

Thermoresponsive Behaviors of Poly(oxypropylene)-amidoamine Functionalized Carbon Nanotubes

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Multiwalled carbon nanotube (MWNT) was organically grafted with poly(oxypropylene)-amine (POP-amine) of 2000 g mol⁻¹ molecular weight and became highly dispersible in water and organic media such as toluene. The presence of the POP pendants may render to the MWNT an inverse temperature transition (ITT) for water dispersion, showing a higher dispersing ability at lower temperature below 21–27 °C, which is detectable by UV–vis transmittance and the naked eye. The temperature-responsive dispersion behavior was further demonstrated in the toluene/water biphasic system, taking advantage of its relative dispersing ability in both media. By varying the temperature around the ITT, the dark-colored carbon nanotube (CNT) was dispersed into either water or toluene phase, in a reversible manner for multiple cycles. The unique thermoresponsive property is attributed to the switching of noncovalent bonding forces of the tethered POP segments between the hydrogen bonding with water and the hydrophobic interaction with toluene. The distinctly different morphologies of dispersion and aggregation were further observed by using atomic force microscopy.

Introduction

Polymeric materials with reversible stimulus-responsive properties may have industrial applications for drug delivery,^{1,2} biomaterial separation,^{3,4} and biosensing devices.^{5,6} The particular functional copolymers could be structurally designed to be responsive to environmental parameters such as solvent,^{7,8} pH,^{9,10} salt concentration,^{11,12} light,^{13,14} and temperature.^{15,16} The properties of these functional copolymers could be tailored by varying their chemical functionalities, molecular weight, composition, and molecular architecture.^{17–21} Recently, there are reports that nanomaterials such as organically modified carbon nanotubes (CNT) were also possibly modified to be sensitive for biological conditions.^{22–26} In general, the responsive behavior requires a well-controlled modification of CNT surfaces by tethering interfacial organics in interaction with the external variables. For example, CNT was modified through an oxidative formation of carboxyl functionalities and subsequent grafting with a temperature-responsive polymer,²⁷ such as poly(*N*-isopropylacrylamide) pendants. The grafting method may involve a reversible addition and fragmentation chain transfer to tether organic polymer onto the CNT surface.²⁸ As a result, the thermoresponsive polymer chains may form a hydrated and expanded conformation in water below the critical temperature, and hydrophobic aggregation above the temperature, generally described as an inverse temperature transition (ITT).^{29–32} These covalently attached polymer chains on the CNT surface greatly influence the CNT dispersing ability in a critical temperature-responsive manner. The organically modified CNT is actually insoluble but dispersible in water with an inverse temperature factor behavior. Such a hybrid has a tendency to aggregate at a higher temperature but disperses well at a lower temperature;

it can be described as having a lower critical aggregation temperature (LCAT).

Research on developing stimulus-responsive nanomaterials is challenging because of the requirement of surface organic reaction in an efficient manner and a proper selection of organic attachments with a stimulus-responsive property. Recently, we have revealed the use of various poly(oxyalkylene)-monoamines and diamines to functionalize multiwalled carbon nanotubes (MWNT).³³ Through oxidation to carbonyl derivatives and consequent amide grafting of poly(oxyalkylene)-amine pendants, it is possible to functionalize MWNT with a series of hydrophilic or hydrophobic polyetheramines in a controllable manner. When grafting with an amphiphilic poly(oxypropylene)-diamine which possesses potential noncovalent bonding of hydrogen bonds and hydrophobic interactions with solvents, the CNT further exhibits a thermoresponsive dispersion property in water or organic solvents.

Experimental Section

Materials. MWNT (prepared from a chemical vapor deposition method) was purchased from Aldrich Chemical Co. The CNTs are 90% in purity, 10–30 nm in diameter, and 1–10 μm in length. Thionyl chloride (99%) was obtained from Acros Co. The poly(oxyalkylene)-diamines, including poly(oxyethylene) (POE) and poly(oxypropylene) (POP) backbone diamines of 2000 *M_w*, with the chemical structure shown in Figure 1, are one of the Jeffamine D-series amines, which are commercially available from Huntsman Chemical Co. or Aldrich Chemical Co.

