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Fabrication of pH- or Temperature-Responsive Single Wall Carbon Nanotubes Via a Graft From Photopolymerization

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*An ultraviolet light initiated ''graft from'' polymerization method to fabricate polymer-functionalized single wall carbon nanotubes (SWNTs) with pendant pH- and temperature-responsive polymer chains is utilized. The attached polymer chains, formed from methacrylic acid and poly(ethylene glycol) methyl ether methacrylate monomers, are well established for its pH-responsive swelling/deswelling behavior. This special property was utilized here to control the aqueous dispersibility of the carbon nanotubes. Furthermore, poly(*N*-isopropylacrylamide), a temperature-responsive polymer, was utilized in the fabrication of SWNTs whose dispersibility was dependent on solution temperature. The morphology of the polymer-functionalized carbon nanotubes was characterized by scanning electron microscopy (SEM) before and after functionalization. Environmental SEM was used to further characterize the morphology of the functionalized SWNTs. In addition, covalent bonding of the polymer to the carbon nanotube surface was established using Raman and Fourier transform infrared spectroscopic techniques. The physical and chemical properties of the functionalized nanotubes were further characterized by energy-dispersive X-ray spectroscopy, thermogravimetric analysis, and differential scanning calorimetry.* © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 2980–2986, 2012
Keywords: PEGylation, carbon nanotubes, functionalization, ''graft from'', polymerization

Introduction

Carbon nanotubes have been extensively studied for over a decade because of their unique mechanical, electrical, optical, and thermal properties.[1–5] One of the most interesting applications of carbon nanotubes is in the bioanalytical field, where the extremely high surface area-to-volume ratio and the material's stability in aqueous environment make nanotubes a great biomolecular carrier.[6] Applications such as sensitive biosensors and biomolecular probes have already been developed in research laboratories.[7–9]

Since the aqueous dispersibility of pristine carbon nanotubes is poor, methods to improve compatibility with aqueous media are needed. Considerable research attention has been focused on producing dispersible carbon nanotubes,[10–14] especially through the addition of polymers chains.[15–18] The functionalization of carbon nanotubes with polymer chains is an appealing technology since these macromolecules not only help to disperse the carbon nanotubes in solvent, but can also be used to provide functional groups for further functionalization, e.g., to provide sites for bonding to the polymer matrix in nanocomposites.[19–22]

Further improvement on the use of carbon nanotubes in biotechnology and biomedicine may come from adding properties which are stimuli-responsive. In this work, we aim to create materials with switchable dispersibility under various pH and thermal conditions through the grafting of polymer chains with these properties. A novel ultraviolet light initiated ''graft from'' polymerization method was used to fabricate pH-responsive and temperature-responsive single wall carbon nanotubes (SWNTs), where the aqueous dispersibility of the SWNTs was altered by environmental changes.

Poly(methacrylic acid) (PMAA) has been studied extensively, especially in the drug delivery area, because of its well-known pH sensitivity.[23–27] PMAA chains may be either swollen or collapsed in aqueous media depending on the surrounding pH value as a result of the protonation/deprotonation of the carboxyl group. At low pH values (<5), the carboxyl groups are protonated, leading to decreased interaction between the PMAA chains and the water molecules. Conversely, at pH values above the pKa value, the carboxyl groups are deprotonated and charged, leading to (1) stronger interactions with surrounding water molecules and (2) strong interchain electrostatic repulsion.

Copolymerization of poly(ethylene glycol) (PEG) macromonomers—in the form of poly(ethylene glycol) methyl ether methacrylate (PEGMA), for instance—with methacrylic acid monomer leads to an amplified swelling/deswelling response.[28–30] Complexation between the pendant PEG chains and the MAA repeating units occurs when the carboxyl group is protonated (lower pH values), leading to greater deswelling than that seen in the PMAA homopolymer. Consequently, the copolymer formed from MAA and PEGMA monomers is well established for its pH-responsive

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behavior, and this material was used to functionalize carbon nanotubes with controllable aqueous dispersibility.

Poly(*N*-isopropylacrylamide) (PNIPPA) is a polymer also studied extensively in biomedical research because the lower critical solubility temperature (LCST) is near body temperature.[31–33] A sharp hydrophilic/hydrophobic phase transition occurs in aqueous solutions of linear PNIPPA upon the change of surrounding temperature. This property will be utilized in the production of temperature-sensitive polymer-functionalized SWNTs.

