361f Controlling the Phase Behavior of Single-Walled Carbon Nanotube – Superacid Dispersions

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Single-walled carbon nanotube (SWNT) liquid crystals are a potential means of producing highly aligned macroscopic articles that manifest some or all of the outstanding electrical, thermal and mechanical properties observed for SWNTs on the nano- to micro- scale. The protonation of SWNTs in superacids enables their dispersion at concentrations up to 12 vol%. With increasing concentration the system goes through several distinct phases: below a critical concentration $\square_I$ the system is completely isotropic, above a second critical concentration $\square_N$ the system is fully liquid crystalline, and at intermediate concentrations the isotropic phase exists in equilibrium with the liquid crystalline phase. The Hammett acidity ($-H_0$) of the solvent has a significant impact on SWNT protonation and phase behavior, particularly $\square_I$. Two methods of determining $\square_I$ were developed and gave similar results. The first method used optical microscopy to qualitatively determine the minimum concentration at which the biphasic region could be visualized. The second method used centrifugation in conjunction with UV-vis-nIR to quantitatively determine the maximum concentration of SWNTs in the isotropic phase. For SWNTs with an average length to diameter ratio of 500 dispersed in 102% sulfuric acid ($-H_0 = 12.0$), $\square_I$ is a mere 140 ppm vol. In contrast, in pure chlorosulfonic acid ($-H_0 = 13.8$), $\square_I$ is 5000 ppm vol. in close agreement with Onsager theory. Hammett acidity also impacts liquid crystalline morphology and the response to non-solvents. These differences in phase behavior have a direct impact on the microstructure of fibers spun from SWNT-superacid dispersions.