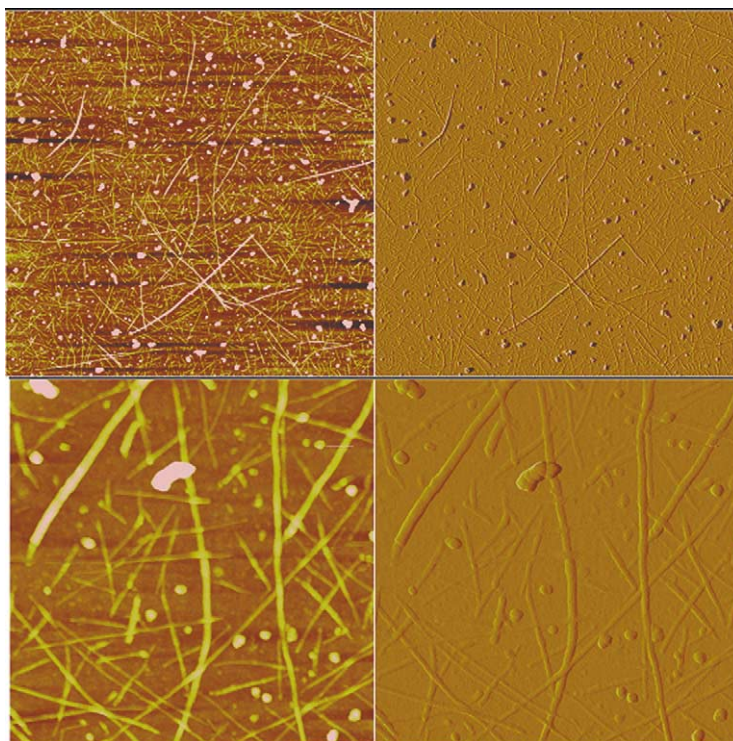

Fig. 1. Tapping-mode AFM images of PVP–SWNTs on a functionalized substrate. 5 μm height image (top left) and amplitude image (top right). 1 μm expanded height image (bottom left) and amplitude image (bottom right).

smaller percentage of ropes consisting of more than one SWNT (Fig. 1). The solutions formed are stable for months, and easily pass through a 1 μm track-etched polycarbonate filter membrane. When the material is dried, it is easily redissolved into pure water with minimal ultrasonication, in dramatic contrast to dried non-polymer-wrapped SWNT material in any other solvent system.

Solubility is a measure of an equilibrium between the dissolved phase and the aggregated phase, so one component to increasing solubility could be the destabilization of the solid. The smooth, uniform interaction surface along pristine SWNTs allows a remarkably robust van der Waals interaction between them [12]. The pair-wise interaction potential between parallel SWNTs has recently been determined by a continuum model [13]. For every nanometer of overlap between two $(10, 10)$ tubes, the binding energy is 950 meV. Thus, summed for a typical SWNT length of 100 nm embedded in a rope, the cohesive energy is a

Fig. 2. Typical paper formed by filtering SWNTs from organic or surfactant suspension, consisting of large ropes (top). Paper formed by filtering PVP–SWNTs (bottom). Scale bars are 500 nm.

staggering 2.9 keV. It might be expected, therefore, that modifications to the SWNTs that disrupt the uniform interactions along their lengths in a hexagonally packed crystal would shift their equilibrium in solvents toward the dissolved phase. Such modifications could be side-wall functionalization [5], end-cap functionalization [4], or wrapping the SWNTs with a polymer. In filtered papers made from non-wrapped SWNT dispersions, the tubes self-assemble into mats of tangled, seemingly endless ropes, wherein a majority of the tubes are in direct van der Waals contact with other SWNTs along their entire length [7,12]. Filtered papers of PVP–SWNTs, on the other hand, exhibit no such large-scale structure (Fig. 2), consistent with the above view.

