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Communications to the Editor

Analogies between Polymer Solutions and Carbon Nanotube Dispersions

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Introduction. Carbon nanotubes are an intriguing new form of carbon, consisting of concentric cylinders of curved graphitic layers. Since their discovery, in 1991, in connection with fullerenes, there has been intense interest as increasing numbers of potentially useful properties have been suggested. Nanotube diameters are 1000 times smaller than conventional carbon or glass fibers and only an order of magnitude larger than typical polymer molecules.[1] Commonly, nanotube aspect ratios are over 1000, although much longer nanotubes have been observed.[2] The combination of their shape with their ability to undergo large deformations without damage suggests that interesting parallels may be drawn with polymeric systems. However, since the stiffness of nanotubes indicates that they will not be subject to significant flexing as a consequence of thermal motion, attention turns to their behavior and potential processability in liquid suspension.

The most common synthesis route for nanotubes is based on an electric arc, which results in a product with a high crystallinity but only in small yields. In this study, catalytically grown nanotubes were used,[3] supplied by Hyperion Catalysis International Inc. The starting material consists of curved nanotubes that are intertwined; it is, however, available in bulk amounts and free of the contaminating nanoparticles that are associated with arc-grown material. The mass per unit length of multiwalled carbon nanotubes is on the order of 10^7-10^8 amu mm^{-1}, the exact value depending primarily on the number of walls.

Experimental Section. The formation of a stable aqueous dispersion of nanotubes was achieved using an acid oxidation treatment, described elsewhere.[4] The result was a colloidal suspension of nanotubes in water, electrostatically stabilized by polar, oxygen-containing, surface groups. A suspension of shortened nanotubes was also prepared by applying a bromine pretreatment, as follows. A 1 g sample of as-supplied nanotubes was covered in bromine for 2−3 days at room temperature and then heated to 80 °C to evaporate the bromine. The material was then heated for 2 h at 300 °C, before being slowly oxidized at 530 °C in an atmosphere of 4% oxygen in argon for up to 62 h. After cooling, the product was then treated with the same acid oxidation treatment as the were the original nanotubes, to produce a stable dispersion.

The dispersal of each type of treated nanotube allowed measurement of the length distributions. Transmission electron microscopy was performed on samples allowed to dry onto carbon films, using a JEOL 2000FX, operating at 200 kV. Micrographs were digitized and loaded into a Seescan image analysis package. The curving paths of the nanotubes were traced, by eye, onto the screen and the lengths calculated by the computer, after suitable calibration.

The viscosity of the dispersions was measured as a function of concentration using a Lauda Viscoboy 2 semiautomated system with Schott Geräte Ubbelohde capillary viscometers. Kinematic viscosities were calculated using the calibration constants supplied with the instrument for the capillaries used, which had diameters of 1.13 and 0.63 mm for concentrations above and below 0.05 vol %, respectively. The temperature was maintained at 25.0 °C using a water bath.

Results. The length distributions for the two dispersions are shown in Figure 1. The mean (number-average) length for the two distributions are 1.1 μm and 370 nm, and since the nanotubes all have the same diameter (10 ± 2 nm), the average aspect ratios are 110 and 37, respectively. Both distributions have the same polydispersivity of 1.65 ± 5. The action of the bromine is to attack the most disordered regions of the nanotubes and to form brominated compounds which in turn act as a preferential sites for oxidation[5] and hence nanotube cleavage.

The viscosity of the dispersions of purely oxidized nanotubes increased with concentration (c) relatively slowly at low concentrations but at a dramatically increased rate above a critical concentration of around 0.5 vol % (see Figure 2). The dispersions of bromine-shortened nanotubes displayed similar behavior with an upturn at a slightly higher concentration around 1 vol %. This behavior is similar to that of polymer solutions that exhibit entanglement transitions and must correlate to significant intertube interactions. As expected, the shorter nanotubes, which have a smaller hydrodynamic volume, do not “entangle” until higher concentrations.

