Phase Behavior and Rheology of SWNTs in Superacids


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ABSTRACT: Single-walled carbon nanotubes (SWNTs) can be dispersed at high concentration in superacids; the protonation of SWNTs sidewalls eliminates wall–wall van der Waals interactions and promotes the dispersion process. At very low concentration, SWNTs in superacids dissolve as individual tubes which behave as Brownian rods. At higher concentration, SWNTs form a highly unusual nematic phase consisting of spaghetti-like self-assembled supermolecular strands of mobile, solvated tubes in equilibrium with a dilute isotropic phase. At even higher concentration, the spaghetti strands self-assemble into a polydomain nematic liquid crystal. Upon the introduction of small amounts of water, the liquid crystal phase separates into needle-shaped strands (~20 μm long) of highly aligned SWNTs, termed alyevices. Under anhydrous condition, the liquid crystalline phase can be processed into highly aligned fibers of pure SWNT without the aid of any surfactants or polymers.

Introduction

Theoretical calculations and experimental measurements on individual SWNTs and SWNT ropes indicate that macroscopic fibers and sheets of neat SWNTs will display remarkable electrical, thermal, and mechanical properties. Neat, well-aligned SWNT fibers and sheets could be the ultimate building blocks of ultra-strong and ultralight materials for aerospace and aeronautical applications and could yield electro-mechanical actuators and sensors with unprecedented performance. Moving from self-assembled microscopic ropes (diameter ~10 to 100 nm, length ~ tens of micrometers) to continuous macroscopic fibers (diameter ≥ 10 μm, continuous length) requires the ability to make and process highly concentrated solutions or dispersions of pristine SWNTs. Since the scalable production of large quantities of SWNTs has been achieved, the lack of a liquid able to disperse significant amounts of pristine SWNTs has been the single most important roadblock to manufacturing macroscopic articles composed solely of SWNTs. SWNTs have been dispersed at moderate concentrations ~1 vol % with the aid of surfactants; however, this route requires large amounts of surfactant, some of which remains in the final product. Removal of the surfactant is not likely to be feasible in large-scale manufacturing processes.

We have successfully dispersed SWNTs at concentrations up to 10 wt % in superacids, e.g., sulfuric acid with various levels of excess SO3, chlorosulfonic acid, and triflic acid. This concentration is over 10 times the highest concentration ever achieved with wrapping or stabilization by surfactants. The high concentrations achievable in superacids are due to the protonation of the SWNTs by a mechanism similar to that occurring in rodlike polymers. The tubes are stabilized against aggregation by the formation of an electrostatic double layer of protons and negative counterions (HSO4⁻ in sulfuric acid).

Experimental Methods

The SWNTs used in this study were produced from the high-pressure carbon monoxide (HiPco) process at Rice University and purified according to literature methods. Oleum (20 wt % excess SO3, density 1925 kg/m³), chlorosulfonic acid, and triflic acid were used as received from Sigma Aldrich. 102% sulfuric acid was prepared by mixing the oleum with 96% sulfuric acid in the ratio 1.1 mL of oleum/mL of H2SO4. 102% sulfuric acid was chosen to ensure that the solubility of the SWNTs would not be affected by the uptake of small amounts of moisture from the environment. Dispersions containing less than 0.5 wt % SWNT were prepared by mixing with a magnetic stir bar for a minimum of 3 days in an anhydrous environment in a glovebox at room temperature. More concentrated dispersions were mixed in an argon-blanketed double-helix mixer (Daca Instruments, Goleta, CA) at 110 °C for a minimum of 3 days. All glassware was flame-dried before use, and the SWNTs were dried in the mixer under vacuum overnight at 80–100 °C before acid was added. Volume fractions of SWNTs were calculated on the basis of a SWNT density of 1450 kg/m³, which is typical of HiPco SWNTs. The measured viscosity and density of the 102% sulfuric acid were respectively 26 mPa s and 1880 kg/m³ at 25 °C.

