Modification of Multiwall Carbon Nanotubes with Initiators and Macroinitiators of Atom Transfer Radical Polymerization

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ABSTRACT: Functionalization on carbon nanotube (CNT) was performed through the addition reaction between the initiators of atom transfer radical polymerization (ATRP) and CNT. The ATRP initiating groups transferred to the CNT surface with this reaction. The modified CNT then served as an ATRP macroinitiator for further modification. Both linear poly(styrene) and V-shaped poly(styrene-*b*-*N*-isopropylacrylamide) block copolymers were therefore covalently bound to the CNT surface. Characterization on the functionalized CNTs was performed with FTIR, Raman spectroscopy, and an X-ray photoelectron spectrophotometer (XPS). The functionalized CNTs exhibited good solubility in organic solvents. In addition, amphiphilic and temperature-responsive properties were observed with the CNTs functionalized with poly(styrene-*b*-*N*-isopropylacrylamide).

Introduction

Covalent surface modification and functionalization of carbon nanotubes (CNTs) derive properties differing from the crude materials.[1−4] The most utilized method to modify CNTs is acid treatment, in which CNTs are treated with concentrated sulfuric acid and nitric acid to cut the CNTs and simultaneously to incorporate carboxylic acid groups to the CNT surfaces.[5,6] Further modification can be done on the incorporated carboxylic acid groups.[7−15] To avoid cutting CNTs in modification, other approaches involving the reactions of the delocalized π electrons of CNT surfaces to modify CNTs were reported.[2,16−18] The active species for the CNT modification reactions include carbenes, nitrenes, azides, and dienes. The addition reactions between free radicals and the π-bonds of CNT surfaces were also reported.[19,20] The radicals can be generated from diazonium salts and peroxides. Besides incorporation of organic moieties to CNT surfaces, preparation of CNTs with covalently tethered polymer chains, especially well-defined polymer architectures, is of interest.[21−24]

Well-defined polymer chains on CNT surfaces can be built up with atom transfer radical polymerization (ATRP).[12,13,24−29] The general routes include steps of (a) CNT surface functionalization, (b) incorporation of ATRP-initiating groups to CNT surfaces via organic reactions, and (c) surface-initiating ATRP using various monomers. Linear homopolymers, block copolymers, and hyperbranched polymers are incorporated onto CNT surfaces through this method. Polymer chains possessing reactive groups, which are reactive toward CNT surfaces, can also be incorporated onto CNT surfaces via the "grafting-to" approach. One example is use of azide-capped poly(styrene) to prepare poly(styrene)-functionalized CNTs.[30,31] However, because radicals are reactive toward CNT surfaces, the growing chain ends of radical polymerization can react onto CNT surfaces to form polymer-functionalized CNTs. Similar results were also reported to controlled radical polymerization. The growing chain ends in the nitroxide-mediated radical polymerization showed reactivity toward CNT surfaces.[32,33]

In this work, we report the attempts to functionalize CNTs with the active species of ATRP. To the best of our knowledge, this CNT functionalization approach has not been reported, although ATRP growing chain ends have shown reactivity toward C_{60} via radical addition reactions.[34] One interesting result is that, after the addition reaction between the ATRP growing species and CNT surfaces, the ATRP active species transfer to CNT surfaces. The modified CNTs could therefore serve as ATRP macroinitiators for further ATRP initiated from the CNT surfaces. Other polymer chains were consequently incorporated to CNT surfaces. Under this modification method, CNTs possessing both poly(styrene) (PS) and poly(*N*-isopropylacrylamide) (PNIPAAm) chains were obtained. The modified CNTs exhibited amphiphilic properties and temperature-responsive behaviors. Therefore, the reported modification route provides a convenient way to incorporate different polymer chains to CNT surfaces and to extend the scope of building up polymer architectures on CNT surfaces.