The solid lines in Figure 2 are based on fittings to the Schulz−Blaschke formula for polymer solutions:[6]

$$\eta_{\mathrm{sp}}/c = [\eta] + k[\eta]\eta_{\mathrm{sp}}$$

where η_{sp} is the specific viscosity and $[\eta]$ and k are constants. This equation was originally entirely empirical,[6] but its form was subsequently justified theoretically by Huggins, who modified his own earlier expression to effectively include polymer−polymer interactions.[7] The parameters in the equation are determined using relative viscosities approximately in the range 1.2−2. Experience has shown that this is the most appropriate range for polymer solutions, to avoid the effects of experimental uncertainty at low concentrations and the

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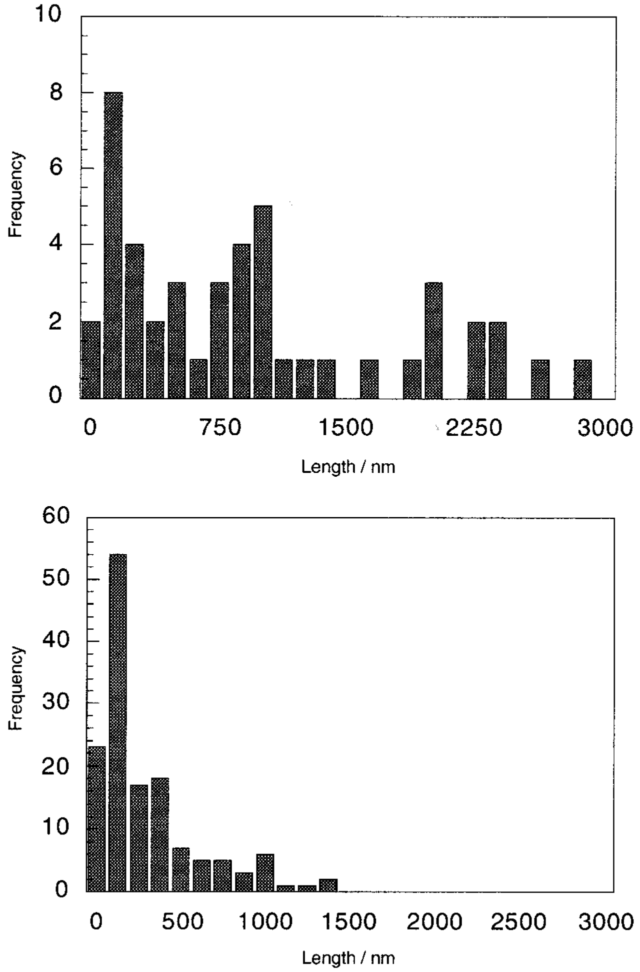

Figure 1. Histograms of nanotube length distribution after oxidation (a, top) and bromination and oxidation (b, bottom).

onset of non-Newtonian behavior at higher concentrations.[8] Using this approach, the equation successfully predicts the observed upturn in viscosity and produces values for the intrinsic viscosity, $[\eta]$, of 100 and 48 cm^3 g^{-1} for the longer and shorter nanotube dispersions, respectively, with k lying between 0.2 and 0.3. The same values for the intrinsic viscosities may also be obtained from the conventional low-concentration extrapolations of (η_{sp}/c) against c and $(\ln \eta_{\mathrm{relative}})/c$ against c. It is interesting to note that the Schulz–Blaschke equation is consistent with the high-concentration data points even though they were not used for the fitting process. The equation is not intended to be applied at high concentration since it tends an infinite viscosity at finite concentration (as a consequence of the simple mathematical model used to describe the increasing restriction of chain motion[7]). However, this trend could be considered to be a manifestation of the development of the gel phase, discussed below, as the chains lock against one another.

Unfortunately, due to the difficulties in preparing nanotube suspensions with different length distributions, the present work only provides two data points toward a Mark–Houwink plot. Nevetheless, it is interesting to follow the methodology for polymer systems to obtain a preliminary estimate for the Mark–Houwink coefficients. Lengths were converted into masses on the basis of a mass per unit length calculated from the observed dimensions and the nanotube density obtained by a liquid immersion technique[9] (found to be 1.75 g cm^{-3} including the central cavity). The intrinsic viscosities were combined with the mass data to obtain estimates for K and a of 10^{-4} cm^3 g^{-1} and 0.7, respectively. These figures are compatible with those found for polymer solutions; for comparison, consider the equivalent values of 10^{-2}–10^{-1} cm^3 g^{-1} and 0.5–0.8 tabulated for poly(vinyl alcohol) in water.[10]