Rheological measurements were made on ARES and RDA III strain-controlled rotational rheometers (Rheometrics Scientific, Piscataway, NJ, now TA Instruments, New Castle, DE). Testing fixtures were made of Hastelloy C or stainless steel 316 to avoid corrosion. Fixture geometries were a large Couette (i.d. = 32 mm, o.d. = 34 mm), parallel plates (25 mm diameter), and cone and plate (25 mm diameter, cone angle = 0.04 rad). Generally, the Couette was used for testing concentrations below 0.5 wt %, and cone and plate or parallel plates were used for testing concentrations above 0.5 wt %. However, several concentrations were tested in multiple fixtures to ensure there were no artifacts in the data due to testing geometry. An anhydrous environment was maintained during loading and testing of all samples by continuous flow of argon into a custom-made environmental control chamber enclosing...
The phase behavior of solutions of Brownian rigid rods is depicted in Figure 1. With increasing concentration, such systems transition from a dilute solution where individual rods do not interact with each other, to a semidilute solution where rotation is inhibited, to an isotropic concentrated solution where both translation and rotation are inhibited. At concentrations above the percolation threshold, steric effects force the system to phase separate into a liquid crystalline phase in equilibrium with the isotropic concentrated phase. Raising the concentration further increases the proportion of the liquid crystalline phase until the system becomes fully liquid crystalline.

**Dilute Regime.** Figure 2 shows a collapse of reduced viscosity $\eta_r \equiv (\eta - \eta_s)/(\eta_s \phi)$ vs shear rate $\dot{\gamma}$ for the three most dilute solutions (27, 54, and 81 ppm vol in 102% sulfuric acid). Measurements at 54 and 81 ppm vol overlap almost perfectly; those at 27 ppm vol agree less well. Data at 27 ppm contain more error because the viscosity of the solution was only ~10% higher than the solvent viscosity. This behavior of the reduced viscosity shows that the viscosity depends linearly on concentration and that the relaxation time is independent of concentration, in accordance with the theory of dilute Brownian rods; thus, below ~90 ppm vol the tubes are dissolved as individuals and do not interact.

The aspect ratio of a sample of Brownian rods can be extracted from the limiting value of the reduced viscosity at low shear rate. Figure 2 shows that shear thinning is incipient at 0.3 s$^{-1}$, near the lowest shear rates that can be measured within the limit of the torque transducer. In the analysis below, the viscosity measured at the lowest accessible shear rate (0.3 s$^{-1}$) is taken as the approximate value of the zero-shear viscosity.

The zero-shear viscosity of a (monodisperse) solution or dispersion of Brownian rigid rods is

$$
\eta_0 = \lim_{\gamma \to 0} \eta(\dot{\gamma}) = \eta_s \left[ 1 + \frac{4}{5} k_B T \tau \right]
$$

where $\eta_s$ is the solvent viscosity, $k_B$ is Boltzmann's constant, $T$ is temperature, $\nu$ is the number of rods per unit volume

$$
\tau = \frac{c L^3}{72 k_B T}
$$

is the rotational relaxation time of the rods, and $c$ is the perpendicular drag coefficient of the rods. The number concentration of rods is related to the volume fraction $\phi$ as $\nu = \phi (\pi R^2 L)$, where $R$ is the rod radius and $L$ is the length. The perpendicular drag coefficient $c$ on a slender cylinder is

$$
c = 4 \pi \eta_s \varepsilon f (\varepsilon)
$$

where

$$
\varepsilon = \frac{1}{\ln(L/R)}
$$

$$
f (\varepsilon) = \frac{1 + 0.64 \varepsilon}{1 - 1.5 \varepsilon} + 1.659 \varepsilon^2
$$

This yields the relationship

$$
\frac{\eta - \eta_s}{\eta_s \phi} = 2 (L/R)^2 \left[ \frac{1 + 0.64}{\ln(L/R)} \right] + \frac{1.659}{(\ln(L/R))^2}
$$

This relationship is simple to apply to the experimental data and gives results in close agreement with the theoretical predictions.

