Synthesis of Water-Soluble Multiwalled Carbon Nanotubes with Grafted Temperature-Responsive Shells by Surface RAFT Polymerization

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Water-soluble multiwalled carbon nanotubes (MWNTs) with temperature-responsive shells were synthesized by grafting poly(*N*-isopropylacrylamide) (PNIPAAM) from sidewall of MWNT via surface reversible addition and fragmentation chain transfer (RAFT) polymerization using RAFT agent functionalized MWNT as chain transfer agent. Carboxylic groups on MWNT were formed by nitric acid oxidation. Then bromoisobutyrate groups were covalently attached to the MWNT by esterification of 2-hydroxyethyl-2′-bromoisobutyrate with carboxylic groups, forming bromoisobutyrate functionalized MWNT (MWNT-Br). RAFT agent functionalized MWNT was produced by substitute reaction of MWNT-Br with PhC(S)SMgBr. ^{1}H NMR, FT-IR, and thermogravimetric analyses (TGA) results showed that PNIPAAM chains grew from MWNT by surface reversible addition fragmentation chain transfer polymerization. The molecular weight of PNIPAAM on MWNT increased linearly with monomer conversion, and its PDI is narrow (around 1.3). TGA showed that the amount of PNIPAAM grown from the MWNT increased with the increase of polymerization time. The MWNT-*g*-PNIPAAM has good solubility in water, chloroform, and tetrahydrofuran. TEM images also showed the MWNT-*g*-PNIPAAM was dispersed individually, indicating that the bundles of original MWNT were separated into individual tubes by surface RAFT polymerization. The produced MWNT-*g*-PNIPAAM has a PNIPAAM shell, which is very sensitive to change of temperature. This method can also be employed to graft other functional polymer chains onto MWNTs.

Introduction

The great interest in carbon nanotubes resides in their possible technological applications in various fields of science, such as molecular wires, molecular electronics, sensors, probes, high-strength fibers, field emission, biological electronics devices, and hydrogen storage.[1−7] The functionalization chemistry of carbon nanotubes is expected to play a vital role in tailoring the properties of these materials and the engineering of nanotube devices. Although a number of research groups have focused on functionalizing carbon nanotubes with various organic, organometallic structures and linear polymers to increase the solubility of carbon nanotubes, and they have made great progress in this field,[8−12] the ability to solubilize separate individual carbon nanotubes in water is still a great challenge.[13−15] Most important, for the applications of carbon-nanotube-based sensors and probes in a biological environment and medical chemistry, how to functionalize a carbon nanotube, to make it water-soluble and responsive to environmental conditions such as pH, temperature, and ionic strength, has been explored very little. This makes it difficult to explore and understand the applications of carbon nanotubes in the biological field, such as for delivery of drugs and protein, or as scaffolds to target different tissues. These studies require carbon nanotubes that are not only water-soluble but also well-controlled with regard to modification of the surface to obtain a shell that is sensitive to environmental conditions. The exploration in this exciting area is not expanding, partially due to the difficulty

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Scheme 1. Outlines of RAFT Agent Fixation on MWNT and PNIPAAM Chain Growing from MWNT via Surface RAFT Polymerization
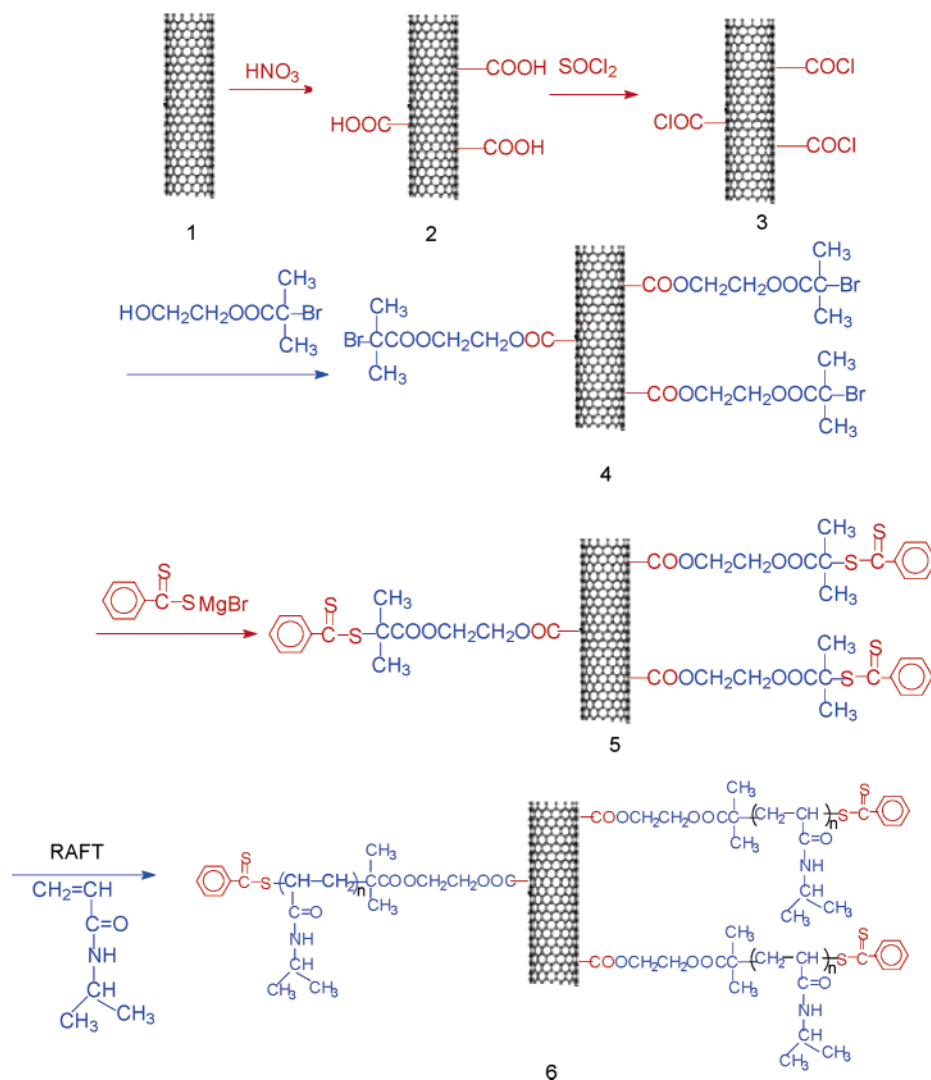
in growing water-soluble, functional polymer chains from carbon nanotubes.[16-18]