Experimental

Materials

Pristine SWNTs (1–2 nm) were purchased from Cheap Tubes (Brattleboro, VT) and were used as received without further treatment. PEGMA macromonomer ($M_n \sim 1100$), methacrylic acid (>98%), *N*-isopropylacrylamide (>99%), and 1-hydroxycyclohexyl phenyl ketone (HCPK, purity $\geq$99%) were purchased from Sigma Aldrich (St. Louis, MO) and all were used as received. Water used in all experiment was purified in an aquaMax ultra purification system (labwater.com, van Nuys, CA) and had a resistivity of 18.2 MΩ/cm.

Fabrication of pH- and temperature-responsive SWNTs

SWNTs (30 mg) were dispersed in 75 mL of a 40:60 (v/v) water: methanol solution and sonicated (Fisher Scientific, 130 W and 40 kHz, Pittsburgh, PA) for 1 h at room temperature. The free radical photoinitiator HCPK was introduced at 1% of the total weight of the solution, which was mildly shaken by a vortex mixer for 10 min to aid in dissolution (Vortex Genie 2, Fisher Scientific, Pittsburgh, PA). The entire 75 mL aliquot of well-dispersed SWNTs solution was divided amongst three Petri dishes and was then stirred at 80 rpm while under UV irradiation. Irradiation of the mixture with ultraviolet light (365 nm, 150 mW/cm^2, IntelliRay 600, UViTron International, West Springfield, MA) was then carried out with direct irradiation of the mixture in a nitrogen atmosphere at room temperature. After 30 min of UV exposure the reaction was stopped. Excess unbound HCPK molecules were removed by centrifugation (Eppendorf, 5810R, Westbury, NY) at 4000*g* and resuspension in water (repeated three times).

To fabricate PMAA-PEGMA-SWNTs, MAA, and PEGMA monomers were introduced in an equal molar ratio to the SWNT solution and polymerization was done using a second 30-min does of UV irradiation. After the polymerization reaction, the suspension was then diluted with water to dissolve any unreacted monomer, and this solution was then removed through centrifugation at 10,000*g*. After three repetitions of centrifugation and resuspension, the functionalized carbon nanotubes were collected on 0.45 μm nylon membrane filters (Whatman, Maidstone, England). These were then washed with DI several times to further remove any weakly adsorbed species. Finally, the resultant pH-responsive SWNTs were dried at 70°C in a vacuum oven (10 kPa) overnight before characterization.

Thermally-responsive materials were fabricated in the same manner, except NIPPA monomer was used in place of the MAA/PEGMA mixtures. All other conditions were identical.

Characterization

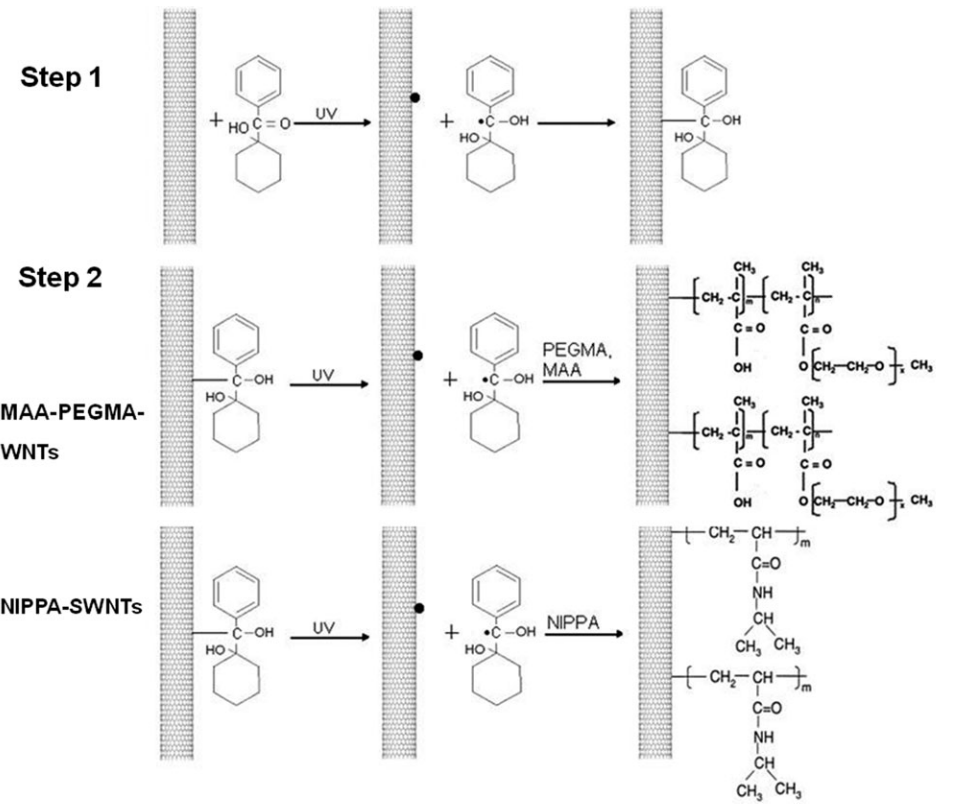
The morphology of the pristine SWNTs was studied by field emission scanning electron microscopy (FE-SEM) on a Hitachi S-4700 (Hitachi, Osaka, Japan). Environmental scanning electron microscopy (ESEM) was recorded on a Quanta FEG-4700 (FEI, Hillsboro, OR) with an accelerating voltage of 30 kV. ESEM was used to investigate the morphology of PMAA-PEGMA-SWNTs and PNIPPA-SWNTs at different pH values and at different temperatures, respectively. Several drops of a suspension containing pristine SWNTs, PMAA-PEGMA-SWNTs, or PNIPPA-SWNTs were sonicated for 20 min before they were stabilized on the aluminum stud for ESEM analysis.