In the polydisperse case, the viscosity contributions of each subpopulation of length are additive, and the intrinsic viscosity is related to the ratio of the third and first moments of the distribution of length. The extrapolated value of the intrinsic viscosity is $[\eta]_{ex} = \lim_{\gamma \to 0} \eta(\dot{\gamma}) = 8300 \pm 830$ (Figure 2); taking this extrapolated value, eq 6 yields an average aspect ratio $L/d = 470 \pm 30$. This result compares well with recent viscosity$^{27}$ and AFM$^{10}$ measurements of individual tubes stabilized in pluronic surfactants. Another way of estimating the critical volume fraction for the transition from dilute to semidilute is to take the reciprocal of the intrinsic viscosity; this estimate yields a critical volume fraction of 120 ppm vol, which compares well to the value of 90 ppm obtained from the overlap shown in Figure 2. In terms of number of rods per unit sphere...
Figure 3. Reduced viscosity, \( \eta - \eta_0 \rangle / \eta_0 \), vs shear rate for 94–452 ppm vol. SWNTs in 100% H\(_2\)SO\(_4\); filled symbols, 94–454 ppm vol. SWNT batch HPR 105 September 2002; hollow symbols, February 2003 103–407 ppm vol. SWNT batch HPR 106.2. Slope of -0.5 is drawn for reference and agrees with the theory of Kirkwood and Plock. Vertical offset between HPR 105 and HPR 106.2 may be partly due to small differences in the initial volumetric dilution.

swept by a rod, the transition concentrations are estimated to be \( v L^3 \approx (4/\pi) \eta_0)=25–33 \), which compares well with literature values.\(^{28}\)

The specific intrinsic viscosity of the SWNTs is \( \eta_0 \) \( = \eta_0 \rangle / \eta_0 \approx 5.7 \text{ mI/kg} = 57 \text{ dL/g} \); this value is comparable to or greater than the highest reported values for high molecular weight poly(p-benzamide) (PBA) in sulfuric acid\(^{29}\) \( \eta_0 \approx 12.5 \text{ dL/g} \) for \( M_w = 64 \text{ 400 g/mol} \), i.e., \( L \approx 400 \text{ nm} \), poly(benzobisthiazole) (PBT) in methanesulfonic acid\(^{30}\) \( \eta_0 \approx 26.5 \text{ dL/g} \) for \( M_w = 37 \text{ 000 g/mol} \), i.e., \( L \approx 190 \text{ nm} \), large poly(benzobisoxazole) (PBO) in methanesulfonic acid\(^{31}\) \( \eta_0 \approx 50 \text{ dL/g} \) for \( M_w \approx 230 \text{ 000 g/mol} \), i.e., \( L \approx 390 \text{ nm} \), and very large molecules of xanthan\(^{32}\) \( \eta_0 \approx 71 \text{ dL/g} \) for \( M_w \approx 5.4 \text{ mg/mol} \), i.e., \( L \approx 2.78 \text{ \mu m} \).

Rods shear thin when the product of the longest rotational relaxation time \( \tau \) and shear rate \( \dot{\gamma} \) exceeds \( \approx 0 \) (i.e., the Weissenberg number \( Wi \equiv \tau \gamma / 0 \) ); because shear thinning starts at \( \gamma \approx 0.3 \) s\(^{-1} \), we estimate that the longest rotational relaxation time is approximately 0.7 s. The estimated value of the longest relaxation time together with eq 2 yields an estimated length \( L \approx 1.5 \text{ \mu m} \) for the longest nanotubes present in the HiPco sample (the diameter is nearly immaterial for the determination of the relaxation time).

Semidilute Regime. The measurements at concentrations between 94 and 600 ppm vol can be collapsed onto a separate master curve of reduced viscosity vs shear rate (Figure 3). Two separate HiPco batches are shown (HPR 105 and 106.2): the SWNTs produced in batch 106.2 display slightly higher reduced viscosity.

At low shear rates, these data depart from the dilute master curve (Figure 2) because the relaxation time is now concentration-dependent, and thus the viscosity starts shear thinning at lower shear rates (below the sensitivity of the rheometer transducer). In this concentration range, the solutions relax slower as concentration increases, as measured by the delay time between transient tests required to get reproducible viscosity data, indicating that 94–600 ppm vol is in the semidilute regime.