Covalently attaching polymer chains onto the surface of carbon nanotubes has recently attracted considerable attention because it endows the surfaces with novel structures and properties. Covalent attachment of polymer chains to the surface can be accomplished by either "grafting to" or "grafting from" techniques. "Grafting to" involves the bonding of a preformed end-functionalized polymer chain to the reactive surface groups on the substrate.[19] The limitation in this technique is that the attachment of a small number of chains hinders diffusion of additional polymer chains to the surface, thereby leading to low grafting density, and also it is difficult to graft functional polymer chain to MWNT. The "grafting from" technique generally involves the immobilizing of initiators onto the substrate followed

by in situ surface-initiated polymerization to generate the tethered polymer chains.[20-25] The advantage of this technique is that many kinds of polymer chains with high grafting density are easily attached on the surfaces of silicon wafers, gold, latex, or carbon black particles and clay by living radical, anionic, cationic, and ring-opening metathesis polymerization methods. Some polymer chains also have been successfully grafted onto the surfaces of carbon nanotubes by this method, and they improved the properties of carbon nanotubes greatly.[26-31] Unfortunately, grafting functional polymer chains from the surface is inherently difficult, because functional monomers typically interfere with most

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living polymerization methods. Therefore, there is no general method reported to graft water-soluble and "smart" (such as temperature, photo, pH, and ionic strength sensitive) polymer chains from the surface of carbon nanotubes in a controlled process. Herein, we report a novel method to graft water-soluble "smart" polymer chains from the surface of multi-walled carbon nanotubes (MWNTs). Different from the present general "grafting from" methods by immobilizing initiators on carbon nanotubes first, here we immobilize RAFT (reversible addition fragmentation chain transfer) agents on carbon nanotubes. Compared with ATRP, anionic, cationic, and ring-opening metathesis polymerization methods, RAFT polymerization can control the polymerization of water-soluble and functional monomers.[32−36] To our knowledge, MWNTs covalently attached with water-soluble, "smart", functional polymer chains may not have been previously attempted, and this is the first report that demonstrates a living polymerization method to graft functional polymer chain onto the surface of MWNTs by surface reversible addition fragmentation chain transfer polymerization.

PNIPAAM, one of the well-known thermo-sensitive polymers, has a low critical solution temperature (LCST) in water at 32 °C and represents probably the most often-used thermoresponsive polymer in biotechnology and medicine. In addition, it can be used to prepare thermo-reversible separators, thermo-responsive soft actuators, automatic gel valves, and smart, reusable catalysts.[37−41] Therefore, MWNTs will be endowed with new potential applications if temperature-sensitive PNIPAAM chains are attached onto MWNTs.

Experimental Section

Synthesis of 2-Hydroxylethyl-2′-bromoisobutyrate (HOCH$_2$-CH$_2$OCOC(CH$_3$)$_2$Br, HEBrIB). HEBrIB was prepared as follows: 42.0 g of ethylene glycol (0.67 mol), 11.2 g of 2-bromo-
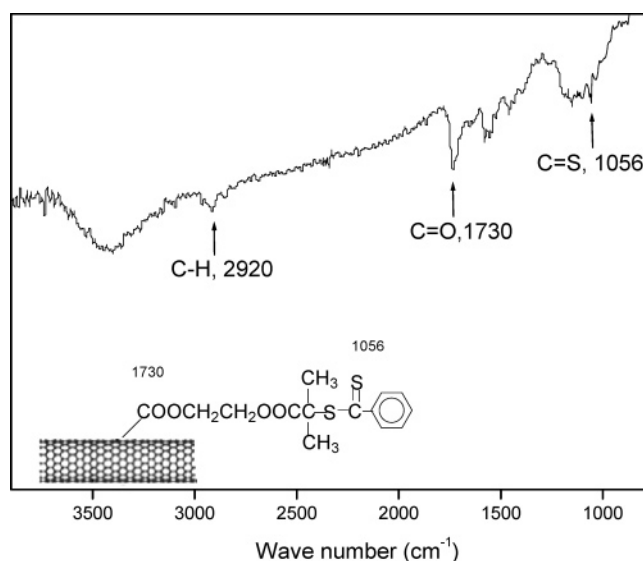

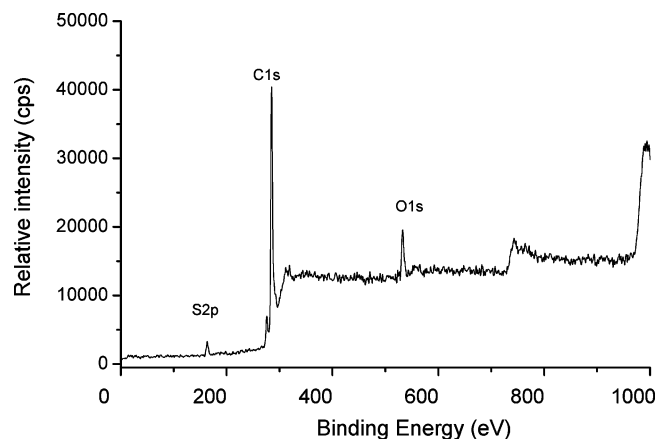**Figure 1.** FT-IR spectrum of MWNT-SC(S)Ph.

