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Temperature Controlled Dispersion of Carbon Nanotubes in Water with Pyrene-Functionalized Poly(*N*-cyclopropylacrylamide)

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Suspensions of single-walled carbon nanotubes (SWNTs) are being studied for variety of applications that include biocompatible transportation,[1] drug delivery systems,[2] and optical sensors.[3] As produced SWNTs are aggregated because of the van der Waals force of attraction and hydrophobic interactions in aqueous environments which severely limit their dispersion, especially in water.[4,5] For this reason, both covalent[6] and noncovalent[7] techniques are used to stabilize SWNTs in water. Recently, the use of pH responsive polymers to stabilize SWNTs in water was examined where changes in conformation and degree of ionization of poly(acrylic acid) (PAA) as a function of pH were utilized for exfoliation and bundling of SWNTs.[8,9] The ability to use temperature to control the level of nanotube exfoliation would be a much more convenient extension of this powerful concept. In this communication, we report the use of a thermo-responsive poly(*N*-cyclopropylacrylamide) (PNCPA) copolymer with 5 mol % pyrene side groups (p-PNCPA), to stabilize aqueous SWNT suspensions. The changes in conformation (i.e., coil to globule transformation) as a function of temperature are believed to control the dispersion state of SWNTs (i.e., stabilized or bundled) in water.

Few attempts have been made to control the dispersion of SWNTs using stimuli-responsive polymers, especially as a function of temperature. Lack of suitable thermo-responsive polymers that have affinity for SWNTs may be one of the reasons for this. Most of the studies reported were based on poly(*N*-isopropylacrylamide) (PNIPAM) due to its transition temperature being near human body temperature (i.e., 32 °C).[10] However, the physical interaction between SWNTs and pure PNIPAM is modest and not sufficient for effective stabilization and/or control of the microstructure of aqueous SWNT suspensions as a function of temperature.[11] Accordingly, there is a need to develop new temperature responsive polymeric systems with better physical interaction with SWNTs.

Pyrene-functionalized PNCPA (p-PNCPA) was synthesized to disperse SWNTs in water (see Supporting Information). PNCPA shows temperature responsive dissolution in water and has a lower critical solution temperature (LCST) of 53 °C.[12,13] Addition of pyrene side groups, however, lowers the LCST of PNCPA to 30 °C for 5 mol % pyrene, due to the hydrophobic effect of the unpolar aromatic system (see Figure 3 and Supporting Information). The pyrene moiety has a strong tendency to adsorb on SWNTs due to $\pi-\pi$ stacking along the sidewalls, but the hydrophilic PNCPA backbone tends to dissolve in water below the LCST.[14] At temperatures above LCST, the otherwise hydrophilic backbone turns hydrophobic and becomes immiscible in water.[15] This transition of the backbone can influence the dispersion state of SWNTs as shown in Figure 1b. The stabilization of SWNTs in water by addition of p-PNCPA is believed due to the presence of a steric layer of polymer on SWNT surfaces. The thickness of the steric layer is greater below the LCST as the backbone exists in an expanded form due to the formation of hydrogen bonds with water.[15] This increased steric layer thickness counteracts the intertube van der Waals force of attraction and restricts the SWNTs from bundling. At temperatures above the LCST, the backbone collapses and assumes the form of a globule, which in turn reduces the steric layer thickness and the obstacle to SWNT aggregation. Similar steric layer thickness controlled dispersion of colloidal suspensions was observed for polystyrene latex stablilized with acidic polysaccharides.[16] The observation of SWNTs in an *"exfoliated"* state at temperatures below the LCST and a more bundled state at temperatures above the LCST of p-PNCPA (see Figure 1a) supports this assertion.

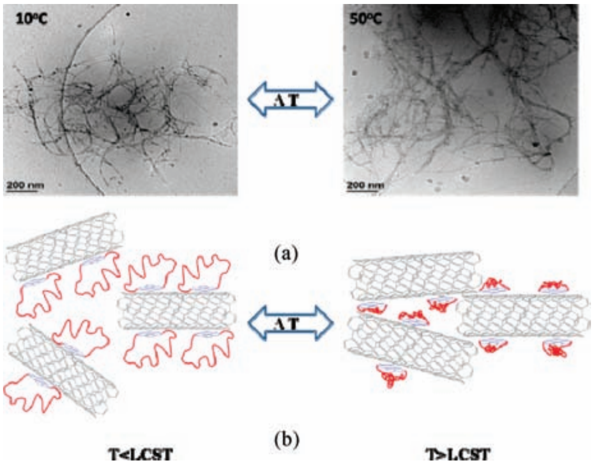

Figure 1. Cryo-TEM of p-PNCPA/SWNT suspensions as function of temperatue (a) and a schematic representing the stabilization mechanism (b).