Measurements. An attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometer (Perkin-Elmer Paragon 500 FTIR) with a horizontal ZnSe crystal accessory (Pike Technology model with a 45° incidence angle and 10 internal reflections) for solid samples was used. A reference spectrum of the ZnSe crystal was collected before the measurements.

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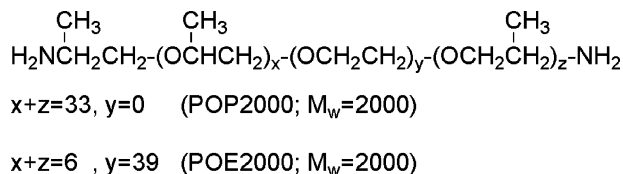


Figure 1. Chemical structure of poly(oxyalkylene)-diamines including poly(oxypropylene)-diamine (POP2000) and poly(oxyethylene)-diamine (POE2000).

Organic fractions were measured by thermal gravimetric analysis (TGA, Perkin-Elmer Pyris 1) at a heating rate of 10 °C/min under air flow. An elemental analyzer (Heraeus CHN-OS Rapid F002) was used to measure C, N, O, S, and H. Samples for LCAT measurement were prepared by dissolving the appropriate amount of MWNT derivatives or amines into deionized water. The temperature-dependent tests on the aggregation of the polymer-modified MWNT were determined with a Jasco V-530 UV-vis spectrophotometer by measuring their relative transmittance at 550 nm wavelength. The dynamic mode atomic force microscopy (DFM) was performed by a SPA-400HV with an SPI3800N controller (Seiko Instruments Industry Co., Ltd.). The cantilever used was fabricated from Si with a spring constant of 13 N/m and a resonance frequency of 139 kHz. Samples were prepared by dispersing MWNT derivatives in deionized water or toluene at 0.5 wt % concentrations and spin-coating on a glass surface at a spinning rate of 1500 rpm for 30 s. The specimen was conditioned by evaluating under a vacuum for 24 h to dryness.

Preparation of Poly(oxypropylene)-amine (POP-Amine) Grafted MWNT by Oxidation and Acylation–Amidation. The synthesis of the POP-amine modified MWNT was reported previously.³³ The typical procedures are described below. MWNT (100 mg) was suspended in H₂SO₄/HNO₃ (3:1 volume ratio, 25 mL) in a 50 mL test tube and agitated by sonication in a water bath for 12 h. The resultant suspension was collected on a polycarbonate membrane filter of 100 nm pore size and washed with deionized water until the filtrates showing a pH of 6–7. The filtered solid was further washed with acetone and dried under vacuum for 24 h at 120 °C to yield MWNT–COOH solid (79 mg, 79% yield). The collected solid was obtained after being dried. The functionalized MWNT is abbreviated as MWNT–COOH and characterized to have absorption of 1722 cm^{−1} under the ATR-FTIR analysis (Figure 2b). The elemental analyses are the following: C, 87.5%; N, 0.5%; O, 7.0%; S, 0.0%; H, 1.5% for MWNT–COOH; C, 88.8%; N, 1.0%; O, 1.9%; S, 0.0%; H, 0.8% for the pristine MWNT; C, 73.2%; N, 1.0%; O, 16.4%; S, 0.0%; H, 6.9% for one of the adducts of MWNT–COOH and POP-amine (abbreviated as MWNT–POP2000). The preparation of the MWNT–POP2000 via an acylation intermediate is exemplified below. A 200 mL three-necked and round-bottomed flask, equipped with a magnetic stirrer, nitrogen inlet–outlet lines, a thermometer, and a Dean–Stark trap, was charged with the suspension of MWNT–COOH (20 mg) in *N,N'*-dimethylformamide (DMF; 150 mL). Thionyl chloride (20 mL) was added the slurry of MWNT–COOH in DMF while stirring. The mixture was heated to 70 °C and maintained at this temperature for 24 h to convert the nanotube surface carboxylic acid into the corresponding acyl chloride. After centrifugation, the pale yellow-colored supernatant was decanted. The solid was washed with anhydrous DMF to remove the excess thionyl chloride. The slurry of the solid was added with POP-amine (5 g, 2.5 mmol) and stirred under N₂ atmosphere at 90 °C for 96 h. After cooling to room temperature, the suspension (23 mg) was collected, washed, and dried. The