Figure 2. XPS spectrum of MWNT-SC(S) Ph.

isobutyric acid (0.067 mol), 0.2 g of *p*-toluenesulfonic acid, and 100 mL of benzene were added into a 250-mL one-neck round-bottom flask equipped with a magnetic stirrer. The mixture was heated at 96 °C while stirring for 36 h, and the water generated by the esterification reaction was removed by an oil−water separator. After distilling at 80 °C/0.1 mmHg for 2 h, the mixture was further kept at 80 °C overnight while stirring. The reaction mixture was then poured into 500 mL of distilled water and the lower, light-yellow, organic phase was separated. After the water phase was saturated with sodium chloride, another small portion of oil was separated. The two organic portions were combined, dissolved in methylene chloride, and dried over anhydrous magnesium sulfate overnight. After filtration from the magnesium salt, and removal of solvent, the 2-hydroxylethyl-2′-bromoisobutyrate was obtained as a colorless liquid (10 g, yield: 70%). ^{1}H NMR (δ, ppm), 1.0 (s, 6H, 2-C*H*$_3$), 3.7 (t, 2H, OCH$_2$C*H*$_2$OH), 4.30 (t, 2H, −COOC*H*$_2$-CH$_2$−).

Synthesis of MWNT-Br. In a typical experiment, crude MWNTs (2.1 g) were added to 60% HNO$_3$ aqueous solution (30.0 mL). The mixture was treated with an ultrasonic bath (40 kHz) for 15 min and stirred for 20 h at reflux. Then the mixture was vacuum-filtered through 0.2-μm Millipore polycarbonate membrane and washed with distilled water until the pH of the filtrate was 7.0. The filtered solid was dried under vacuum for 28 h at 50 °C, obtaining MWNT-COOH (1.4 g).

A 250-mL round-bottomed flask was charged with 1.30 g of the carboxyl-functionalized MWNT, 100 mL of SOCl$_2$, and 20 mL

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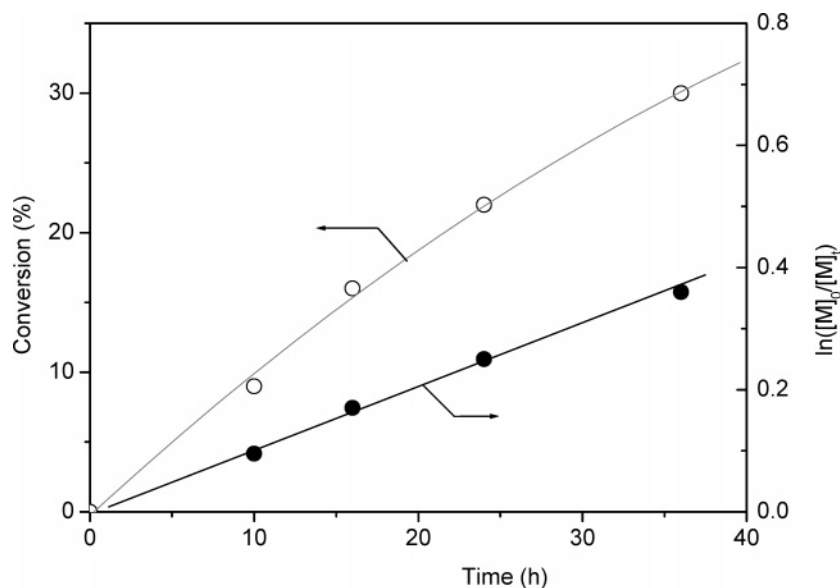
Figure 3. Relationships of conversion of NIPAAM and $\ln([M]_0/[M]_t)$ with polymerization time.

of benzene. The flask was fitted with a water condenser, and the mixture was stirred at 70 °C for 24 h. The solvent was removed under vacuum. The remaining solid (MWNT-COCl) was washed three times with anhydrous THF and was vacuum-dried at 25 °C for 4 h. A mixture of the solid (MWNT-COCl), 2-hydroxyethyl-2′-bromoisobutyrate (8.3 mL), and 100 mL of anhydrous toluene was added into a 250-mL round-bottomed flask and refluxed for 30 h. The solid was separated by filtration through a 0.2-μm poly-(tetrafluoroethylene) (PTFE) membrane, thoroughly washed with ethanol and diethyl ether, and vacuum-dried for 10 h to yield 1.1 g of MWNT-Br. TGA showed 14.1% weight loss before 500 °C from MWNT-Br. The weight loss corresponds to 8.2 bromoisobutyrate functional groups per 1000 carbons of MWNT-Br.

Synthesis of MWNT-SC(S)Ph. Phenylmagnesium bromide was prepared from bromobenzene (24.0 g) and magnesium turnings (3.4 g) in dry tetrahydrofuran (150 mL). The solution was warmed to 40 °C and carbon disulfide was added over 10 min, then the reaction mixture was kept at 40 °C for 1 h. To the resultant brown mixture was added MWNT-Br (0.98 g) and the reaction temperature was kept at 70 °C for 60 h. Ice hydrochloric acid (1.0 M, 50 mL) was added, the product was washed with distilled water 5 times, then washed with ether 5 times. The RAFT agent functionalized MWNT (MWNT-SC(S)Ph) obtained was dried under vacuum at room temperature.