Suspensions with well-dispersed SWNTs are known to have lower viscosities as compared to those that have agglomerated or bundled SWNTs, due to lack of entanglements.[8] To investigate this behavior, viscosity measurements were made on dilute suspensions containing 0.011 wt % SWNT and 0.1 wt % p-PNCPA at temperatures below and above the LCST of the polymer (i.e., 50 and 10 °C), as shown in Figure 2. It can be seen that, at 10 °C, the suspension shows a nearly Newtonian behavior with little change in viscosity as a function of shear rate. However, suspension viscosity at 50 °C exhibits a *shear-thinning* behavior (i.e., decrease of viscosity with increasing shear). Concentrated solutions of SWNTs show *shear- thinning* behavior because of the high degree of entanglements that look like polymeric solutions.[17]

Also, cryo-TEM micrographs of the suspensions (see Figure 1a) show SWNT microstructure to be bundled at 50 °C and more exfoliated at 10 °C. The results obtained from viscosity measure-

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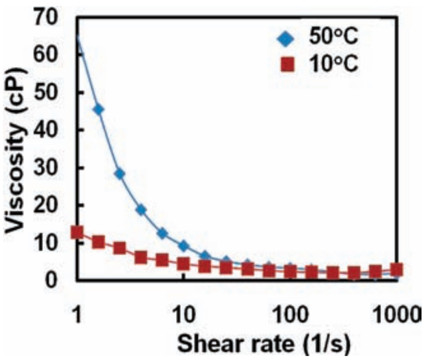

Figure 2. Viscosity of p-PNCPA/SWNT suspensions as a function of shear rate at 10 and 50 °C.

ments are complementary to cryo-TEM, and thus it is reasonable to deduce that p-PNCPA/SWNT suspensions are well dispersed at 10 °C and relatively bundled at 50 °C.

To understand the temperature response of p-PNCPA in the presence of SWNTs, turbidity (actually decadic absorbance) at 400 nm was examined in the absence and presence of SWNTs, as shown in Figure 3. It can be seen that there is a significant increase in turbidity of the p-PNCPA solution at 30 °C, and this is because of the coil−globule transition of p-PNCPA. The p-PNCPA/SWNT suspensions also show a small but significant increase at ∼30 °C, which corresponds to the transition temperature of p-PNCPA. Thus, the thermo-responsive characteristics of p-PNCPA are retained in the presence of SWNTs.

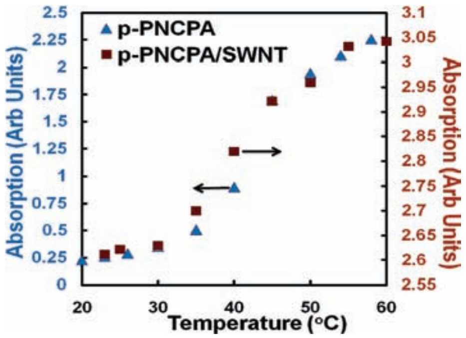

Figure 3. Turbidity as a function of temperature for aqueous p-PNCPA/SWNT neat suspension and p-PNCPA solution in water.

To investigate the solid-state microstructure, suspensions of p-PNCPA/SWNT were dried at temperatures below and above LCST (i.e., 20 and 50 °C, respectively) to form thin composite films. Scanning electron microscopy was performed on the dried composite films. Results (see Supporting Information) show a high degree of aggregation in the films dried at 50 °C. Electrical conductivity measurements made on these composites (see Table 1) showed significantly higher conductivity for films dried at 50 °C at all the concentrations studied (i.e., 10 and 20 wt % SWNT). This improved electrical conductivity for the film dried at 50 °C is due to better nanotube−nanotube contacts resulting from weaker polymer−nanotube interaction. This leads to a more aggregated, more heavily networked microstructure, much like the case in the liquid suspension. In the film dried at 20 °C, the closer association between polymer and nanotube restricts the electron flow by creating an insulating layer and reducing the contact points between tubes. This method of tailoring microstructure in the liquid state to control the microstructure and behavior in the solid state will have potential applications in polymer nanocomposite preparation.

Table 1. Electrical Conductivity of p-PNCPA/SWNT Composite

wt % SWNT	drying temp (°C)	electrical conductivity (S/m)
10	20	0.04
	50	0.26
20	20	0.91
	50	2.29

To conclude, we have synthesized a novel thermo-responsive polymer with 5 mol % pyrene side groups (p-PNCPA) to disperse SWNTs in water. Cryo-TEM micrographs obtained at temperatures above and below the LCST of this thermo-responsive polymer revealed the bundled and exfoliated microstructure of SWNTs, respectively. Viscosity measurements show shear-thinning and nearly Newtonian behavior of the suspensions above and below LCST. Turbidity measurements suggest that p-PNCPA retains its intrinsic thermo-responsive properties in the presence of SWNTs, with no significant change in the transition temperature. Evaluation of dried composite films suggests that the microstructure in the liquid state is preserved in the solid state to a large extent. Temperature controlled dispersion of SWNTs in water provides a new technique for controlling properties in the liquid and solid states that could impact nanotube-based sensing and composites respectively.

Acknowledgment. The authors would like to acknowledge financial support for this work from the Texas Engineering Experiment Station (TEES) and the National Science Foundation (CMMI 0644055). Dr. Christos Savva is thanked for his assistance with cryo-TEM (part of the Microscopy and Imaging Center [MIC] at Texas A&M). The acquisition of the FEI Quanta 600 FE-SEM was supported by the National Science Foundation (DBI 0116835), the VP for Research Office, and TEES. The University of Mainz is gratefully acknowledged for financial support.

Supporting Information Available: Synthesis scheme of p-PNCPA, experimental details, ^{1}H NMR spectra of p-PNCPA, UV/vis absorption and fluorescence emission spectra of p-PNCPA, SEM of dried composite films, and hydrodynamic radius of p-PNCPA as a function of temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA905803F