Raman spectroscopy (633 nm, Horiba Jobin YVON, Edison, NJ) was utilized to elucidate the chemical structure of the pristine SWNTs, PMAA-PEGMA-SWNTs, and PNIPPA-SWNTs. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Nicolet 6700, Thermoelectron Corporation, Madison, WI) was used to further characterize the functional groups associated with the pristine and functionalized SWNTs. The spectra were collected from 4000 to 850 cm^{-1}, with a 1 cm^{-1} resolution and a total of 128 scans. Energy-dispersive X-ray spectroscopy (EDS, Helios Nanolab 600, FEI, Hillsboro, OR) analysis was used to investigate the surface elements of the pristine SWNTs, PMAA-PEGMA-SWNTs, and PNIPPA-SWNTs. Low resolution survey scans of carbon and oxygen were taken. Thermogravimetric analysis (TGA, Netzsch, Exton, PA) experiments were carried out under nitrogen using a heating rate of 10°C/min, up to 700°C. Differential scanning calorimetry (DSC) (TA Instruments, New Castle, DE) was used to determine the LCST of the grafted PNIPPA chains of the PNIPPA-SWNTs. A small amount of sample (~10 mg) was loaded on to an aluminum pan with a cover. Experiments were performed on 20 mg of the specimen, heating from room temperature to 50°C at a heating rate of 1°C/min.

Results and Discussion

There are two main methodologies for the covalent attachment of polymeric substances to the surface of carbon nanotubes, commonly defined as "graft to" and "graft from" methods. The former relies on the addition of a previously formed polymer molecule to a functionalized or otherwise prepared nanotube surface. The graft from method is based on the covalent immobilization of an initiator or polymer precursor on the nanotube surface, with a subsequent polymerization reaction occurring in the presence of monomer. In the graft to method, sonochemical treatment is frequently used to introduce reactive sites (typically carboxyl groups) on the SWNT surface. Polymer molecules are then synthesized and grafted to the SWNT surface through various chemical reactions. Steric hindrance from previously attached chains slows further macromolecular addition, a distinct disadvantage of this method. Additionally, the pristine carbon nanotube's surface must be first functionalized to accept polymer grafts, a process which can partially destroy the electrical or mechanical properties.[34]

Alternatively, Mylvaganam et al.[35] noted that conducting a free radical polymerization in the presence of carbon nanotubes led to termination of the propagating species at the nanotube surface. A separation step could then be conducted to remove polymer-functionalized nanotubes from the unbound chains.



Scheme 1. Illustration of the fabrication of pH and temperature-responsive single wall carbon nanotubes.

A graft from method was used here where polymer molecules are synthesized from initiation sites first added to the nanotube surface. We have adopted the method proposed by Ma et al.[36] for the modification of poly(propylene) surfaces and tailored it for use with carbon nanotubes. Irradiation of dissolved photoinitiator leads to dissociation into radical fragments which subsequently attack the nanotube surface. Unbound photoinitiator is then removed by centrifugation or dialysis. Further irradiation leads to cleavage of this newly formed bond and, in the presence of monomer, the creation of a site for polymerization (Scheme 1).