PNIPAAM Growing from MWNT by Surface RAFT Method. MWNT-SC(S)Ph (50.0 mg), NIPAAM (1.0 g), and AIBN (0.5 mg) in 2 mL of benzene were added into a polymerization tube. The polymerization tube was sealed under vacuum and placed in a thermostated oil bath at 100 °C. The polymerization was stopped by cooling to 25 °C and opening the polymerization tube to air. The mixture was diluted with 200 mL of THF, bath-sonicated for 20 min, and filtered through a 0.2-μm PTFE membrane. The solid was washed with THF to remove the free polymer. After 10 washings there was no cloudiness when 10 drops of filtrate was added to 10 mL of diethyl ether, indicating that little or no soluble PNIPAAM remained. A gray or black solid was obtained after vacuum-drying for 24 h.

Cleavage of PNIPAAM from MWNT. PNIPAAM chain can be cleaved from the MWNT at ester bond under basic conditions. For this purpose, the MWNT-*g*-PNIPAAM was dispersed in a mixture of MeOH/aq. 20% NaOH (2:1) and stirred at 60 °C under nitrogen overnight for 48 h. The reaction mixture was filtered though a 0.2-μm PTFE membrane. The filtrate was by acidified

with formic acid, MeOH and water was evaporated. Then the solids obtained were dissolved in chloroform. After extraction with a small amount of hot distilled water (45 °C), the organic phase was isolated and dried with anhydrous magnesium sulfate for 12 h. After filtration from magnesium salt, homoPNIPAAM was obtained by removal of chloroform. The molecular weight of homoPNIPAAM was analyzed by SEC.

Measurements. Fourier transform infrared spectra were recorded on a Bruker VECTOR-22 IR spectrometer. [1]H nuclear magnetic resonance (NMR) spectra were analyzed on a Bruker DMX-500 instrument with D_2O as solvent. Thermal gravimetric analyses (TGA) were carried out on a PE TGA-7 instrument with a heating rate of 20 °C/min. Transmission electron microscopy (TEM) analyses were conducted on a JEOL JEL2010 electron microscope at 200 kV, and the samples for TEM measurements were prepared by placing one drop of sample on copper grids coated with carbon. Molecular weight and PDI were measured on an SEC Waters 2690 with RI, RALLS, and DV detectors. DSC studies were performed from 10 to 50 °C (heating rate 2 °C/min) on a 2920 modulated DSC (TA Instruments) under a nitrogen atmosphere.

Results and Discussion

Immobilization of Surface RAFT Agent onto MWNT. Dithiobenzoate is an excellent RAFT agent for living radical polymerization of (meth)acrylate and styrene monomers, so we should fix dithiobenzoate onto MWNT in order to prepare MWNT grafted with PNIPAAM. After treatment with nitric acid, MWNT was functionalized with carboxylic groups at the open ends and at defects of the sidewalls. Scheme 1 shows the method for RAFT agent fixation to MWNT and PNIPAAM chain growing from MWNT via surface RAFT polymerization. The produced RAFT agent functionalized MWNT (MWNT-SC(S)Ph) dispersed into organic solvents such as terahydrofuran (THF), dimethylformamide (DMF), and chloroform well enough to observe very broad bands in ^{1}H NMR spectra, but it flocculates as black fiber bundles suspended in clear solvent in less than one week. The FT-IR spectrum (Figure 1) of MWNT-SC(S)Ph clearly shows the characteristic C−H, C=O, and C=S stretching vibrations centered at 2920, 1730, and 1056 cm^{-1}, respectively. For these reasons we conclude that the RAFT agents are
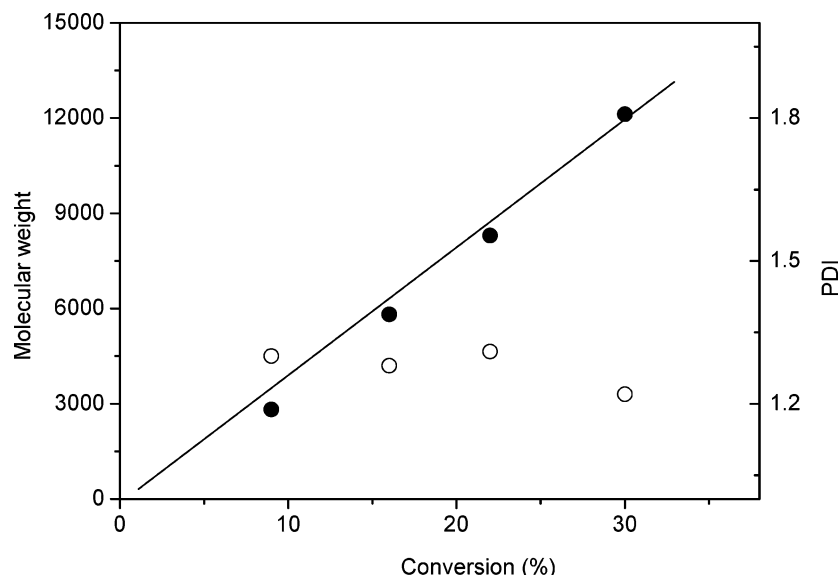
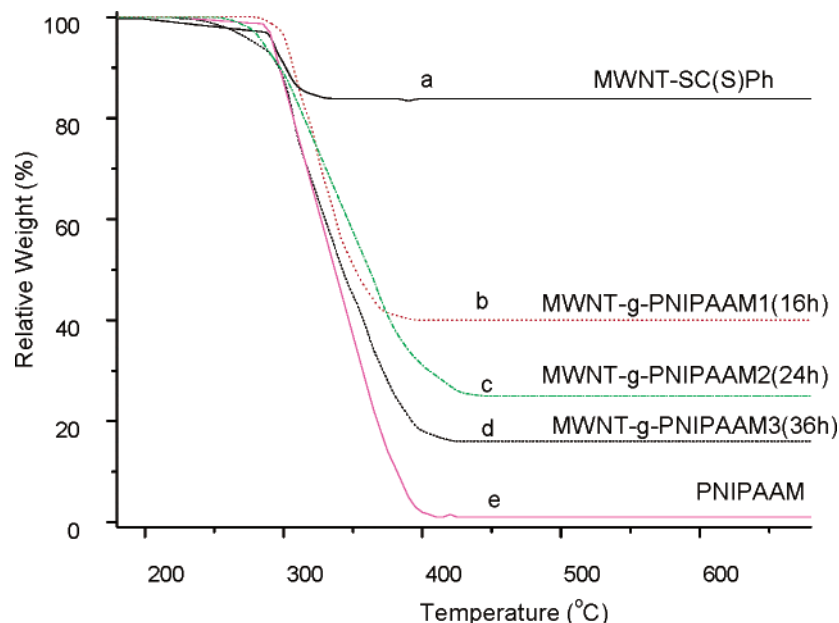**Figure 4.** Variations of molecular weight and PDI of PNIPAAM with monomer conversion.