Experimental Section

Materials. Multiwalled carbon nanotube (MWNT) supplied by the CNT Co., Ltd., Incheon, Korea, was used as received. 1-Bromoethylbenzene (BEB, Tokyo Chem. Ind., purity >95%), 1,1,4,7,7-pentamethyldielthylenetriamine (PMDETA, Aldrich, 99% in purity), copper(I) bromide (CuBr, Aldrich, 99.999% in purity), 2,2′-bipyridyl (Aldrich, 99% in purity), and *N*-isopropylacrylamide (NIPAAm, Aldrich, 97% in purity) were used as received. Styrene was purchased from Acros Chem. Co. and was distilled out under reduced pressure prior to use. Tetrahydrofuran (THF), *N*-methyl-2-pyrolidinone (NMP), and diphenylether (TEDIA Chem. Co.) were used as solvents in reactions.

Characterization. Raman spectra were obtained using a Renishaw InVia Raman spectrometer employing a He−Ne laser of 1 mW radiating on the sample operating at 632.8 nm. FTIR-ATR spectra were obtained with a Perkin-Elmer Spectrum One FTIR equipped with a multiple internal reflectance apparatus and a ZnSe prism as an internal reflection element. X-ray photoelectron spectroscopy (XPS) analysis was conducted using a VG MICROTECH MT-500 ESCA (British) using a Mg Kα line as a radiation source. The background pressure in the analytical chamber was 1.0×10^{-5} Pa. The molecular weights of polymers were measured with gel permeation chromatography (GPC) composed of a LAB-Alliance Series III pump, an RI 2000 refractive index detector, and a PLgel Mixed D column with poly(styrene) gel particles of 5 μm in diameter as stationary phase. The elution was performed using

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THF with a flow rate of 1.0 mL/min at 40 °C. Mono-dispersed styrene samples were used as standards for molecular weight calibration.

Thermogravimetric analysis (TGA) was performed with an instrument from Thermal Analysis Incorporation (TA-TGA 2050) at a heating rate of 10 °C/min under nitrogen atmosphere. The glass transition temperatures of prepared materials were measured with a differential scanning calorimeter (DSC, TA-DSC Q100) at a heating rate of 20 °C/min. Evolved gases analysis was performed with collecting the evolved gases from a TGA (Perkin-Elmer TGA 7 with a heating rate of 10 °C/min under a helium gas flow of 100 mL/min) by an automatic thermal desorption instrument (Perkin-Elmer ATD 400). The collected gases were then transferred to a hyphenated gas chromatography−mass spectrometer (GC−MS, Clarus 500 GC-Clarus 500 MASS with electron ionization, 120 V). The desorption was performed at 250 °C with a helium flow of 30 sccm. The heating program for the GC analysis is from 0 °C (inlet temperature) to 250 °C at a heating rate of 10 °C/min, then remaining isothermal at 250 °C until the analysis is completed.

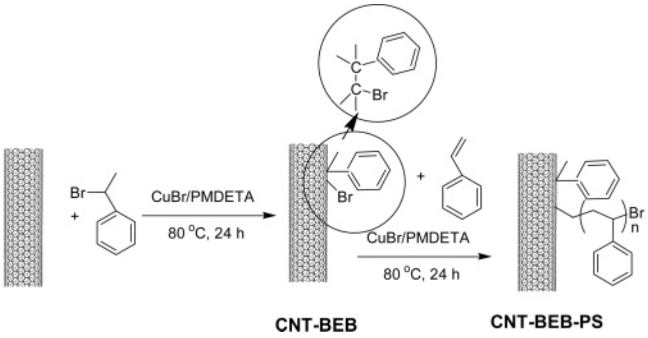
Preparation of Poly(styrene) from ATRP. ATRP initiator end-capped poly(styrene) (PS-Br) was prepared from ATRP polymerization. Styrene (10.4 g, 100 mmol), CuBr (0.14 g, 1.0 mmol), and 2,2′-dipyridyl (0.468 g, 3 mmol) were charged in a 20 mL round-bottom flask. After the mixture was purged with dry argon for 15 min, BEB (0.185 g, 1.0 mmol) was added into the reaction system. The reaction system was degassed three times and then reacted at 80 °C for 24 h. The reaction mixture was diluted with THF (20 mL). PS-Br was obtained with precipitation from excess methanol and purified by a repeated dissolution−precipitation process three times. The product yield is 80%. The number-average molecular weight (M_n) and the polydispersity index (PDI) of PS-Br measured with GPC are 7300 g/mol and 1.2, respectively.