3.2. Robust association between polymer and SWNTs

A modified flow field-flow fractionation (FFF) technique was used to test the stability of polymer wrapping. 20 μl of a dissolved 0.46 g/l PVP–SWNTs were injected into the flow FFF instrument (Universal Fractionator Model F-1000, FFFractionation, LLC) with zero cross-flow and a channel flow of water with 0.02% sodium azide (a bacteriocide). When the sample entered the cross-flow region, the channel flow was halted and a cross-flow of 0.5 ml/min was initiated, pinning the sample against the accumulation membrane. The sample was washed by the cross-flow against the membrane for 40 min, after which the cross-flow was halted and the channel flow reinitiated, allowing the sample to be collected when it exited the flow FFF. The final samples were compared to the starting material by tapping-mode AFM, and found to be unchanged within experimental error. The observed length distribution was 137 ± 130 nm before and 167 ± 138 nm after. In all cases, a large percentage of the tubes had heights consistent with known individual nanotube heights plus a monolayer coating of the polymer. No nanotubes were observed surviving this treatment in a control experiment where the SWNTs were suspended by Triton X-100.

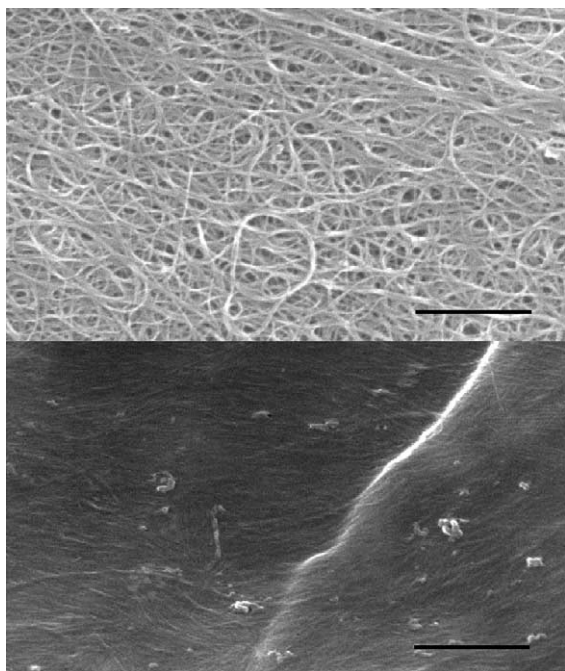During the sample preparation, the nuclear magnetic resonance (NMR) signal for the polymer

disappears after several centrifugation/decanting/ resuspension cycles, although by absorption spectroscopy, there is still a significant amount of polymer left in solution. We conclude that the polymer that is tightly associated with the SWNTs is dramatically broadened by some combination of factors, including inhomogeneities in the local magnetic field induced by the diameter and helicity-dependent diamagnetism of the SWNTs themselves (i.e., an 'antenna' effect), the slow motion of such large objects in solution preventing rotational averaging, and at least partial alignment of the SWNTs in the magnetic field [14,15]. Therefore, NMR spectroscopy quantifies the amount of free polymer in solution, and by subtraction from the total amount of polymer as determined by absorption spectroscopy, we can quantify the amount of polymer that is associated with the SWNTs. These NMR measurements are possible due to recent developments in the purification techniques for SWNTs, particularly with respect to removing residual metal catalyst from the samples [9,11].

Taken together, these results are strong evidence that the polymer and SWNT comprise a single entity that can be manipulated as a whole, rather than solubilization by a dynamic equilibrium of the supramolecular association.

3.3. Tight, uniform wrapping

The individual PVP–SWNTs appear by AFM to be of uniform diameter along their lengths with heights consistent with monolayer coverage of the SWNTs, supporting the interpretation that the polymer is uniformly wrapped around the tubes rather than associated with the side walls at various points as random coils.

