

# LIQUID CRYSTALLINITY AND FIBER SPINNING OF DOUBLE-STRANDED DNA STABILIZED SINGLE-WALLED CARBON NANOTUBE DISPERSION

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## Introduction

Single-walled carbon nanotubes (SWNTs) are one of the most promising materials in nanoscale science and technology in a wide range of application [1-3]. Integration of SWNTs with natural biopolymers, especially dsDNA improves the biocompatibility of the system while preserving the intrinsic properties of nanotubes. SWNTs liquid crystalline (LC) phases are a favorable starting material for producing macroscopic objects. In addition to obtaining nematic SWNT-dsDNA dispersions, we have also obtained the first cholesteric SWNT liquid crystal. Rheology of the dispersions also supported LC phase behavior. The production of fibers and films from the cholesteric dispersions has also been demonstrated.

## Experimental

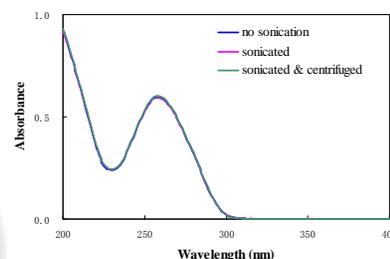
Purified high-pressure carbon monoxide process (HiPco) SWNTs from Rice University and Unidym Inc. were dispersed in aqueous solutions of salmon testes dsDNA with 5.4 % sodium salt (Sigma-Aldrich). To calculate the volume fractions of SWNTs, 1.45 g/cm<sup>3</sup> and 1.7 g/cm<sup>3</sup> were used as density of SWNTs and dsDNA respectively. In a typical experiment, SWNTs were mixed with aqueous solutions of dsDNA, and the mixtures were sonicated for 30 min at power level of 50 W in an ice bath. Dispersions with an initial concentration of 0.75 wt % dsDNA and 0.1 wt % SWNT were chosen for further treatment by centrifugation. Evaporation of the supernatant resulted in a cholesteric liquid crystal phase formation. Samples were collected at different time intervals during slow evaporation at room temperature. The concentrations of SWNTs were estimated by thermal gravimetric analysis (TGA). It should be noted that 27 % of the dsDNA remains even after 45 minutes hold at 800 °C under nitrogen. Liquid crystalline phase formation was confirmed by both optical microscopy (Nikon (Melville, NY) Eclipse 80i optical microscope) and rheology (Anton Paar (GmbH) Physica MCR 301 rheometer).

Wet jet solution spinning of cholesteric dsDNA-SWNT dispersions was controlled by Harvard Apparatus (Holliston, MA) PHD 4400 Hpsi high force/high pressure programmable syringe pump which has an average linear force of >200 lbs. The surface morphology of the resulting fibers was characterized by using JEOL 7000F FE-scanning electron microscope (SEM) (Tokyo, Japan).

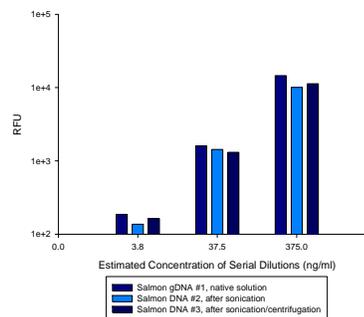
Double-stranded characteristics of dsDNA dispersions were verified using an Ultrospec 2100Pro UV-Vis spectrophotometer and SPECTRAFluor Plus fluorescence spectroscopy (TECAN, Instrument serial number 94385) by assaying dsDNA with picogreen reagent (Invitrogen, cat#P11495) and measuring the relative fluorescent units (RFU); dsDNA fragments were determined to be 750 bp after sonication by running on 1% agarose gel in 0.5 x TAE buffer with Bionexus Hi-Lo dsDNA marker.

## Results and Discussion

In order to confirm that the dispersion process did not denature the DNA, UV spectroscopy was performed on nonsonicated, sonicated, and sonicated and centrifuged dispersions. As shown in Figure 1, all three samples had the same intensity UV absorbance peak at 260 nm. Since ssDNA has a 40% higher absorbance than dsDNA[4], the uniformity of the spectra shows that dsDNA is retained. Furthermore, fluorescence spectroscopy of picogreen assays showed that all samples had similar relative fluorescence units (Figure 2); this provides further support that the majority of DNA retained its helical structure.