Preparation of CNT-BEB. MWNT (0.3 g), CuBr (0.2 mmol, 0.03 g), PMDETA (0.35 mmol, 0.06 g), and 8 mL of *N*-methyl-2-pyrolidinone (NMP) were charged into a 20 mL reactor. After the mixture was purged with dry argon for 15 min, BEB (3.8 mmol, 0.7 g) was added into the reaction system. The reaction system was degassed three times and then reacted at 80 °C for 24 h. The reaction mixture was poured into excess THF. CNTs were collected by filtration, washed with THF and hot water several times to remove the physically adsorbed compounds, and then dried under vacuum to give the product of CNT-BEB (0.41 g). The ratio of BEB in CNT-BEB is about 13 wt % from TGA measurement at 400 °C. FTIR (KBr, cm^{-1}): 2957, 2921, 1499, 696.

Preparation of CNT-BEB-PS (PS-Grafted CNT from Grafting-From Method). Styrene (0.5 g, 4.8 mmol), CuBr (0.047 g, 0.33 mmol), PMDETA (0.056 g, 0.33 mmol), and 3 mL of diphenylether were charged into a 10 mL reactor. After the mixture was purged with dry argon for 15 min, CNT-BEB (0.15 g) was added into the reaction system. The reaction system was degassed three times and then reacted at 80 °C for 24 h. The reaction mixture was poured into excess THF. CNTs were collected by filtration, washed with THF and hot water several times to remove the physically adsorbed compounds, and then dried under vacuum to give the product of CNT-BEB-PS (0.21 g). FTIR (KBr, cm^{-1}): 2957, 2921, 1525, 1499, 696. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.3−7.5 ppm (aromatic protons), δ 1.8 ppm (−C*H*−), δ 1.4 ppm (−CH_2−).

Preparation of CNT-PS (PS-Grafted CNT from Grafting-To Method). MWNT (0.2 g), CuBr (0.047 g, 0.33 mmol), 2,2′-bipyridyl (0.16 g, 1.0 mmol), and 3 mL of NMP were charged into a 10 mL reactor. After the mixture was purged with dry argon for 15 min, PS-Br (2.0 g) was added into the reaction system. The reaction system was degassed three times and then reacted at 80 °C for 24 h. The reaction mixture was poured into excess THF. CNTs were collected by filtration, washed with THF and hot water several times to remove the physically adsorbed compounds, and then dried under vacuum to give the product of CNT-PS (0.24 g). FTIR (KBr, cm^{-1}): 2926, 1520, 700. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.5−7.3 ppm (aromatic protons), δ 1.8 ppm (−C*H*−), δ 1.4 ppm (−CH_2−).

Scheme 1. Surface Functionalization of Carbon Nanotube (CNT) with Atom Transfer Radical Polymerization (ATRP) Initiators and Surface-Initiated ARTP of Styrene[a]



[a] CuBr and 1,1,4,7,7-pentamethyldielthylenetriamine (PMDETA) were used as a catalyst and a ligand, respectively.

Preparation of CNT-PS/PNIPAAm (PS-*b*-PNIPAAm-Grafted CNT from Sequential Polymerization Method). NIPAAm (2.0 g, 17.7 mmol), CuBr (0.01 g, 0.07 mmol), PMDETA (0.03 g, 0.18 mmol), and 3 mL of distilled water were charged into a 10 mL reactor. After the mixture was purged with dry argon for 15 min, CNT-PS (0.1 g) was added into the reaction system. The reaction system was degassed three times and then reacted at 80 °C for 24 h. The reaction mixture was poured into excess distilled water. CNTs were collected by filtration, washed with THF and hot water several times to remove the physically adsorbed compounds, and then dried under vacuum to give the product of CNT-PS/PNIPAAm (0.13 g). FTIR (KBr, cm^{-1}): 3372, 2926, 2861, 1722, 1603, 1520, 1499, 700.