PVP–SWNTs, after centrifuging in water at 200 000 g for 2 h, form a gelatinous pellet that is found to be ca. 2% SWNTs and 2% PVP by weight. Examination of 10–50 μm thick films between crossed polarizers revealed large (ca. 100 μm), well-defined birefringent domains, suggesting that the material behaves nematicly (Fig. 3). This further supports the interpretation that the nanotube surface area is uniformly covered by the associated polymer. The system is almost certainly a nematic solid, and may require the traditional addition of highly entropic side chains to transform the material into a true liquid crystal.

At maximum coverage, the 40 kD PVP:SWNT ratio by weight is found to be 5:8 for HiPco material and 1:1 for laser-oven material. 360 kD PVP is found to associate with the SWNTs at higher ratios, 1.7:1 and 2:1 for laser-oven material and HiPco material, respectively. It is likely that these
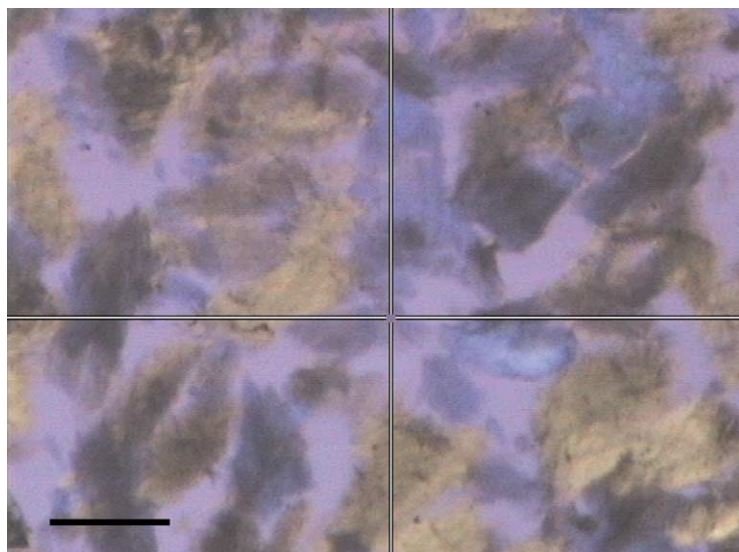

Fig. 3. Birefringent domains of PVP–SWNTs as observed between crossed polarizers. Scale bar is 40 μm.

longer polymers are more likely to entangle during the wrapping process, thus associating more un-wrapped polymer for a given surface area coverage. Further, presuming the same polymer/SWNT surface area ratio as was observed in the 40 kD case, a single strand of 360 kD PVP would more than cover the entire surface area of a single SWNT of typical observed length.

3.4. Wrapping: a general phenomenon

SWNTs can also be successfully solubilized by wrapping with other polymers, including polystyrene sulfonate (PSS), poly(1-vinyl pyrrolidone-co-vinyl acetate), poly(1-vinyl pyrrolidone-coacrylic acid), poly(1-vinyl pyrrolidone-co-dimethylami-noethyl methacrylate), polyvinyl sulfate, poly(sodium styrenesulfonic acid-co-maleic acid), dextran, dextran sulfate, and bovine serum albumin. Other polymers were unsuccessful, including poly(methyl methacrylate-co-ethyl acrylate), polyvinyl alcohol, polyethylene glycol, and poly-allyl amine.

We propose that the wrapping of the SWNTs by water-soluble polymers is a general phenomenon, driven largely by a thermodynamic drive to eliminate the hydrophobic interface between the tubes and their aqueous medium. Within this interpretation, changing the solvent system to remove the strong hydrophobic thermodynamic penalty should induce the PVP–SWNT complexes to disassociate, and in fact NMR-silent PVP–SWNTs, upon addition of tetrahydrofuran, recovers the PVP NMR spectrum.