Figure 1 shows the ATR-FTIR spectra of pristine SWNTs, PMAA-PEGMA-SWNTs, and PNIPPA-SWNTs. The pristine SWNTs curve is featureless. From the PMAA-PEGMA-SWNTs spectrum, the peak at 1696 cm^{-1} indicates the C=O double-bond stretching vibration in the carboxylic acid groups of PMAA and the peaks at $\sim$1110 cm^{-1} were attributed to the C—O symmetric stretch of the PEG sidechain. The peak at $\sim$2890 cm^{-1} represents the stretch mode of C—H bond vibration. From the PNIPPA-SWNTs spectrum, the peaks at 3300 cm^{-1} and 1550 cm^{-1} are attributed to the N—H deformation vibration in the amide groups of PNIPPA. The peak at 1650 cm^{-1} represents the C=O double-bond stretching vibration in the amide groups. Also, the peak at 1366 cm^{-1}, attributed to C—H bond vibration associated to the methyl groups in PNIPPA, is observed in the spectrum.

To confirm the importance of the polymerization reaction, a control experiment was conducted where nanotubes were mixed with MAA/PEGMA monomers but no reaction was conducted. After conducting the washing and filtration protocol outlined previously, complete removal of the free macromonomer was indicated by its absence in the ATR-FTIR scans. The ATR-FTIR spectra illustrated the effectiveness of the photoinitiated polymerization reaction and also further reinforced that hypothesis that the PEG-rich chains were covalently bonded to the CNT surface.

Raman spectroscopy was utilized to investigate grafted chain bonding after carbon nanotube functionalization, using an excitation laser with a wavelength of 633 nm (Figure 2). The Raman spectra of pristine SWNTs show typical breathing modes at 190–250 cm^{-1} and tangential modes at 1590 cm^{-1} (G-band). Comparing curves a, b and c in Figure 2, an obvious increase in relative intensity at 1301 cm^{-1} (D-band)

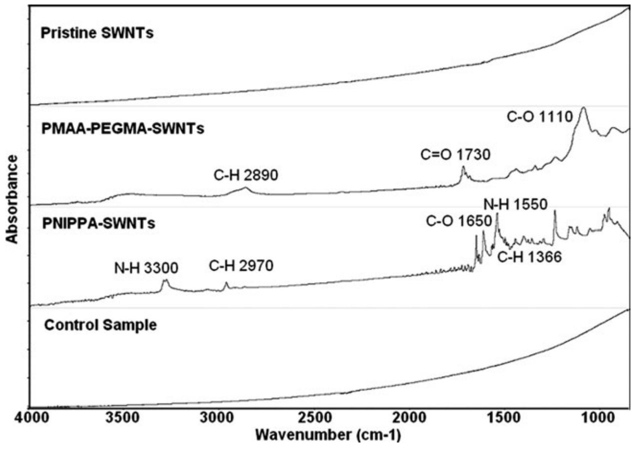


Figure 1. ATR-FTIR spectra of pristine SWNTs, PMAA-PEGMA-SWNTs, and PNIPPA-SWNTs.

Control sample refers to nanotubes incubated in monomer but without photoinitiation.

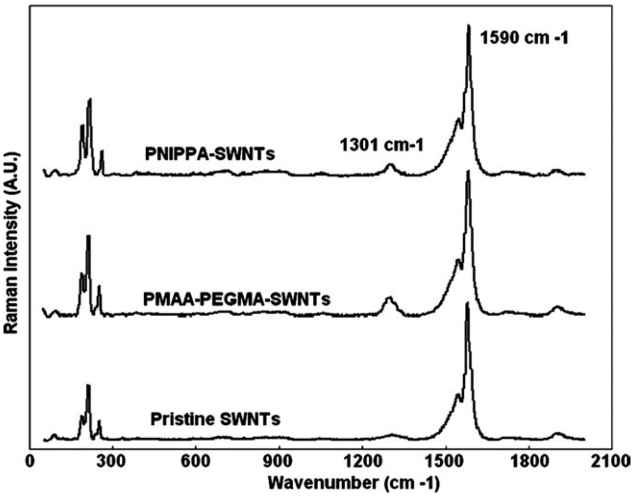


Figure 2. Raman spectra of pristine SWNTs, PMAA-PEGMA-SWNTs, and PNIPPA-SWNTs.

with respect to the G-band can be observed. It is reported that covalent functionalization and subsequent conversion of sp^2 hybridized carbon atoms to sp^3 will disrupt the π—conjugation system, leading to an increase in the D-band signal intensity.[37] The increasing intensity at 1301 cm^{-1} (D-band) after functionalization indicates the formation of sp^3 hybridized carbon atoms, additional evidence that the polymer chains were covalently grafted to the SWNT surface.