Figure 5. TGA thermograms of MWNT-SC(S)Ph (a), MWNT-*g*-PNIPAAM1−3 taken at different time intervals (b−d), and homoPNIPAAM (e) under nitrogen.

covalently bound to the surface of MWNT. TGA result showed about 0.76 RAFT agent functions per 100 carbon atoms calculated from the weight loss from MWNT-SC(S)-Ph at 280−420 °C. In addition, X-ray photoelectron spectroscopy (XPS) analysis was employed to determine the composition of the MWNT immobilized with RAFT agent functions on the surface. The result is shown in Figure 2. The major peak component at the binding energy (BE) of about 284.60 eV is assigned to the C1s, the minor peak component at the BE of 533.30 eV is attributable to O1s of the ester groups on the surface of MWNT, and the small peak at the BE of 163.30 eV corresponds to S2p of the RAFT agent functions on MWNT. The mole content of the RAFT agent functions on the surface of MWNT is about 0.8% with respect to carbon, which is similar to the result obtained from TGA.

Growth of PNIPAAM Chains from MWNT via Surface RAFT Polymerization. Previous research showed that polymer chains can be easily grafted from the solid surface and microsphere surface with a controlled behavior via surface RAFT polymerization in the presence of RAFT agent functions immobilized on solid surface and microsphere surface.[35,42,43] Surface RAFT polymerization of NIPAAM was performed in benzene in the presence of MWNT-SC-(S)Ph, and PNIPAAM chains grew from the surface of MWNT via the RAFT process. After the polymerization, the reaction mixture was diluted with THF, and the resultant products were washed thoroughly with THF, and then filtered to remove soluble homopolymers unimmobilized on MWNT. Washing was done until no polymer was found in the filtrate. The water-soluble and temperature-sensitive polymer functionalized MWNTs (MWNT-*g*-PNIPAAM) were collected with black or gray color. The weight of MWNT-*g*-