This can be understood by estimating the dominant thermodynamic factors in wrapping an idealized water-soluble polymer around a SWNT. Due to the free rotation about the backbone bonds in the polymers studied here, they generally form random coils in solution. The entropic cost of forcing a linear polymer into a wrapping conformation around a nanotube can be estimated as being at most that of restricting each polymer backbone bond to one of its three rotational minima, which is simply

$$\Delta S = -k \times \ln(W) = -k \times \ln\left(3^{n-2}\right)$$
$$= -k(n-2)\ln(3),$$

where n is the number of backbone carbon atoms. In an effort to evaluate the generality of a proposed thermodynamic driving force, we will consider the isoenergetic case, recognizing that polymers with favorable enthalpic interactions can likely be chosen (e.g., PVP is a close polymer analog to NMP, an excellent solvent for laser-oven SWNTs [3]). From the observed 40 kD PVP:SWNT mass ratio and assuming a 1.0 nm diameter tube [8], we find an average of 8.1 monomer units/nm of HiPco SWNT, resulting in an entropic penalty of ca. 56 J/mol K. Assuming a negligible enthalpic contribution to the free energy as discussed above, this gives a maximum free energy penalty for polymer conformational restriction at 25°C of 17 kJ/mol nm of SWNT wrapped.

Offsetting this effect is the loss of hydrophobic surface achieved by shielding the nanotube from the water in which it is immersed, which for SWNTs can be estimated from the surface tension of the corresponding hydrophobic cavity. For a cavity the size of a 1.0 nm diameter nanotube, this is ca. 136 kJ/mol for each nm of SWNT length at room temperature. Clearly, the free energy cost of forcing the polymeric wrapping into a regular wrapping arrangement is significantly smaller than the gain achieved by overcoming the hydrophobic penalty between the SWNTs and their surrounding water.

Of the successful wrapping polymers, the ionic polymers provide an instructive contrast to the non-ionic case described. PSS, for example, can solubilize SWNT material up to 4.1 g/l. However, during the wrapping procedure, the higher ionic strength of the solutions induced aggregation during the wrapping step as a consequence of electric double-layer solubilization, requiring that the dispersion and association steps take place simultaneously. This double-layer effect could be used to good advantage, however, in the purification step through intentional salting out of the ionic-polymer wrapped SWNTs, significantly reducing the required centrifugation forces. The absorption spectroscopy/NMR technique for quantifying the amount of wrapping polymer present was verified in this case by electron microprobe analysis for sulfur content. PSS–SWNTs

had less-reproducible polymer to SWNT mass ratios than did PVP–SWNTs, ranging up to 1:2 and 2:1 for laser-oven and HiPco materials, respectively. This irreducibility is a result of a lower binding of polymer to the tubes, as evinced by the continued removal of polymer by repeated centrifugation/decanting/resuspension steps. Removing the PSS wrapping by ultrasonication in concentrated phosphoric acid for 1 h followed by washing with water reduced the sulfur microprobe signal by over two orders of magnitude, to within baseline noise.

3.5. Molecular picture

From the key observations described, solubilization with near monolayer coverage of tightly associated polymer around individual SWNTs, a molecular-level picture of the association geometry is suggested: helical wrapping. A single tight coil, however, would necessarily introduce significant bond-angle strain in the polymer backbone, enough to offset the thermodynamic drive for wrapping described above. Multi-helical wrapping (Fig. 4), on the other hand, allows high-surface area coverage with low-backbone strain, where, at least locally, multiple strands of polymer coil around the SWNT at close to their nascent backbone curvature. Given such a picture, it is natural to expect that successive strands of polymer wrapping would have different binding constants, particularly when the polymer strand is charged as in the case of PSS, explaining the lower binding of PSS relative to PVP.