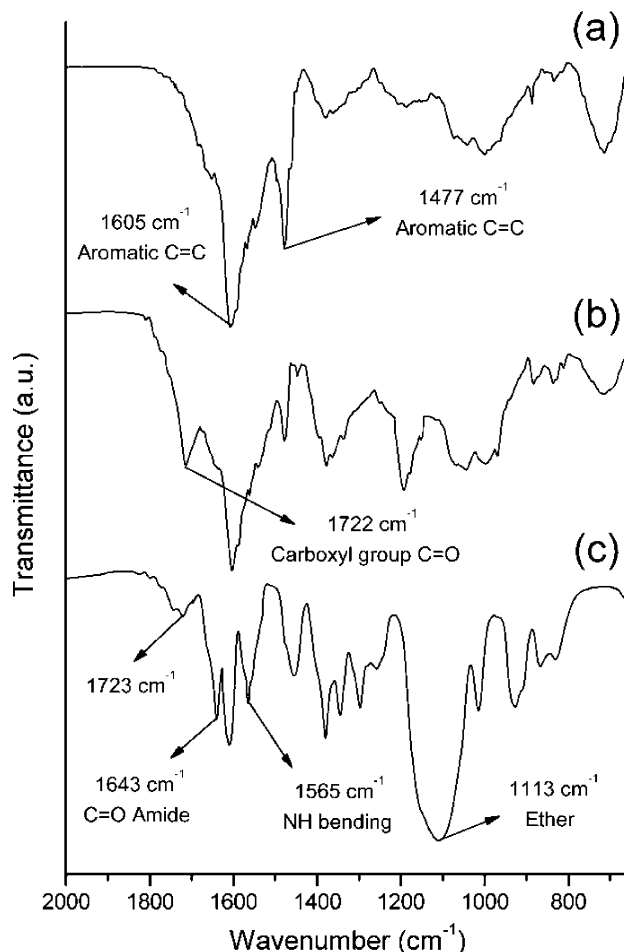


Figure 2. FTIR adsorptions of (a) pristine MWNT, (b) MWNT–COOH, and (c) MWNT–POP2000.

formation of amide functionalities in MWNT–POP2000 was evidenced by the presence of 1643 cm^{−1} (C=O stretch of amide carbonyl), 1723 cm^{−1} (residual C=O stretch of carboxyl), 1565 cm^{−1} (stretch of C–N and bend of N–H in the amide), and 1113 cm^{−1} (C–O–C ether), as shown in Figure 2c.

Results and Discussion

Preparation and Characterization of the POP-Amine Grafted MWNT. The synthetic route for preparing the POP-grafted MWNT³³ is illustrated in Scheme 1. The MWNT–COOH was first prepared, consequently converted into the corresponding acyl chloride intermediate, and followed by amidation with the POP-amine under mild conditions. The first-step formation of carboxylic acid functionalities on the MWNT surface was characterized by the FTIR absorption. The content of carboxyls was measured by elemental analysis (EA) and the organic fraction analysis by TGA. On the basis of the oxygen EA, the carboxyl content was ca. 0.16 mol for 100 g of MWNT–COOH. On the basis of TGA decomposition curves, the organic component was differentiable from MWNT which had a high thermal stability up to 400 °C and evaporation at 700 °C (Figure 3a). It was found that the MWNT–COOH was less stable, reasonably explained by the presence of defect structure on the nanotube surface caused by the HNO₃ oxidation (Figure 3b). The organic POP segments, grafted on MWNT through covalent bonding, had gained an enhanced stability, shown by the relative thermal stability compared with that of the physically mixed POP in MWNT. Under the standard TGA heating profile, the organics exhibited a delay of the decomposi-