Results and Discussion

Reactions between ATRP Initiators and CNTs. The initiating reaction of ATRP is carried out by the reaction between the carbon radicals formed from the initiators and the −C═C− bond of the monomers. Besides the addition reaction between the initiator and the monomer molecules, the halide atom of the initiator also transfers to the monomer to form a new active group for the further propagating reaction. The unsaturated linkages on CNT surfaces are reactive toward radicals. Therefore, the initiating species of ATRP should be reactive toward CNT surfaces to perform the above-mentioned addition and halide atom transfer reactions. As shown in Scheme 1, with uses of CuBr as a catalyst and PMDETA as a ligand, BEB, which is an ATRP initiator, is covalently incorporated onto CNT surfaces. The bromide atoms also transfer to the CNT surfaces after the reaction. Further reactions between the C−Br groups and another nanotube are inhibited due to steric hindrance. The BEB groups covalently bound to CNT were observed in the FTIR spectrum of CNT-BEB with the absorption peaks at about 3010 (C−H in aromatic ring), 1499 (aromatic ring), and 665 (C−Br) cm^{-1} (Figure 1a). The Br atoms transferring from BEB to CNT surfaces were also observed in the XPS spectrum of CNT-BEB with the Br$_{3d}$ absorption at about 68 eV (Figure 1b). In addition, the performance of CNT side-wall functionalization was also examined with Raman spectroscopic analysis (exciting at 633 nm) (Figure 1c). The signals at 1315 and 1590 cm^{-1} represent the disorder sp^3 mode (D band) and the tangential mode (G band) of CNTs, respectively.[11] The intensity ratio of D band over G band (D/G ratio) for the unmodified CNT was about 0.998, which shows an increase to 1.334 with BEB functionalization. This D/G ratio change indicates that some sp^2 hybridized carbons in CNTs convert to sp^3 hybridization after BEB functionalization, demonstrating the success of bonding BEB to CNT side walls. The presence of BEB moiety in CNT-BEB is further character-

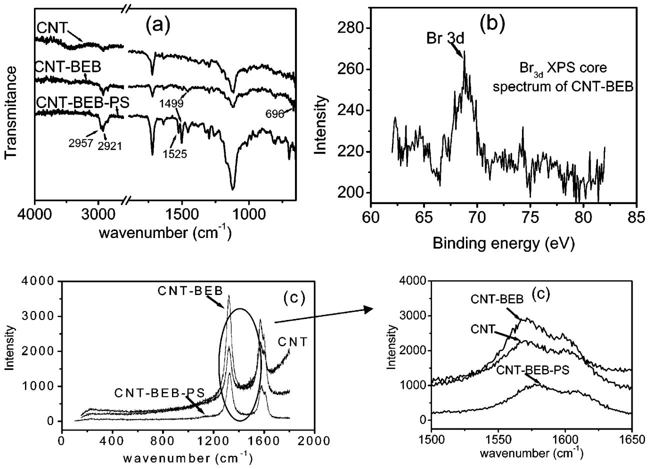


Figure 1. Characterizations on carbon nanotubes functionalized with 1-bromoethylbenzene (CNT-BEB) and poly(styrene) (CNT-PS) with (a) FTIR, (b) X-ray photoelectron spectroscopy (XPS, CNT-BEB only), and (c) Raman spectroscopy.

ized by an evolved gas analysis on the degradation products of CNT-BEB. The gaseous products collected from the sample degradations were analyzed by GC−MS. 1-Bromoethylbenzene was found as one of the major products in CNT-BEB degradation. Because the physically absorbed BEB on CNT was washed out with THF in preparation, the results from evolved gas analysis demonstrate that BEB was covalently bonded on CNT.

Surface-Initiating Polymerization of Styrene from CNT-BEB. The above results demonstrate that surface functionalization of CNTs could be performed with the active species of ATRP, with in situ atom transfer to CNT surfaces and incorporation of ATRP-initiating species on CNT surfaces. The modified CNTs then serve as macroinitiators to perform the surface-initiating ATRP from CNT surfaces. With uses of styrene as a monomer (Scheme 1), polystyrene-tethered CNT (CNT-BEB-PS) was prepared from the surface-initiating ATRP from CNT-BEB. The grafted poly(styrene) (PS) chains of CNT-BEB-PS were characterized with the absorptions at around 2800−2850 cm^{-1} (C−H in $-CH_2-CH-$) and 1499 cm^{-1} (phenyl group) in its FTIR spectrum (Figure 1a). Graft of PS also results in a significant decrease in the intensity of the C−Br absorption at 665 cm^{-1}. Moreover, the D/G band ratio of CNT-BEB-PS read from its Raman spectrum is 1.363 (Figure 1c), which is similar to that of CNT-BEB. The change in D/G band ratio indicates that the surface-initiating ATRP of styrene did not alter the carbon hybridization status of CNTs. On the other hand, the absorption peaks of the diameter-dependent radial breathing mode (at about 180−260 cm^{-1}) and the tangential mode (at about 1590 cm^{-1}) shifted to low frequency (Figure 1c), indicating the increase in the nanotube diameters with PS-grafting. The presence of PS chains on CNT-BEB-PS is also demonstrated by the evolved gas analysis on its degradation products, in which styrene was found as the major component.