Biphasic Regime. Optical microscopy shows that at 1000 ppm vol (0.1 vol %) the system is biphasic. The morphology of SWNTs in this biphasic region is remarkable. The SWNTs self-assemble into seemingly endless strands of supermolecular aggregates. These strands are in equilibrium with the isotropic phase and are termed hereafter “SWNT spaghetti”. The SWNT spaghetti are nematic liquid crystalline domains where tubes are free to translate along the length of the strand (Figure 4). Imaging successive z-planes shows that the strands continue through multiple focal planes and fails to reveal any ends. The constant optical density along the length of the strand suggests that the spaghetti have a uniform diameter below 600 nm (part of the measured diameter is due to diffraction). At room temperature, the SWNT spaghetti phase first appears between 600 and 1000 ppm vol. A more precise determination is difficult because at lower concentration it is necessary to scan at high magnification increasingly larger regions of the sample. The biphasic region is expected to be quite wide because the SWNTs are polydisperse in length and diameter.\(^{10,28,33}\)

On the basis of the minimum of the viscosity vs concentration curve (Figure 6) and on measurements on solid structures induced by phase separation (Figure 10 and also ref 34), we believe that the SWNTs in the spaghetti phase are spaced by approximately 2–3 nm, i.e., by roughly four to six molecules of sulfuric acid, and that they are highly aligned because of their stiffness and because of the steric constraints present on narrowly spaced object of such high aspect ratio. Presently, we cannot explain the peculiar shape of the SWNT spaghetti nematic phase; it may be related to the large polydispersity of the sample (the ratio between the length of the longest and shortest SWNTs is at least 20) and also to the differences between SWNTs and rodlike polymers. SWNTs have much higher bending stiffness than rodlike polymers (see Appendix A); they have cylindrical rather than locally planar cross section and in the absence of acid have a high van der Waals...
attraction of $\sim 0.5$ eV/nm between side walls. The morphology of the spaghetti phase may be related to the molecular stiffness and geometry or to residual long-range attractive intermolecular forces in the acids.

**Single-Phase Nematic Liquid Crystal: Optical Microscopy.** Optical microscopy shows that the fraction of the SWNT spaghetti phase increases as the bulk concentration of SWNTs is raised, until only the SWNT spaghetti is present, yielding a single phase polydomain lyotropic nematic liquid crystal at approximately 4 vol % in 102% sulfuric acid. This single phase shows strong birefringence under polarized light (Figure 5). The polydomain structure is evidenced by rotating the sample between cross polars and observing that different domains turn bright and dark based on the relative alignment between their director and the polarization vector of the light. We believe that the polydomain structure results from the local coalescence of spaghetti strands that have ordered. On large length scales (\sim 100 \mu m), the domains are randomly oriented with respect to each other. The healing time for defects at the boundaries of the spaghetti strands is expected to be quite long and can be estimated by using typical properties of nematic liquid crystalline polymers. The healing time $t_\alpha$ for the spontaneous disappearance of a defect from a nematic liquid crystalline polymer of viscosity $\eta$ and thickness $h$ is

$$t_\alpha \approx \frac{\eta h^2}{K},$$

where $K$ is the characteristic Frank constant. The viscosity of nematic SWNT/acid dispersions is between 400 and 500 Pa s. The effective “director diffusivity”, $K/\eta$, of SWNTs is unknown; typically it ranges between $K/\eta \sim 10^{-8}$ and $10^{-10}$ cm$^2$/s in polymeric nematics,\textsuperscript{28} thus, a 500 \mu m thick sample would take nearly 1 year to form a uniform monodomain liquid crystal.

**Single-Phase Nematic Liquid Crystal: Rheology.** The nematic nature of SWNT/superacid solutions is evidenced further by key rheological signatures unique to lyotropic liquid crystals formed by high-molecular-weight rodlike molecules: the viscosity–concentration curve has a maximum; the viscosity vs shear rate curve often shows three distinct regions, usually termed regions I, II, and III; with increasing shear rate, the first normal stress difference $N_1$ changes sign from positive to negative and back to positive; in transient shearing tests the shear stress and first normal stress difference oscillate for \sim 100 shear units or more before reaching steady state; and the Cox–Merz rule is not obeyed.