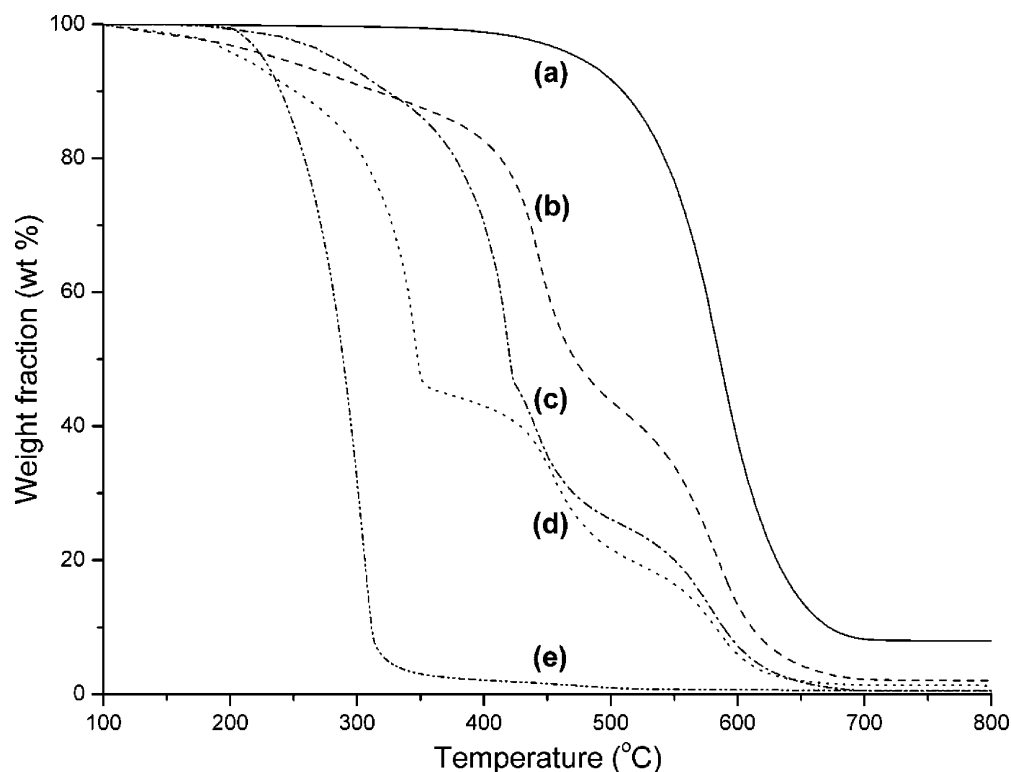
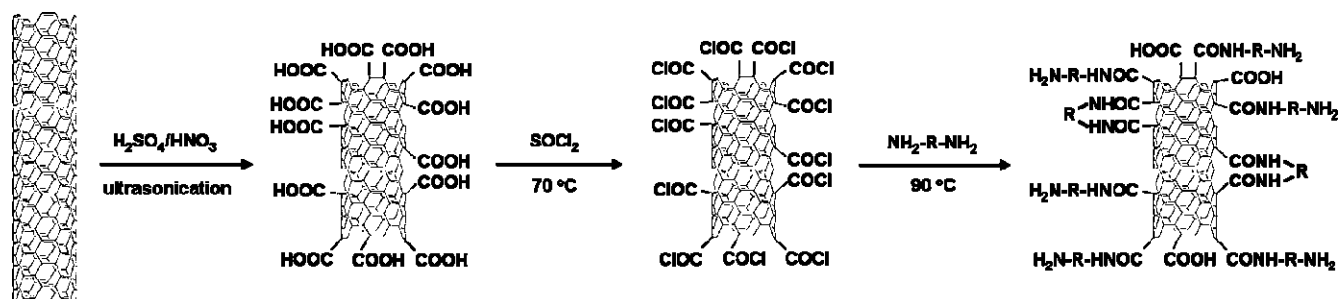


Figure 3. Relative thermo-oxidative stability by thermal gravimetric analysis (TGA) in air: (a) pristine MWNT, (b) MWNT-COOH, (c) MWNT-POP2000, (d) physical mixing of MWNT-COOH + POP-amine (56 wt %), and (e) POP2000.

SCHEME 1: Synthesis of MWNT-Amidoamines from the Grafting of Poly(oxypropylene)-amine (POP-amine) onto MWNT-COOH by the Acylation-Amidation Method



tion midpoint from 330 to 400 °C (Figure 3, parts c and d). This observation provided another evidence of the POP grafting. On the basis of TGA and EA, it represents 62.8% of carboxylic acid conversion into amidoamine.