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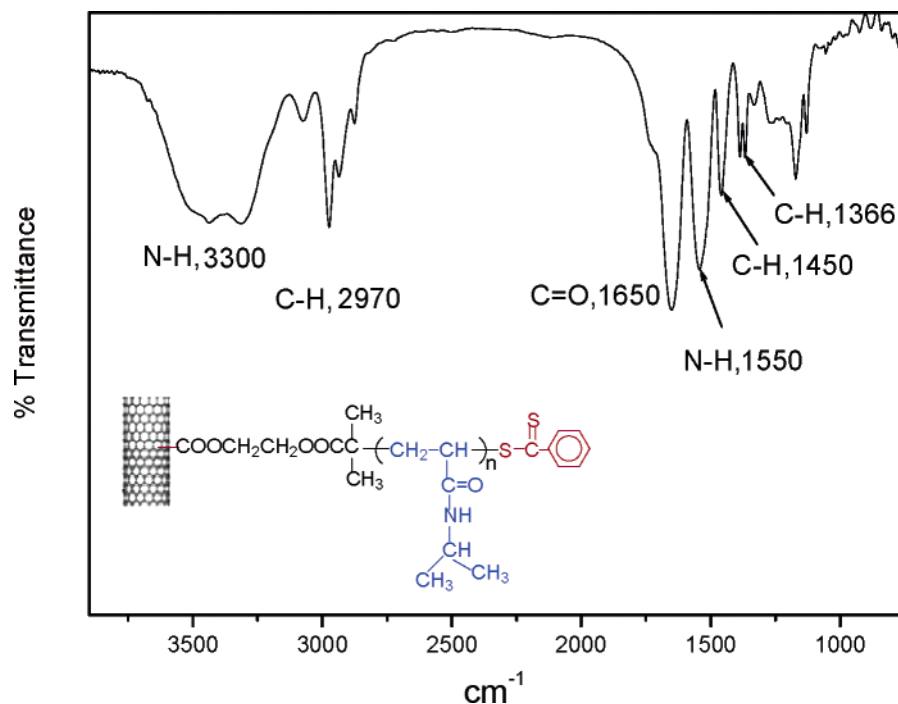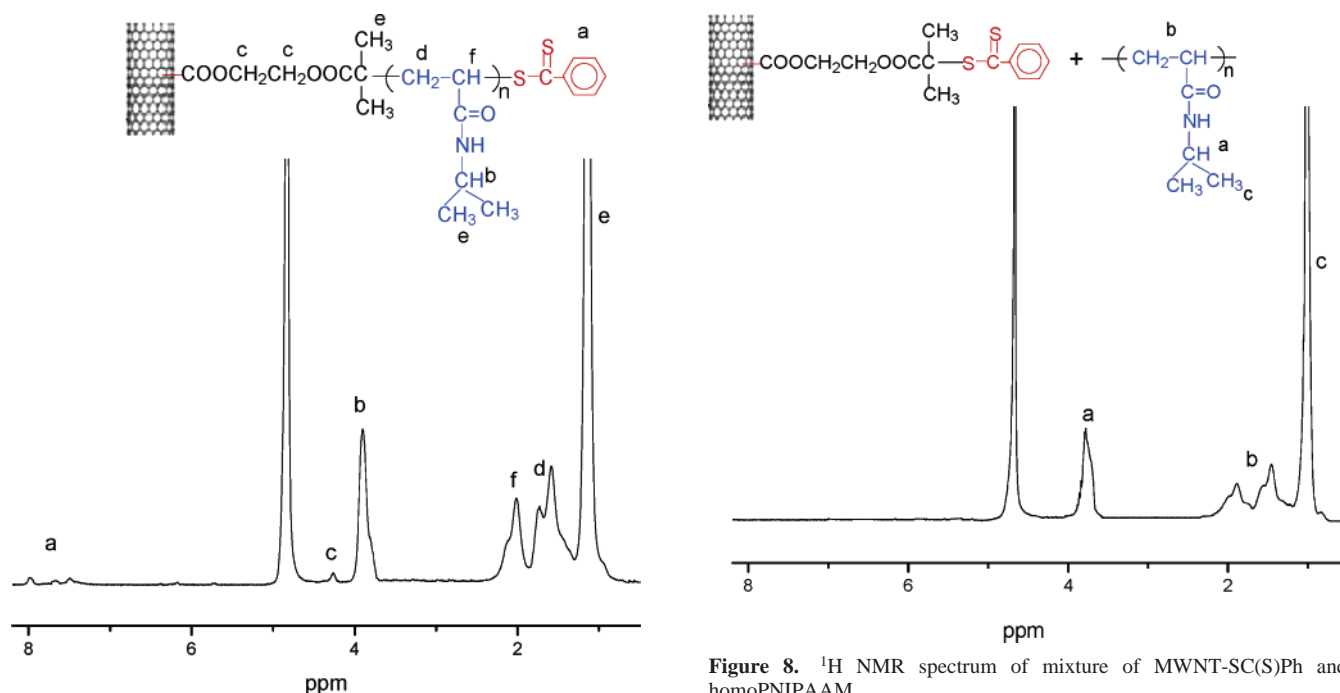
Figure 6. FT-IR spectrum of MWNT-*g*-PNIPAAM.

Figure 7. ¹H NMR spectrum of MWNT-*g*-PNIPAAM.

Figure 8. ¹H NMR spectrum of mixture of MWNT-SC(S)Ph and homoPNIPAAM.

PNIPAAM obtained was much greater than that of the MWNT-SC(S)Ph added, indicating the presence of surface-grown PNIPAAM via RAFT process. The NIPAAM conversion was obtained by ¹H NMR method. Conversion and $\ln([M]_0/[M]_t)$ vs polymerization time were plotted as shown in Figure 3; the $\ln([M]_0/[M]_t)$ exhibited a linear increase of polymerization time. The PNIPAAM chains on MWNT were cleaved from MWNT, and their molecular weights (MWs) and polydispersity indexes (PDIs) were determined on SEC. The molecular weight of PNIPAAM chains on MWNT increased linearly with NIPAAM conversion as shown in Figure 4, indicating that chain length of PNIPAAM on

MWNT is controllable. In addition, SEC analyses of the cleaved PNIPAAM showed the PNIPAAM grafted on MWNT had a narrow molecular weight distribution.

Characterization of MWNT-*g*-PNIPAAM. The pristine MWNT will decompose around 500 °C in the presence of air, and decomposes around 800 °C under nitrogen. The relative amounts of PNIPAAM and RAFT agent functions on MWNT, compared with that of MWNT, were determined from TGA. TGA analyses of MWNT-*g*-PNIPAAM showed one major decomposition in the temperature range 280−450 °C corresponding to surface grown temperature-sensitive polymer on MWNT as shown in Figure 5. The amount of PNIPAAM attached to MWNTs determined by TGA varies
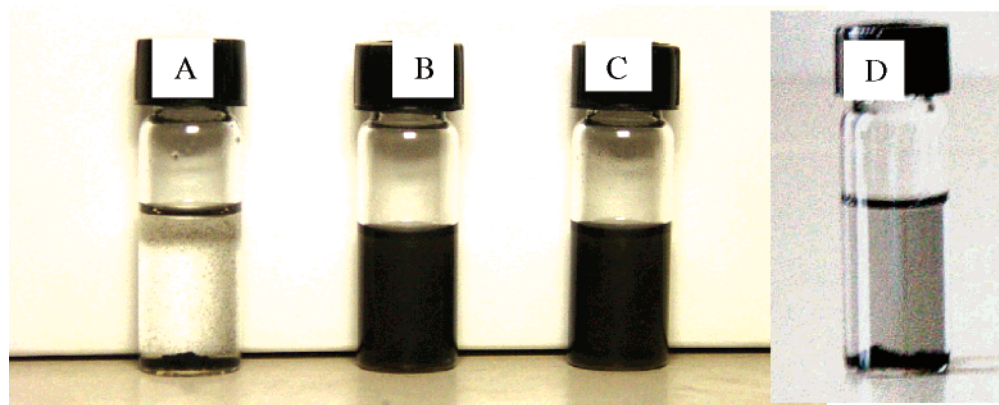
Figure 9. MWNT-SC(S)Ph in water (A), MWNT-*g*-PNIPAAM in THF (B) and water (C), and MWNT-SC(S)Ph (35%) and homoPNIPAAM (65%) in H₂O (D).