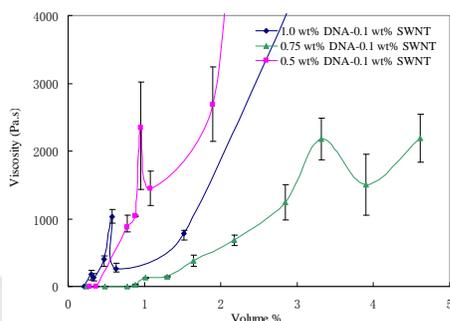
**Fig. 1** UV-Vis absorbance spectra for dsDNA solutions with initial concentration of 0.75 wt% before and after sonication/centrifugation.



**Fig. 2** Fluorescence quantification of dsDNA solutions before and after sonication/centrifugation using picogreen.

Slow dispersion evaporation increases the concentrations of both dsDNA and SWNT resulting in phase transitions from isotropic to biphasic to fully liquid crystalline. For dispersions of individual and small bundles of SWNTs, Figure 3 shows that with increasing concentration the viscosity versus concentration curve goes through a maximum as expected for lyotropic liquid crystal dispersion. The transition to a single phase liquid crystal occurs near the minimum in the viscosity

versus concentration curve. The curves in Figure 3 also highlight that phase transitions depend on the relative concentrations of SWNT and dsDNA. It also depends on the length to diameter ratio of the SWNTs which varies by batch. Optical microscopy on these samples supported nematic phase formation similar to previous observations for SWNT-ssDNA[5]. In contrast evaporation of supernatants of SWNT-DNA resulted in the fingerprint structure characteristic of a cholesteric liquid crystal. When rotating the specimen relative to the polarizers, different domains of the polydomain microstructure change color; this is known as Pseudo Bragg reflections and one of the characteristic optical properties of a cholesteric phase[6]. The liquid crystalline nature of dsDNA-SWNTs dispersions is further evidenced by the viscosity versus concentration curve (Figure 5).

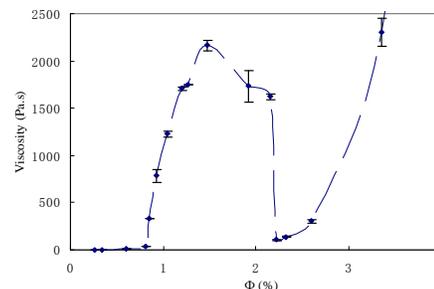


**Fig. 3** Relationship between viscosity and concentration for dsDNA-SWNTs dispersion obtained from 10:1 (HiPco), 7.5:1 (Unidym), and 5:1 (HiPco) dsDNA:SWNTs without centrifugation at a shear rate  $0.1 \text{ s}^{-1}$ . The system transition to a single-phase LC occurred near the minimums at 0.63, 3.90, and 1.07, vol% respectively.

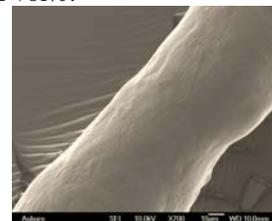


**Fig. 4** 2.32 vol% SWNTs under cross-polarized light. The scale bar is 50  $\mu\text{m}$ .

Carbon nanotube fibers from the high-concentration of cholesteric dsDNA-SWNT dispersions were obtained by wet jet solution spinning using alcohols such as ethanol (95 %), 2-propanol (99.8 +%), and tert-butanol (Figure 6). These results showed that the surface morphology is readily tunable due to the relative solubilities and diffusion rates of dsDNA and SWNT in the various alcohols. Surface morphologies obtained included spherical bumps (with diameter 70-150 nm) and rod-like (60-80 nm in width and several hundred nm in length) striations, wavy or smooth structures.



**Fig. 5** Relationship between viscosity and concentration for supernatants of dsDNA-SWNTs dispersion at a shear rate  $0.1 \text{ s}^{-1}$ . The system transition to a single-phase LC occurred at approximately 2.2 vol%.



**Fig. 6** Scanning electron microscope image of fiber extrude from cholesteric dispersion of dsDNA-SWNTs (1.98 vol% of SWNTs) in 2-propanol. The fiber diameter is  $\sim 81 \mu\text{m}$ . The scale bar is  $10 \mu\text{m}$ .

## Conclusions

We have observed the cholesteric LC phase formation in aqueous SWNTs-dsDNA dispersions. The SWNT:dsDNA ratio was found to have a significant effect on phase behavior as evidenced by rheology and cross-polarized optical microscopy. Macroscopic assembly of the cholesteric phase of dsDNA-SWNTs dispersions into fibers showed coagulant dependent surface textures.

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## References

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