Thermoresponsive Behaviors of the POP2000-Grafted MWNT in Water. Various organic fractions in MWNT-POP2000 and their corresponding ability to disperse in water are summarized in Table 1. It was demonstrated that all of these POP-amide functionalized MWNT prepared from different degrees of acid treatment had an ITT, dispersing well at low temperature but aggregating at an elevated temperature. The temperature-sensitive aggregating or dispersing phenomenon is attributed to the tethered POP organic portions that enable it to dissolve in water at lower temperatures through hydrogen-bonding interaction and show a behavior of ITT. Since the POP organics could render the CNT dispersible at a lower temperature but allow aggregation at a higher temperature, it can be described as having a lower critical aggregation temperature, or LCAT. This inverse temperature dispersing behavior for the MWNT could be measured by temperature-variable optical UV transmittance in 2×10^{-2} wt % aqueous suspensions. A series of MWNT-POP2000 with different grafted organic amounts, prepared by the acylation-amidation method, was analyzed by

TABLE 1: Thermal Gravimetric Analysis and LCAT of Various MWNT-POP Amidoamines Prepared from Different Degrees of Acid Treatment in Water

MWNT-POP	MWNT-COOH (acid treatment, h)	MWNT-COOH/POP (mg/g)	based on TGA		
			MWNT fraction (wt %)	organic fraction (wt %)	LCAT (°C)
I	6	20/1	49	51	22
II	6	20/0.4	56	44	24
III	12	20/3	48	52	26
IV	12	20/0.8	55	45	27
V	18	20/5	44	56	22
VI	18	20/1	50	50	25
VII	24	20/8	42	58	21
VIII	24	20/3	46	54	24

TGA to have the organic compositions in the range of 44–58 wt %. All of these samples demonstrated an LCAT when dispersed in water. For example, the MWNT-POP2000 of 44 and 51 wt % organics were shown to have their LCAT of 24 and 22 °C, respectively. The presence of hydrogen bonding in the POP-amide structure facilitated the water dispersing ability at lower temperature, but aggregation occurred when the medium temperature increased. The trend for the higher POP fraction was observed to have a lower LCAT. In Table 1, the

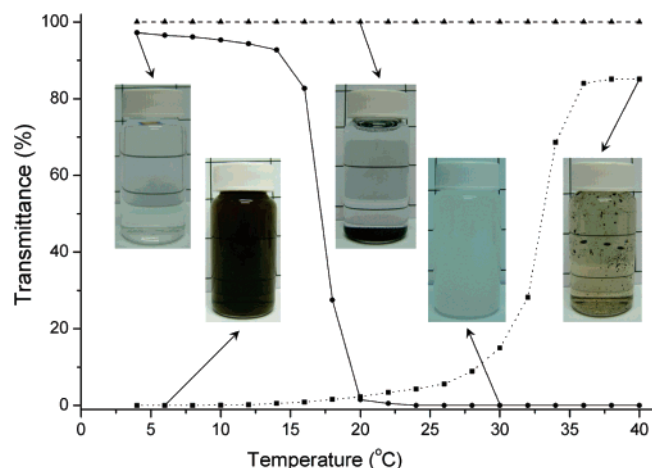


Figure 4. Relative transmittance ability of POP2000-amine (●), pristine MWNT (▲), and MWNT-POP2000 IV (■) in the range of 4–40 °C in water.

trend of LCAT was summarized for POP-modified MWNT, in corresponding with different organic amounts grafting from the carboxyl functionalities.

The starting material, POP-diamine of 2000 g mol⁻¹ M_w , is insoluble at ambient temperature in water due to the presence of the hydrophobic POP backbone. As shown in Figure 4 (solid curve with circles), the POP-diamine became soluble at a lower temperature below 20 °C, measured by the optical absorption at 550 nm at the concentration of 3 mg/mL in water. The ITT was found by plotting its solution transmittance (%) against the temperature in the range of 4–40 °C. The POP-amine solubility decreases at a critical-point manner, due to the hydrogen-bonding disruption at this temperature. The transmittance decreased significantly at the transition range of 14–20 °C when the POP aggregation occurred, and turbidity appeared. The characteristic of the POP2000 solubility in water is significantly different from its POE2000 analog which has a majority of oxyethylene segmental composition. As a comparison, the POE2000 diamine of 2000 g mol⁻¹ M_w is highly water-soluble at any temperature, because the hydrogen bonding of the POE backbone is more intensive than that of the POP backbone. Before the organic grafting, as indicated in Figure 4 (dashed curve with triangles), the pristine MWNT shows a constantly clear transmittance in the temperature range because of the MWNT bundles entangled and precipitated at the bottom of the water layer. From the naked eye, the upper phase solution was clear, while the pristine MWNT aggregated at the bottom. The POP grafting altered the dispersing behaviors of the MWNT. For example, Figure 4 (dotted curve with squares) exhibits the transmittance of MWNT-POP2000 IV with 45 wt % of POP compositions as a function of temperature. As the temperature increased gradually, the transmittance increased slightly in the range of 4–26 °C and dramatically between 28 and 36 °C. After the sharp transition at 36 °C, the transmittance was very high (85%). In the range of 4–26 °C, the presence of well-dispersed MWNT reduced the optical transparency. This measurement of the transmittance is parallel to the darkness of the suspension observed by the naked eye. The results imply that the tethered POP organics certainly play the role of influencing the dispersion or aggregation of the MWNT hybrids around 24–32 °C. It is interestingly noted that the shifting of opaque MWNT dispersion to a clear upper phase solution with MWNT aggregated at the bottom is a reversible process over a number of temperature cycles.