Table 1. Binding Energy and Atomic Concentration of Pristine SWNTs, PMAA-PEGMA-SWNTs, and PNIPPA-SWNTs, as Measured by EDS

	Pristine SWNTs		PMAA-PEGMA-SWNTs		PNIPPA-SWNTs	
Element	keV	At%	keV	At%	keV	At%
C	0.284	96.72	0.284	78.16	0.284	75.91
O	0.532	3.28	0.532	21.84	0.532	16.71
N	0.400	0	0.400	0	0.400	7.38

To determine the composition of the grafted polymer chains, EDS analysis was used. The results are shown in Figure 3. Table 1 summarizes the binding energy and the composition of every element in the surface. The major peak component at the binding energy (BE) of about 0.284 keV is assigned to carbon, the minor peak component at the BE of 0.532 keV is attributed to oxygen of the PEG chain and the carbonyl groups in PMAA and PNIPPA. Only trace amounts of oxygen were detected in the pristine carbon nanotube samples, likely from the metal oxide catalysts used in carbon nanotube manufacture. Another peak component at the BE of 0.400 keV is attributed to nitrogen of the amide group in PNIPPA. Compared to pristine SWNTs (atomic oxygen percentage of only 2.75%), the atomic oxygen percentages rose significantly in both PMAA-PEGMA-SWNTs and PNIPPA-SWNTs samples to 21.84% and 16.71%, respectively, after 30 min of polymerization, confirming the presence of polymer. In addition, the existence of nitrogen confirmed the successful introduction of PNIPPA.

The weight of grafted polymer on the nanotube was determined by TGA. In Figure 4, the TGA curves for pristine carbon nanotubes, PMAA-PEGMA-SWNTs, and PNIPPA-SWNTs samples are shown. The pristine carbon nanotubes have good thermal stability and no obvious weight loss was observed below temperatures of 500°C. The PMAA-PEGMA-SWNTs samples started to decompose when the temperature reached 200°C, with drastic decomposition and weight loss between 300 and 400°C. The PNIPPA-SWNTs samples were less stable, with large amounts of decomposition occurring between 100 and 200°C. The percentage weight loss curves of the two polymer-functionalized samples indicate overall weight losses of 45.2 and 55.1% for PMAA-PEGMA-SWNTs and PNIPPA-SWNTs, respectively.

As the pristine carbon nanotubes showed little decomposition below 500°C, the functionalized SWNTs weight loss at that temperature was used to estimate the relative weight of grafted polymer on the surface of SWNTs. The weight loss differences at 500°C were calculated to be 33.2% between the pristine and PMAA-PEGMA-SWNTs samples and 43.1% between the pristine and PNIPPA-SWNTs samples. Such

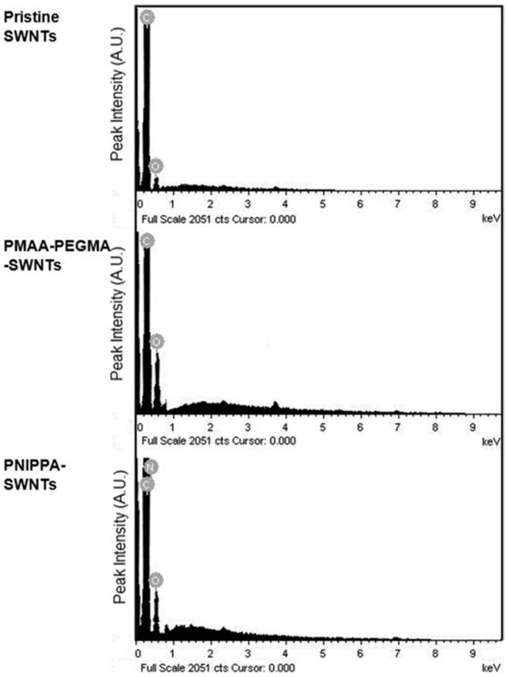


Figure 3. Survey EDS spectra of pristine SWNTs, PMAA-PEGMA-SWNTs, and PNIPPA-SWNTs.