from 35 to 87 wt % when polymerization time increased from 9 to 36 h. The FT-IR spectrum of MWNT-*g*-PNIPAAM showed characteristic bands for PNIPAAM (in KBr: C−H at 2970, 1450, and 1366 cm⁻¹; C=O at 1650 cm⁻¹ and N−H at 3300, 1550 cm⁻¹ in Figure 6). The chemical structure of MWNT-*g*-PNIPAAM was also determined from ¹H NMR and is shown in Figure 7. In its ¹H NMR spectrum, the characteristic peaks of PNIPAAM, such as the peak at $\delta = 3.9$ ppm ascribed to methine proton of isopropyl unit, the peak at $\delta = 1.1$ ppm ascribed to methyl protons, and the peak at $\delta = 1.5-2.5$ ppm corresponding to methine and methylene protons in the main chain of PNIPAAM, were clearly found. Moreover, some small peaks originating from RAFT agent functions on MWNT, such as peaks at $\delta = 7.2-8.0$ ppm ascribed to benzene ring protons and the peak at $\delta = 4.2$ ppm ascribed to ester methylene protons, were also found in this ¹H NMR spectrum, which indicates that the RAFT agents on MWNT participated in the polymerization of NIPAAM. For comparison, the ¹H NMR spectrum of mixture MWNT-SC(S)Ph (35%) and homoPNIPAAM (65%) in D₂O was also recorded and is shown in Figure 8. Different from the ¹H NMR spectrum of MWNT-*g*-PNIPAAM, there was no peak originating from RAFT agent functions on MWNT found except the characteristic peaks of PNIPAAM. This difference may result from the units coming form RAFT agent functions on MWNT located at ends of PNIPAAM chain after RAFT polymerization of NIPAAM, which makes these small units soluble in D₂O, and thus the small peaks ascribed to RAFT agent functions on MWNT could be found in the ¹H NMR spectrum of MWNT-*g*-PNIPAAM. While in the mixture of MWNT-SC-(S)Ph and homoPNIPAAM, RAFT agent functions on MWNT have no strong interaction with homoPNIPAAM, the RAFT agent functions on MWNT are insoluble in D₂O, and thus there was no small peak corresponding to RAFT agent functions found in the ¹H NMR spectrum of the mixture. This further verified that PNIPAAM chains were covalently bonded and not adsorbed on MWNT.

Dispersion of RAFT agent functionalized MWNT into an organic solvent and aqueous solution was very difficult even after the carbon nanotubes had been subjected to sonication; sedimentation of MWNT-SC(S)Ph from THF appeared a few minutes after sonication. However, the MWNT-*g*-PNIPAM was soluble in water, THF, and chloroform. Figure 9 shows

the solubility of MWNT-SC(S)Ph in aqueous solution and MWNT-*g*-PNIPAAM in aqueous solution and THF. It is clear that MWNT-SC(S)Ph is insoluble in water, and there was much sedimentation of MWNT-SC(S)Ph at the bottom of a small bottle. However, the MWNT-*g*-PNIPAAM (50 mg) is soluble in water (1.0 mL) and THF (1.0 mL), forming a homogeneous solution; there was no sedimentation observed even after 10 days as shown in Figure 9B and C. For comparison, we attempted to disperse the mixture of MWNT-SC(S)Ph (35%) and homoPNIPAAM (65%) into water, and the result has shown that homoPNIPAAM is a poor dispersant for MWNT-SC(S)Ph, and MWNT-SC(S)Ph precipitated from the solvent after a few hours as shown in Figure 9D. All of the evidence supports solubilization of the MWNT by covalently bound PNIPAAM and not by adsorbed homoPNIPAAM. The TEM image of MWNT-SC(S)Ph showed that the MWNTs were piled up, but the MWNT-*g*-PNIPAAM was dispersed individually (as shown in Figure 10), indicating that original MWNTs can be separated into individual tubes by surface RAFT polymerization of NIPAAM.