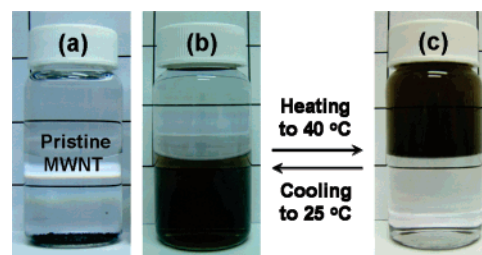


Figure 5. Thermoresponsive cycles of the POP2000-amine grafted MWNT in toluene/water phases: (a) pristine MWNT (25 °C), (b) MWNT-POP2000 (25 °C), and (c) MWNT-POP2000 (40 °C).

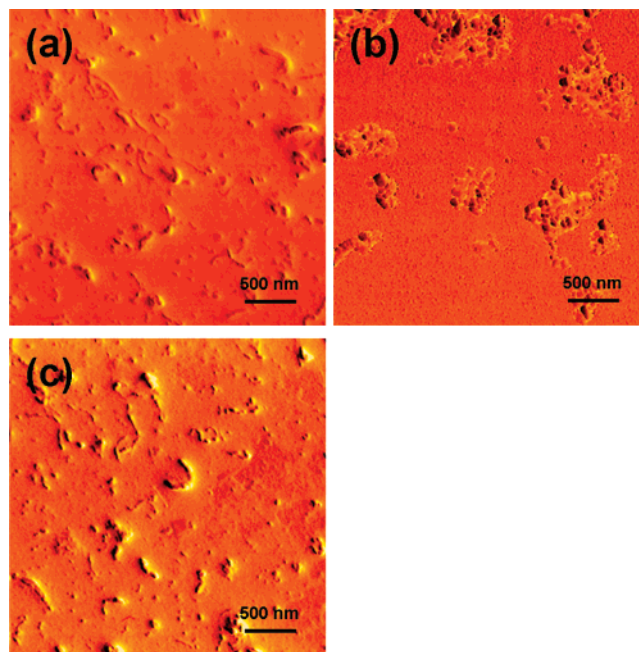
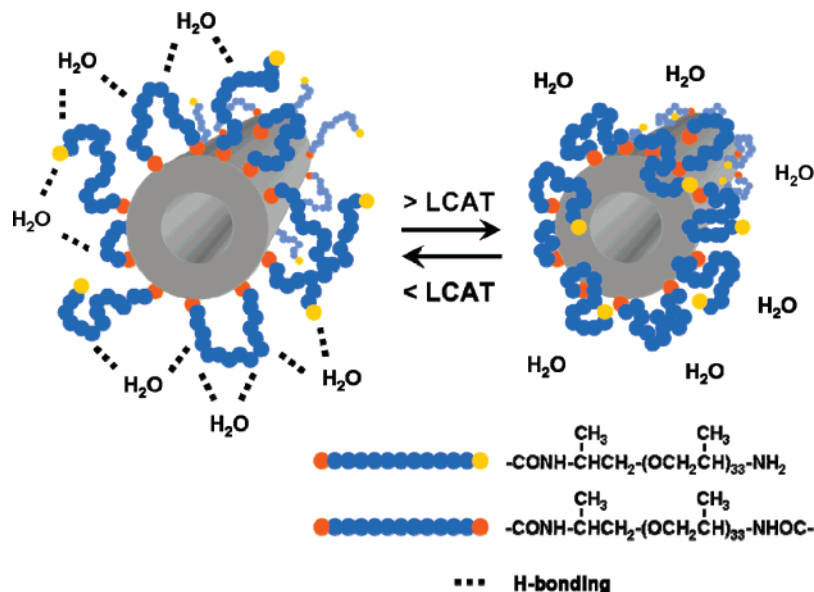