To confirm that the formation of CNT-BEB-PS is only from the BEB bound on the CNT surfaces, a control experiment was also done using pristine CNTs to replace CNT-BEB in the PS grafting system.[26] After 24 h, the collected CNTs were applied to TGA measurement. No major weight loss was observed in the tests. The results demonstrate that BEB was successfully incorporated onto CNT surfaces and the ability of the anchored BEB to serve as initiating sites for surface-initiating ATRP.

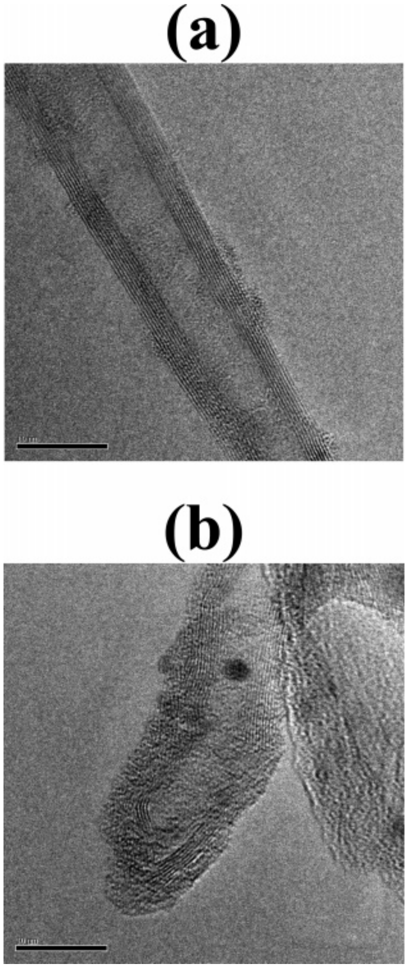


Figure 2. High-resolution transmission electron microscopy (HR-TEM) micrographs of (a) unmodified carbon nanotube and (b) poly(styrene) grafted carbon nanotube (CNT-BEB-PS) from surface-initiating atom transfer radical polymerization.

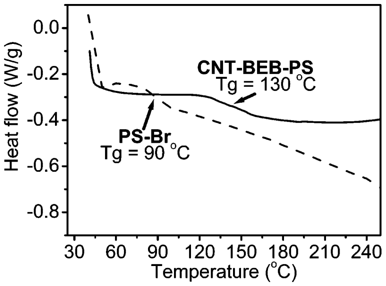


Figure 3. Differential scanning calorimetric thermograms of poly(styrene) (PS-Br) and poly(styrene) grafted carbon nanotube (CNT-BEB-PS).

The weight fractions of organic moieties of the modified CNTs were measured with TGA (figures shown in the Supporting Information), and the obtained values are 13 and 42 wt % for CNT-BEB and CNT-BEB-PS, respectively. The structure of the PS-functionalized CNTs was observed with HR-TEM (Figure 2). The diameters and walls of the crude CNTs were observed. Figure 2b displays the images of CNT-BEB-PS, which exhibits a polymer layer with a thickness of about 2.5−3.0 nm. The polystyrene layer fully covered the CNT surface. Moreover, CNT-BEB-PS exhibited a glass transition temperature of about 130 °C (Figure 3), which is due to the presence of PS chains. It is noteworthy that the T_g of CNT-BEB-PS is higher than that measured with poly(styrene) (PS-Br). This increase in T_g supports that the polystyrene chains are covalently bound to the CNT surface. Surface functionalization on CNTs also dramatically alters their solubility in organic solvents. Unmodified CNT cannot be homogeneously dispersed in organic