Figure 6 shows that SWNTs in superacids exhibit this nonmonotonic relationship between viscosity and concentration. The transition from a biphasic system to a single-phase liquid crystal occurs in the concentration range between the maximum and the minimum in viscosity;\textsuperscript{28} thus, the single-phase nematic liquid crystal forms between 3.5 and 5.1 vol %, a slightly higher concentration than that estimated by Flory theory (12.5d/L \sim 2.7 vol % based on an average aspect ratio of L/d \sim 470). Experimental observations on other systems have shown that Flory theory typically underpredicts the transition to a single-phase liquid crystal.\textsuperscript{33,35–41}

Figure 7 shows the viscosity $\eta$ and first normal stress difference $N_1$ vs shear rate curve of SWNT/superacid solutions at 4.5 vol %, where the dispersion is predominantly or wholly anisotropic. Notably, the viscosity shear thins at low shear rate, then seems to plateau at $\gamma \approx 1$ s$^{-1}$, and then shear thins again at high shear rates; the first normal stress difference is negative at shear rates above 1 s$^{-1}$. The three-region shear viscosity curve was first observed by Onogi and Asada;\textsuperscript{42} it is generally associated with tumbling nematics and is not exhibited by all lyotropic nematic polymeric liquid crystals.\textsuperscript{40} The origin of the three region curve is still a subject of investigation and debate. One explanation is that the first shear thinning region, region I, is a result of tumbling and the evolution of texture. At intermediate shear rates (region II) there is a competition between tumbling and the steady alignment of the director with flow; as a result, the rods “wag” about a single director. At higher shear rates, region III, the director aligns in
the flow direction, resulting in shear thinning.\textsuperscript{28,40,43} SWNTs in 102\% H\textsubscript{2}SO\textsubscript{4} display nearly constant viscosity in a narrow region of shear rates around 1 s\textsuperscript{-1}, which indicates that there may be a very narrow region II plateau between the two shear thinning regions. Region III (shear-aligning behavior) begins at shear rate \( \approx 3 \) s\textsuperscript{-1}, indicating that moderate shear should be sufficient to align nematic domains of SWNTs. The facile alignment is manifested by the high degrees of collective alignment in SWNT fibers produced by simply pushing the SWNT/superacid dispersion through a syringe needle into a coagulation bath,\textsuperscript{34,44} as shown in Figure 10. As the shear rate exceeds a critical value (about 10 s\textsuperscript{-1} for 4.5 vol \%), the SWNT/superacid dispersion ejects itself from the rheometer gap.

The negative first normal stress difference \( N_1 \) displayed by SWNT dispersions (Figure 7) is generally\textsuperscript{69} associated with lyotropic nematic liquid crystalline polymers.\textsuperscript{28} At low shear rate, \( N_1 \) is positive and increases with shear rate as observed in polymer solutions. At a critical shear rate, \( N_1 \) suddenly drops and switches to a large negative value. As shear rate is increased further, \( N_1 \) turns positive again.\textsuperscript{35,38,43,50} The origin of negative \( N_1 \) has been the subject of considerable research and is still not completely understood.\textsuperscript{28,38,51–53} Essentially, negative \( N_1 \) is believed to be a consequence of director tumbling. For systems where negative \( N_1 \) is observed, the change from positive to negative occurs in region II as a consequence of the transition from “tumbling” to “wagging”.\textsuperscript{54} In the shear aligning region, region III, \( N_1 \) becomes positive again.

Figure 8 shows that the response of 7.6 vol \% SWNT/superacid to start-up of steady shearing at shear rate 5 s\textsuperscript{-1}. Both the shear stress and the first normal stress difference oscillate for hundreds of shear units (product of shear rate and time). This behavior is also typical of lyotropic liquid crystalline polymers and quite different from that of isotropic suspensions and polymer solutions, where oscillatory transients last a few shear units at most.\textsuperscript{55} Long oscillatory transients were displayed by all concentrated samples (\( \phi > 4.5 \) vol \%).

A final rheological signature demonstrated by SWNT/superacid solutions is that the steady and dynamic viscosities do not exhibit the same behavior as a function of shear rate and frequency;\textsuperscript{30,55} i.e., the Cox–Merz rule is not obeyed (Figure 9). This empirical rule states that at a given frequency \( \omega\) and shear rate \( \dot{\gamma} \) the dynamic viscosity \( \eta' (\omega) \) and the steady shear viscosity \( \eta (\dot{\gamma}) \) are equal when \( \omega = \dot{\gamma} \). Lyotropic polymeric liquid crystals do not obey the Cox–Merz rule.