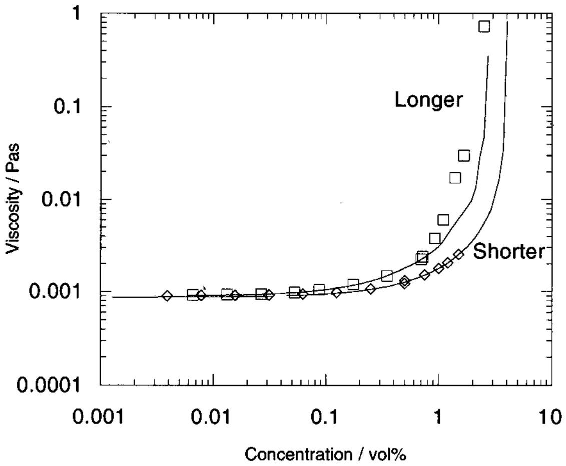

Figure 2. Plot showing the viscosities of oxidized and bromine-shortened nanotube dispersions as a function of concentration (data points). The two fitted lines are based on the Schulz–Blaschke equation. Note that the predictions of the Schulz–Blaschke equation have been plotted in terms of dynamic viscosity rather than specific viscosity for ease of comparison.

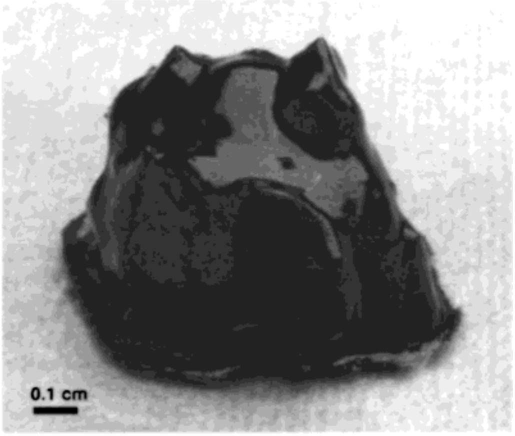

Figure 3. Photograph of a viscoelastic gel formed from an aqueous dispersion of oxidized nanotubes (~5 vol %).

The K value for the nanotubes is relatively low, but this result would be expected for a polymer with a large mass per unit length. The value of a, the Mark–Houwink exponent obtained, though very typical of polymer systems with randomly coiled molecules, is lower than a figure approaching 2 expected for a perfectly rigid straight rod and hence a perfect nanotube. In fact, this reduced value is not surprising in view of the intrinsic random curvature of these defective nanotubes, which gives them a conformation that is probably rather similar to that of a polymer molecule. It should be noted that, as a result of their size and stiffness, nanotubes are unlikely to change conformation in suspension. There is also a potentially more subtle difference between the two experimental samples; if the bromination attacks defects and hence points of curvature in the nanotubes, the brominated nanotubes may be proportionately straighter than the longer material.

Such an effect is difficult to confirm since the curvature observed on a TEM grid depends on deformation during drying and cannot be directly related to the intrinsic curvature in suspension.

Since oxidized nanotubes have ionizable groups on their surface, it is worth considering whether they might be expected to display the same type of viscosity behavior as polyelectrolyte polymers. Such polymers display a distinctive viscosity behavior due to the variation in chain conformation as a function of the ionic strength of the solution. However, since nanotubes are unlikely to change their conformation in solution, regardless of ionic strength, it is not suprising that they display nonelectrolytic behavior.

On raising the concentration of the dispersions further, above approximately 5 vol %, a viscoelastic gel was found, a photograph of which is shown in Figure 3. The gel appeared to be thixotropic and did not display any brittle behavior. Although the gel redispersed in excess water and reversibly re-formed on partial drying, complete drying was irreversible with subsequent solvent exposure leading to swelling but not dissolution. As reported previously, dried films have a high density of 1.3 g cm^{-3}, corresponding to a high packing fraction and in some cases to domains of parallel order.[4]

Conclusions. Stable aqueous dispersions of nanotubes of controlled molecular mass can be produced using chemical treatments. They exhibit polymeric behavior, in terms of an entanglement-like transition, and can be characterized using equations taken from polymer science to produce typical fitting parameters. Further work, based on a fuller rheological study, particularly of the gel material, might raise further interesting parallels, including the possibility of flow-induced alignment. Manipulation of assemblies of nanotubes and control of their alignment is one the key issues for many of the suggested applications of carbon nanotubes.

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