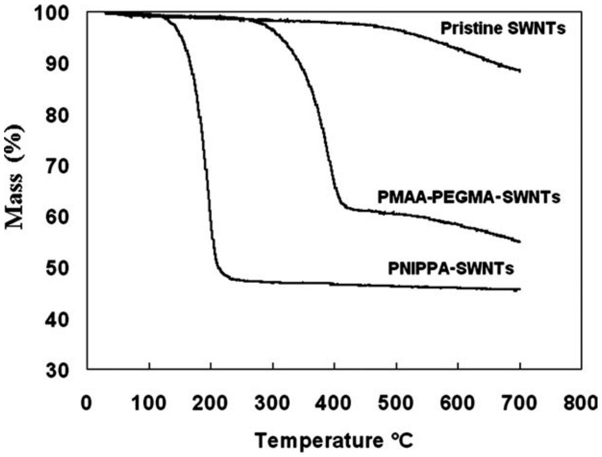


Figure 4. TGA curves of pristine SWNTs, PMAA-PEGMA-SWNTs, and PNIPPA-SWNTs.

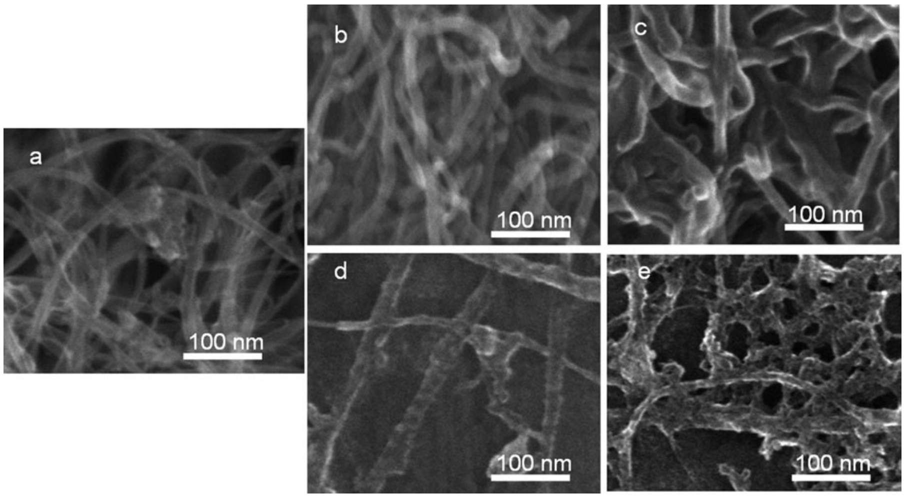


Figure 5. SEM images of (a) pristine SWNTs, (b) PMAA-PEGMA-SWNTs at pH 10, (c) PMAA-PEGMA-SWNTs at pH 4, (d) PNIPPA-SWNTs at room temperature, (e) PNIPPA-SWNTs at 35°C.

high weight loss further confirms the previously shown EDS results and demonstrates this graft from polymerization route was effective, yielding nanomaterials with high levels of polymer grafting.

The SWNTs used in this work were produced by Cheap Tubes and had an average diameter of 2 nm. SEM images of pristine SWNTs, PMAA-PEGMA-SWNTs at different pH values, and PNIPPA-SWNTs at different temperatures are shown in Figure 5. ESEM was used to identify the presence of a polymer layer on the SWNTs samples and also to visualize the response of the grafted polymer chains to changes in pH or temperature. Images were taken of pristine SWNTs, PMAA-PEGMA-SWNTs samples at pH 4 and pH 10, and PNIPPA-SWNTs at room temperature (22°C) and 35°C. The pristine SWNT is clearly observed in Figure 5a, and the surface is clean. The average diameter of the pristine SWNTs was determined to be 8 nm, indicating the nanotubes were not individually dispersed and that small nanotube bundles may exist. Figure 5b shows a PMAA-PEGMA-SWNTs sample in a pH 10 solution. The average diameter of the nanotubes has increased to 15 nm, indicating the existence of a polymer layer on the surface of the SWNTs. In addition, the well-dispersed nature of this sample shows the utility of polymer functionalization. When the pH of the solution was adjusted to a value of 4 through the addition of 1.0 M HCl, relatively coarse and more aggregated nanotubes resulted, as can be seen in Figure 5c. Figure 5d shows PNIPPA-SWNTs at room temperature. The sheathed structure can be clearly observed, attributed to coverage by covalently attached PNIPPA chains. At room temperature, which is below the LCST, the hydrophilic PNIPPA chains help to disperse the PNIPPA-SWNTs in aqueous solution. When the temperature increased to 35°C, a phase transition occurs, with a resultant collapse of the grafted PNIPPA chains. As a result, the PNIPPA-SWNTs at this temperature were more aggregated, with an average diameter of 30 nm.