Figure 6. DFM phase images of MWNT-POP2000 on the glass surface: (a) in water at 25 °C, below LCAT, (b) in water at 40 °C, above LCAT, and (c) in toluene at 40 °C and dried.

Since the MWNT-POP2000 hybrid is also dispersible in toluene, the relative ability of dispersing in water or toluene is investigated. In the biphasic toluene/water, the hybrids were shown to be temperature-dependent for dispersing in water or in toluene. At a lower temperature below 25 °C, the hybrid would only disperse in the aqueous phase rather than in toluene, as indicated in Figure 5b. When the temperature was increased to or above 40 °C, the dispersion favored the toluene phase. Interestingly, the sample dispersed in toluene would return into the water phase when the temperature was lowered below 25 °C. This reversible process of dispersion migration provides a macroscopic evidence for the hydrophilic and hydrophobic transformation of the modified CNTs. Depending on the temperature, the noncovalent bonding between the hydrogen bond and the hydrophobic interaction influenced the dispersion in water and in toluene, respectively. It is noteworthy that this reversible process is fast and the sample is stable in the biphasic system over a 2 month period of time in air.

Direct DFM Observation of MWNT-POP2000 Dispersion. Due to the high aspect ratio and lengthy geometric shape, the pristine MWNT tends to aggregate in bundles and precipitate out from common organic solvents. Through the organic modification, the modified MWNT-POP2000 becomes dispersible in toluene and also in water, depending on the temperature. In order to differentiate the dispersing and aggregating states, their morphologies were examined by using a DFM. The

SCHEME 2: Reversible Mechanism of MWNT–POP2000 Hybrids in Thermoresponsive Dispersion or Aggregation through POP Expansion


MWNT–POP2000 in water, dispersed at 25 °C, and spin-coated on a glass slide, was observed to be well-distributed (Figure 6a). By contrast, the same sample prepared at 40 °C showed the aggregated morphology with the average clusters in nearly micrometer scale or averaged 300 nm in diameter, as indicated in Figure 6b. In Figure 6c, MWNT–POP2000 was dispersed at 40 °C in toluene and then spin-coated, showing the individual nanotubes in a fine distribution. These DFM observations revealed the different morphologies between the dispersed and aggregated MWNT, that existed below and above the LCAT.

Mechanism of Temperature-Responsive Dispersion. Under the DFM analysis and other observations mentioned above, the temperature-responsive mechanism can be rationalized (Scheme 2). At the temperature below the LCAT, there exists a hydrogen-bonding interaction between the grafted POP segments and water molecules and, consequently, the conformation of expanded POP molecular coils in water. As a result, the tethered MWNT were dispersed well through the POP solubility in water. Above the LCAT, the hydrogen-bonding force between the POP chains and water molecules is thermodynamically unstable. The POP molecular coils shrink in water, but in toluene, the POP coils expand again into the good solvent. As a result, the temperature change determines the dispersing behavior in the biphasic water/toluene system.

Conclusion

The grafting of POP-amide functionalities on MWNT rendered the hybrids dispersible in both toluene and water. In water dispersion, the MWNT–POP2000 hybrids exhibited a lower critical temperature behavior at the range of 21–27 °C. Furthermore, the MWNT with the tethered POPs (2000 g mol^{−1} *M_w*) enabled us to reversibly shift the dispersion in toluene or in water, depending on the environmental temperature. The dual dispersing behavior, fast and reversible, was influenced by the POP molecular coil interaction with water by hydrogen bonding or with toluene by hydrophobic interaction. The DFM analysis provided a direct observation of dispersed and aggregated morphologies. The thermally responsive behavior in the biphasic system may broaden the MWNT applications in the areas of drug targeting or biosensing devices.

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