Temperature-Responsive Property of the Shell. It is known that the conformation and solubility of PNIPAAM chains in water can change with temperature. At temperatures below the LCST, the intermolecular hydrogen bonding between the PNIPAAM chains and water molecules is predominant; the PNIPAAM chains were of coil-structure and soluble in water. However, at temperatures above the LCST, intramolecular hydrogen bonding between C=O and N−H groups in the PNIPAAM chains results in a compact and collapsed conformation of PNIPAAM chains, which makes it difficult for the PNIPAAM chain to be soluble in water. The MWNT-*g*-PNIPAAM has good solubility in water below the LCST, however, MWNT-*g*-PNIPAAM gradually precipitated from aqueous solution when temperature increased to 35 °C. This results from the fact that at low temperature, the loosely coiled conformation of PNIPAAM chains and intermolecular hydrogen bonding with water molecules leads to MWNT being soluble in water. However, at temperatures above the LCST, intramolecular hydrogen bonding between C=O and N−H groups in the PNIPAAM chain results in a compact and collapsed conformation of PNIPAM chains, which makes it difficult for the hydrophilic C=O and N−H groups to interact with water molecules, and the PNIPAAM chain exhibits hydrophobicity, and the
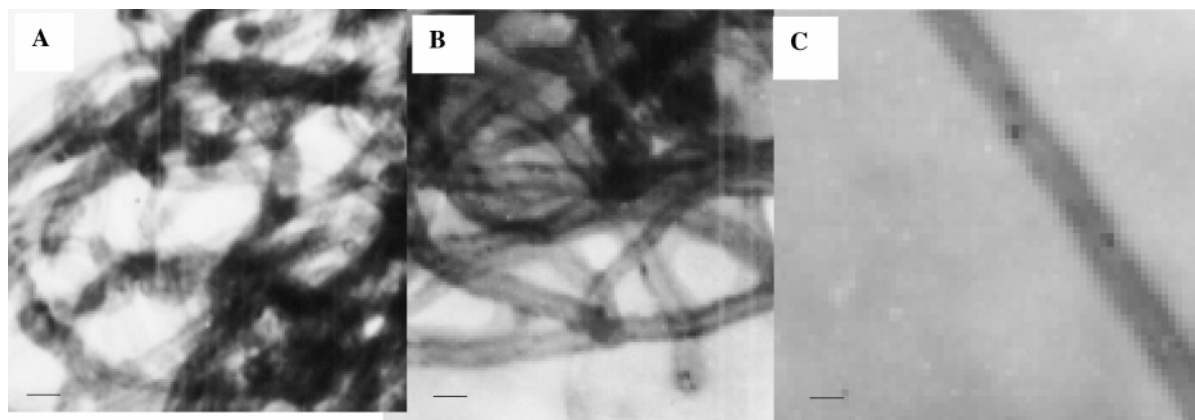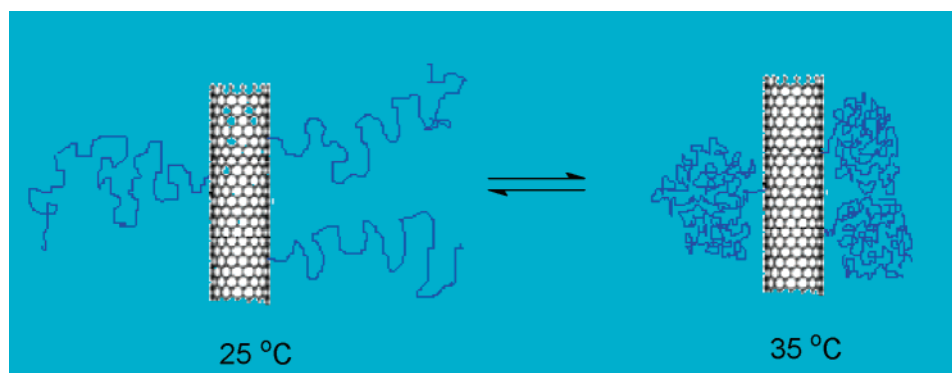
Figure 10. TEM images of pristine MWNT (A), MWNT-SC(S)Ph (B), and MWNT-*g*-PNIPAAM (C) (10 nm).

Scheme 2. Outline for Conformation Changes of PNIPAAM Chains on MWNT

MWNT-*g*-PNIPAAM gradually precipitated from aqueous solution.[44,45] The shell of MWNT-*g*-PNIPAAM responses to temperature reversibly as outlined in Scheme 2. Generally, this response to temperature was determined by the change of R_h by LLS, the transmittance of aqueous solution, NMR method, and phase transition by DSC.[46−48] Due to the darkness of MWNT grafted with PNIPAAM in aqueous solution, the change of transmittance is not clear; R_h change cannot be obtained because PNIPAAM is immoblilized on MWNTs. MWNT-*g*-PNIPAAM is soluble in water, and this phase transition of PNIPAAM chain can be determined by DSC. Figure 11 is the DSC curve: it is clear that the phase transition temperature is about 34 °C, which has shown that reversible switching shell between hydrophilicity and hydrophobicity of MWNT-*g*-PNIPAAM can be intelligently controlled through the external stimuli of temperature.
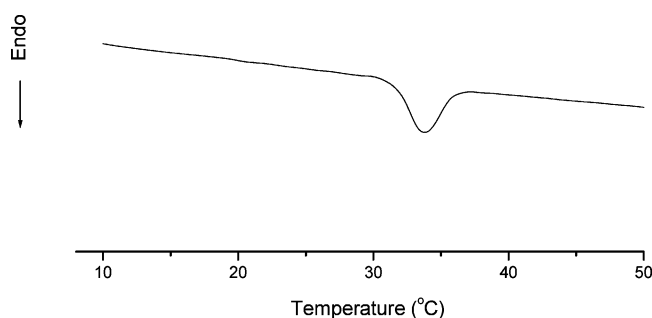

Figure 11. DSC thermogram of MWNT-*g*-PNIPAAM in water at heating rate of 2 °C/min.

Conclusion

Dithiobenzoate has been successfully attached to the surface of MWNT, and water-soluble and temperature-sensitive PNIPAAM chain grew from the surface of MWNTs by surface RAFT polymerization of NIPAAM using dithiobenzoate immobilized on MWNTs as surface chain transfer agent. The PNIPAAM shells of MWNT-*g*-PNIPAAM can respond to temperature. At temperature below LCST, PNIPAM chains were of coil to form an expanded shell at the surface of MWNT; however, PNIPAAM chains collapsed onto the surface of MWNT to form a barrier-like shell when temperature increased to 35 °C. These MWNT-*g*-PNIPAAMs with temperature-sensitive shell should have potential application in "smart" sensor and probes, reusable catalyst, delivery of drug and protein, "smart" separator, and scaffolds to target different tissue. This surface RAFT method can be extended to graft various stimuli-responsive functional polymers (pH or ionic strength) from MWNT to form a pH- or ionic-strength-responsive surface on MWNT; also this method can be employed to graft various functional block copolymers from MWNT.

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