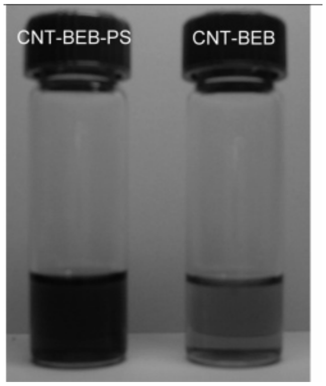
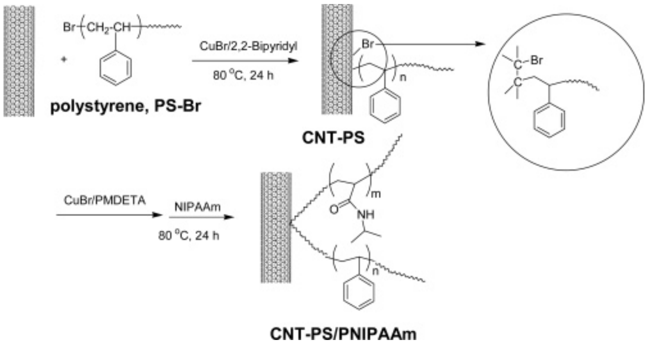


Figure 4. Solubility of modified carbon nanotubes in tetrahydrofuran (THF) after standing for 2 months. The testing samples are 1-bromoethylbenzene (BEB)-modified carbon nanotube (CNT-BEB, right) and poly(styrene) grafted carbon nanotube (CNT-BEB-PS, left).

Scheme 2. Incorporation of Amphiphilic V-Shaped Poly(styrene)-*b*-poly(*N*-isopropylacrylamide) (PS-PNIPAAm) Polymers onto Carbon Nanotube Surface through Sequential "Grafting-To" and "Grafting-From" Techniques[a]



[a] PMDETA: 1,1,4,7,7-pentamethyldielthylenetriamine.

solvents. On the other hand, CNT-BEB-PS can be homogeneously dispersed in THF, and the dispersed CNTs did not sediment in 2 months (Figure 4). The high solubility of CNT-BEB-PS is attributed to the presence of poly(styrene) chains bound to CNT surfaces.

Buildup of Polymer Architectures to CNT Surfaces through Sequential "Grafting-To" and "Grafting-From" Approach. Polymer chains prepared from ATRP method naturally possess active species of ATRP at chain ends, which is demonstrated to be reactive toward CNT surfaces. This reaction therefore can be a simple approach to polymer-functionalized CNTs by the "grafting-to" method. Here, a poly(styrene) (PS-Br) from ATRP (number-average molecular weight of 7300 g/mol and polydispersity index of 1.2) was utilized in the preparation of PS-functionalized CNTs (Scheme 2). In this reaction, the bromine atoms at PS-Br chain ends transfer to CNT surfaces to form tertiary C−Br groups on the PS-grafted CNTs (CNT-PS) surfaces. The tertiary C−Br groups then serve as ATRP initiators. In this work, surface-initiating ATRP from CNT-PS surfaces was performed with uses of NIPAAm as a monomer to incorporate poly-NIPAAm chains onto CNT-PS surfaces. Through the sequential "grafting-to" and "grafting-from" method, V-shaped polymer brushes, in which one arm is PS and the other arm is PNIPAAm, are bound to CNT surfaces (CNT-PS/PNIPAAm).