The stability of the nanotube's dispersibility and propensity to aggregate was studied at different pH values. The pH-responsive aqueous dispersibility of the functionalized nanomaterials is shown in Figure 6. Three different pH values—4, 7, and 10—were chosen. Each change of pH was followed by 10 min of sonication. First, the PMAA-PEGMA-SWNTs were dispersed in solution at a pH of 10. After 10 min of sonication, a dark homogenous solution was formed. No noticeable change in dispersibility was observed when the solution's pH value was adjusted to 7 though the dropwise addition of 1.0 M HCl. However, when the pH value was adjusted to 4, the dispersion became unstable and the PMAA-PEGMA-SWNTs soon precipitated out of solution. By adjusting the pH back to 7 through gradually addition of 1.0 M NaOH, the dark homogeneous solution was recovered. As shown in Scheme 2, at low pH (<5.6), the carboxyl groups are protonated, leading to a collapse of the PMAA chains due to intramolecular hydrogen bonding. This collapsed structure makes the SWNTs very difficult to disperse in aqueous solution. At higher pH values, deprotonation occurs, leading to strong inter-chain repulsion and to enhanced interaction between the chains and the surrounding aqueous environment.

The temperature-responsive behavior of the PNIPPA-SWNTs in solution was tested by placing ~8 mL of the solution (in a 20 mL glass bottles) into a water bath which was preheated 40°C for 2 min and then cooling down to

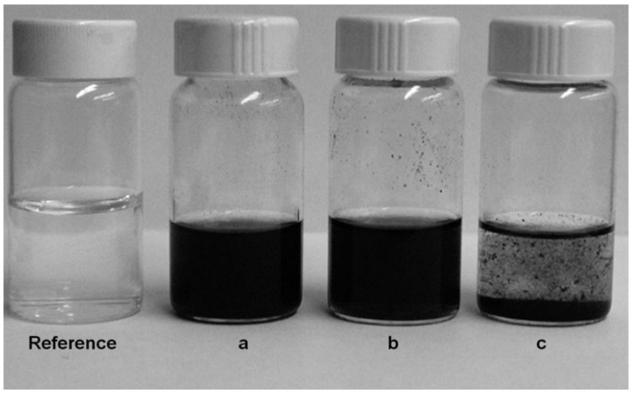
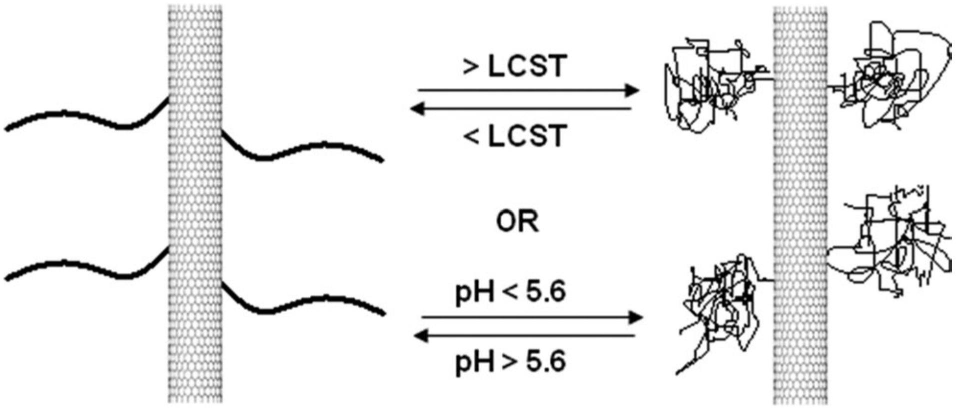


Figure 6. Photographs of pH-responsive nanomaterials dispersed in aqueous solution at room temperature.