**Aligned Solid Materials from Nematic Liquid Crystalline Phase.** In addition to optical and rheological signatures in the liquid state, the nematic structure of SWNT/superacid dispersions is evidenced by scanning electron microscopy of materials quenched from the high-concentration dispersions. Scanning electron microscopy of ether-quenched SWNT/superacid dispersions shows that the SWNTs are free to rearrange into a variety of aligned species (Figure 10). Buckypapers prepared from SWNT/superacid solutions show the typical mat of entangled super-ropes. Such super-ropes are approximately 300–1000 nm wide, about 2 orders of magnitude wider than the original thin ropes (10–20 nm) generated by the HiPco reaction; the super-ropes come from the fast coagulation of liquid crystalline spaghetti domains which were not aligned with respect to each other. The introduction of moisture into the system deprotonates the nanotubes, reduces the electrostatic stabilization, and causes the precipitation of tactoid structures similar to those formed by inorganic liquid crystals of vanadium pentoxide.\textsuperscript{56} These structures are nearly monodisperse in dimension for a given starting concentration of SWNTs and show a high degree of alignment along their axis of 14:1 as measured by Raman.\textsuperscript{15} These tactoid structures have been named “alewives” for their resemblance to a Great Lakes fish. We believe that they are crystal solvate phases analogous to those formed by solutions of rodlike polymers in acids upon exposure to moisture.\textsuperscript{57} In the absence of moisture, the same starting concentration can be used to make highly aligned fibers with 20:1 axial to perpendicular alignment even in the absence of drawing\textsuperscript{54} as well as well-ordered sheets.\textsuperscript{58}
Conclusions

The protonation of single-walled carbon nanotubes in superacids allows them to be dispersed at high concentration, more than an order of magnitude higher than typical concentrations achieved in surfactants or organic solvents. The phase behavior of SWNTs in acid shows many parallels with that of lyotropic nematic rodlike polymer solutions. The notable distinction is that in the biphatic region the anisotropic phase consists of extremely long self-assembled strands. At sufficiently high concentrations, approximately 4 vol % in 102% H2SO4, a novel type of single phase nematic liquid crystal is formed. The nematic structure of SWNT/acid solutions is evidenced by the ability to form aligned species, birefringence, and rheological signatures including a maximum in the viscosity vs concentration curve, changes in sign of the first normal stress difference, and long oscillatory transients. In addition, the viscosity vs shear rate curve is suggestive of the three-region behavior associated with many lyotropic nematic polymeric liquid crystals. Exploiting successfully this phase behavior will be key to designing and optimizing a process for forming macroscopic objects comprised solely of highly aligned SWNTs.

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Appendix A

The persistence length of SWNTs can be estimated by calculating the bending stiffness of a hollow cylinder
\[ \kappa = \frac{\pi D^3}{8} \]
and by using the relationship between persistence length and bending rigidity \( L_p \approx \kappa/(k_BT) \). Taking \( C = 345 \text{ N/m as characteristic in-plane rigidity of SWNTs} \)
and \( d = 0.93 \text{ nm as characteristic HiPO4 diameter} \)
yields \( L_p \approx 27 \mu m \) at room temperature. In contrast, the persistence length of the stiffest rodlike polymers (e.g., PBO, PBZT, PBA, PBLG) is usually reported to range between 50 and 200 nm.

Appendix B

If rodlike macromolecules are modeled as inextensible Brownian threads with finite bending stiffness, three dimensionless groups can be defined that characterize their behavior in a shear flow: the ratio of contour to persistence length (see Appendix A), the Weissenberg number, i.e., the product of the shear rate and rotational relaxation time \( Wi = \gamma \tau \equiv \gamma L^2/72k_BT \) (see eq 2), and the elasticity number \( El \), i.e., ratio of viscous forces induced by the flow and elastic forces due to the bending stiffness, \( El = \gamma \tau \equiv \gamma L^4/4k_BT = \gamma L^4/4k_BT \), where \( \alpha \approx 4.73 \) is the eigenvalue of the most dangerous buckling eigenmode.

References and Notes