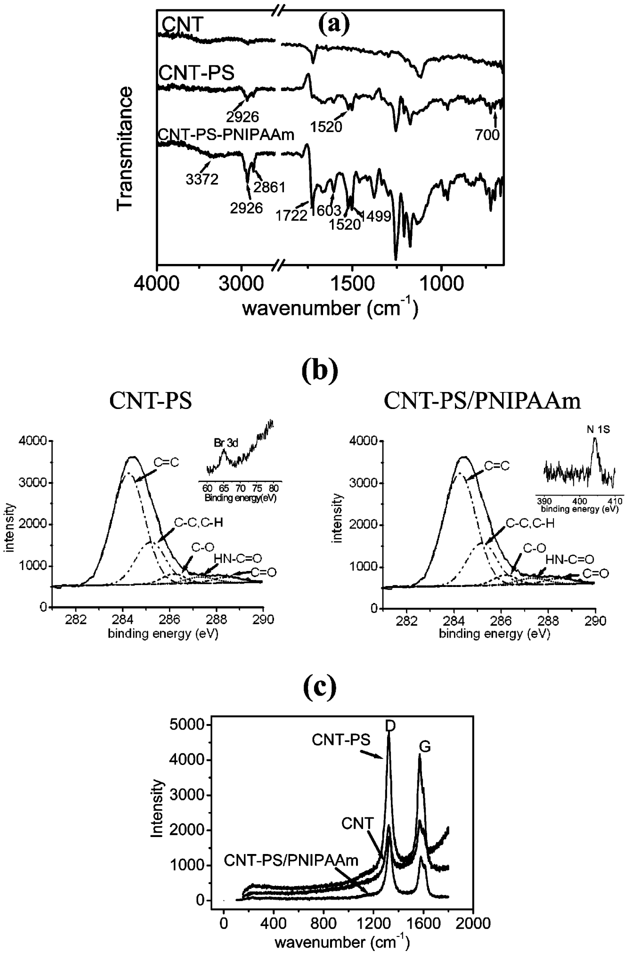


Figure 5. Characterizations on V-shaped poly(styrene)-*b*-poly(*N*-isopropylacrylamide)-modified CNT (CNT-PS/PNIPAAm) with (a) FTIR, (b) X-ray photoelectron spectroscopy, and (c) Raman spectroscopy.

The presence of PS and PNIPAAm chains in CNT-PS/PNIPAAm was characterized by FTIR and XPS (Figure 5). In addition to absorption peaks arising from the grafted poly(styrene) (PS) chains, CNT-PS/PNIPAAm was also characterized with the absorptions at around 1721 cm^{-1} (C═O in PNIPAAm chains) and 3372 cm^{-1} (N−H in PNIPAAm chains) in its FTIR spectrum. The PS chains were observed with an intensity increase in the C−H absorption peak in the CNT−PS C_{1s} core shell spectrum. The PNIPAAm structure was confirmed with the appearance of the absorption peaks of C−N and C═O in the C_{1s} core shell spectrum and the appearance of the absorption peak in the N_{1s} core shell spectrum. The CNT sidewall functionalization status was also examined with Raman spectra from exciting at 633 nm (Figure 5c). The D/G band ratio for the unmodified CNT was about 0.998. After functionalization with PS-Br, the D/G band ratio increased to 1.136 observed with CNT-PS. This change in D/G band ratio indicates that some sp^2 hybridized carbons in CNTs were converted to sp^3 hybridization after PS-Br functionalization and supports that PS chains have been successfully bonded to CNT side walls through the reaction. On the other hand, the absorption peaks of the diameter-dependent tangential mode of CNT at about 1590 cm^{-1} exhibited about 10 and 21 cm^{-1} shifts to lower frequency with PS-Br and PS-*b*-PNIPAAm functionalization, indicating this functionalization increases the CNT diameters.

Evolved gas analysis on the functionalized CNTs was also performed with a TGA-GC/MS. Styrene appeared as the major degradation component of the thermal degradation products of CNT-PS. In addition to styrene, ethylamine appeared in the degradation products of CNT-PS/PNIPAAm, demonstrating the success of incorporation of poly-NIPAAm chains to CNT surfaces. The PS amount grafted on CNT-PS is about 22 wt % measured with TGA. The weight ratio of PS over poly-NIPAAm

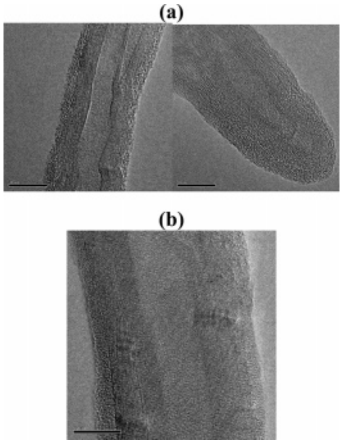


Figure 6. High-resolution transmission electron microscopy (HR-TEM) micrographs of (a) poly(styrene) grafted CNT (CNT-PS) and (b) V-shaped poly(styrene)-*b*-poly(*N*-isopropylacrylamide)-modified CNT (CNT-PS/PNIPAAm).