Shown are reference vial (water only) and dispersions containing PMAA-PEGMA-SWNTs at: (a) pH = 10, (b) pH = 7, and (c) pH = 4.



Scheme 2. Illustration of the conformational changes of grafted PMAA and PNIPPA chains upon pH or temperature manipulation.

room temperature. As shown in Figure 7, at room temperature the PNIPPA-SWNTs were well dispersed and the resultant mixture was homogeneous. However, after heating for the short (2 min) period, the PNIPPA-SWNTs precipitated from the aqueous solution rapidly. When the solution was returned to room temperature, a homogenous solution was recovered with the help of 2 min sonication. Sonication of the solution at 40°C, however, did not result in the formation of a homogenous solution.

PNIPPA is a polymer studied extensively in biomedical research because the LCST is near body temperature.[31–33] A sharp phase transition occurs in aqueous solutions of linear PNIPPA upon the change of surrounding temperature. When the temperature is lower than LCST, the C=O and N—H bonds in PNIPPA will form intermolecular hydrogen bonds with water, and the PNIPPA molecules are in a hydrophilic, loosely coiled structure. SWNTs functionalized with PNIPPA correspondingly have higher dispersibility under these conditions. However, at temperatures above the LCST, C=O and N—H groups form intramolecular hydrogen bonds, leading to the formation of a collapsed state and precipitation of PNIPPA-SWNTs out of the aqueous solution. The pH- and temperature-response behavior is illustrated in Scheme 2.

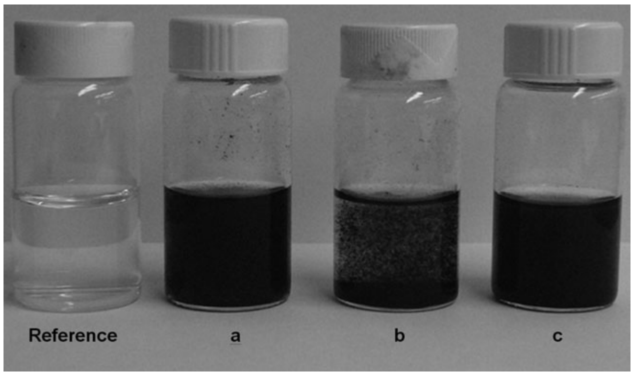


Figure 7. Photographs of temperature-responsive nanomaterials dispersed in aqueous solution.

Reference material (water only) and dispersions: (a) at room temperature, (b) at 40°C, and (c) a sample cooled from 40°C back to room temperature.

DSC was used to study the hydrophilic/hydrophobic phase transition of PNIPPA functionalized SWNTs. It can be clearly seen in Figure 8 that the hydrophilic/hydrophobic phase transition temperature is around the expected LCST of 32°C.

Conclusions

In this work, a novel UV-initiated graft from polymerization method for the fabrication of pH- or temperature-responsive SWNTs was demonstrated. The dispersibility of the functionalized SWNTs could be switched on/off through manipulation of the solution pH value or temperature. This technique allowed for carbon nanotube modification without harsh oxidative treatment. The demonstrated technique features grafted structures secured by stable C—C bonds, a significant advantage over potentially hydrolysable linkages introduced in other treatments. The switchable dispersibility could be used in advanced materials for biomedical purposes. Also, this technique provides a means for the highly dispersible nanomaterial to be easily reclaimed from aqueous solution, which is environmentally beneficial.

Acknowledgments

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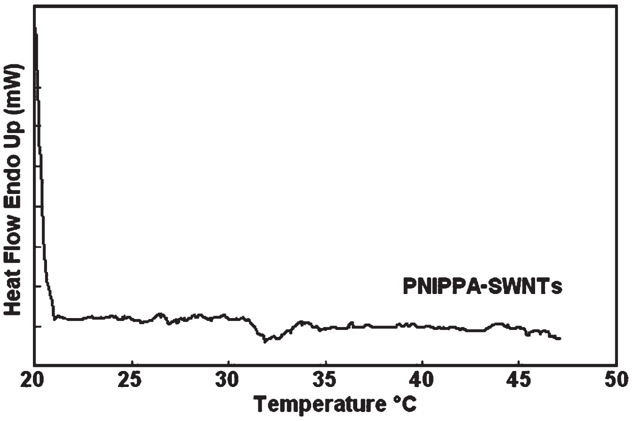

Figure 8. DSC curve of PNIPPA-SWNTs in water

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