3.6. Biologically relevant conditions

PSS–SWNTs are largely solubilized by the electric double-layer effect, making solution stability sensitive to its ionic strength. HiPco PSS–SWNT solutions at a concentration of 11 mg/l of tubes salt out at NaCl concentrations of 20 ± 5 mM, and $MgCl_2$ concentrations of 2 ± 1 mM. PVP–SWNTs also salt out, albeit at higher ionic strengths (135 ± 20 mM NaCl and 10 ± 2 $MgCl_2$ for 11 mg/l of tubes), suggesting that these tubes also carry a charge, similar to the dimethylformamide and dimethylsulfoxide dispersions of
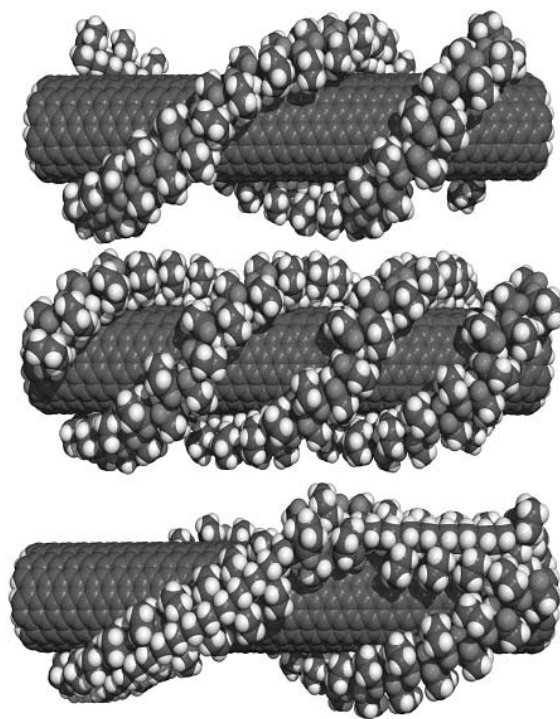

Fig. 4. Some possible wrapping arrangements of PVP on an 8, 8 SWNT. A double helix (top) and a triple helix (middle). Backbone bond rotations can induce switch-backs, allowing multiple parallel wrapping strands to come from the same polymer chain (bottom).

SWNTs previously reported [5]. The solution stability of PVP–SWNTs at these high-ionic strengths raises the possibility that a similar system will be solubilized in biologically relevant conditions. BSA and dextrans also stably solubilized SWNTs at high-ionic strengths, more directly making the connection to the biological world. This is currently under further investigation.

3.7. Applications

The solubilization of SWNTs by the procedures described here opens up the possibility of functionalization chemistry, both on the tubes themselves [16] and on the wrapping polymer [17], and solution-phase separations. For example, purification of the SWNTs from any residual catalytic material can be efficiently performed by HGMS [11]. Also, PVP–SWNTs can be length-fraction-
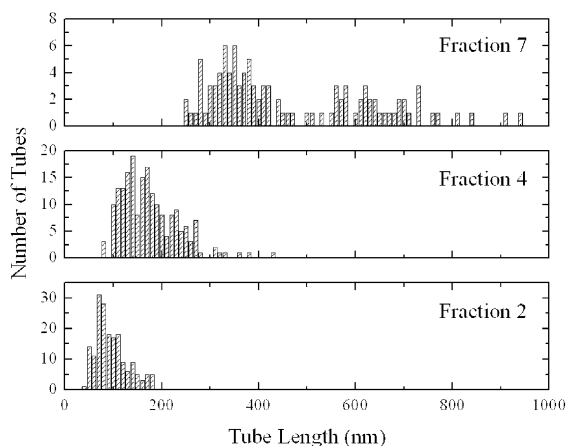
Fig. 5. PVP–SWNT lengths as separated by gel electrophoresis.

ated by gel electrophoresis. Fractions, as measured from a maximum migration of 18 cm along a 0.5% agarose gel in a glycine/SDS buffer and subjected to 100 V for 5 h, were investigated by AFM to reveal significant separation by length (Fig. 5).

4. Conclusions

SWNTs have been reversibly solubilized in water by wrapping them with a variety of linear polymers. We have demonstrated that the association between the polymer and the SWNT is robust, not dependent upon the presence of excess polymer in solution, and is uniform along the sides of the tubes. A general thermodynamic driving force for such wrapping in an aqueous environment has been identified. This solubilization provides a route to more precise manipulation, purification, fractionation, and functionalization than was possible before, as well as allowing SWNTs to be introduced to biologically relevant systems.

Acknowledgements

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