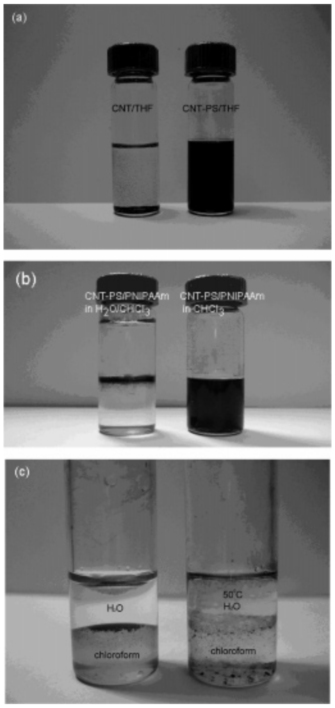


Figure 7. Solubility behavior of modified carbon nanotube (CNT): (a) unmodified CNT and poly(styrene) grafted CNT (CNT-PS) in tetrahydrofuran, (b) V-shaped poly(styrene)-*b*-poly(*N*-isopropylacrylamide)-modified CNT (CNT-PS/PNIPAAm) in $CHCl_3$ and $H_2O/CHCl_3$, and (c) CNT-PS/PNIPAAm in $H_2O/CHCl_3$ at 20 (left) and 50 °C (right).

on the CNT-PS/PNIPAAm surfaces was about 1.0. The presence of CNTs coated with amorphous polymeric materials was demonstrated with TEM analysis, in which the individual nanotube can be observed (Figure 6). Unmodified CNTs exhibit multiwall nanotube bundles. The nanotubes were coated with a polymer layer of about 3 nm in thickness after PS functionalization. The surrounding polymeric materials appear at both the middle sections and the ends of nanotubes. Sequential functionalization of poly-NIPAAm does not result in a significant increase in polymeric layer thickness, because the poly-NIPAAm chains grow up from the CNT surfaces, not from the chain ends of PS. The diameter increases of CNTs along with the surface functionalization are observed with AFM analysis. The diameters of unmodified CNT, CNT-PS, and CNT-PS/PNIPAAm were found to be 25, 35, and 59 nm, respectively. Although the diameters of MWNT were not completely identical in the analysis, the diameter increases might still provide some support to the success of bonding polymeric layer to CNT surfaces.

Solubility Behaviors of CNT-PS/PNIPAAm. CNT-PS exhibits good solubility in organic solvents, as does CNT-BEB-PS. CNT-PS/PNIPAAm was soluble in chloroform and formed a special film at the chloroform−water interface in a chloroform/water mixture (Figure 7b). Gao et al.[35] reported a similar phenomenon observed with CNTs decorating with amphiphilic polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA). Therefore, this result gives more support to the presence of amphiphilic PS-*b*-PNIPAAm block copolymers on CNT-PS-PNIPAAm surfaces. In addition, because poly-NIPAAm is temperature-responsive and has a lower critical solution temperature (LCST) of 32 °C, the CNT-PS/PNIPAAm might be temperature-responsive.[36] As mentioned above, CNT-PS/PNIPAAm formed a film at the chloroform−water interface in a chloroform/water mixture. When the water temperature was raised to 50 °C, CNT-PS/PNIPAAm moved from the chloroform−water interface toward the chloroform phase (Figure 7c), due to that poly-NIPAAm lost its solubility in water at temperatures above its LCST. When the temperature was down to 25 °C, CNT-PS/PNIPAAm gathered again at the chloroform−water interface, to demonstrate the temperature-responsive properties of CNT-PS/PNIPAAm.[37]

Conclusions

ATRP is able to directly incorporate organic moieties, including small molecules and polymer chains, to the CNT surface. Linear PS and V-shaped PS-*b*-PNIPAAm polymer chains were successfully incorporated on CNT through the "grafting-from" and sequential "grafting-on" and "grafting-from" method, respectively. With the functionalization, CNT-PS exhibited good solubility in THF and chloroform, and CNT-PS/PNIPAAm was dissoluble in chloroform and showed amphiphilic behavior at the water/chloroform interface. This functionalization approach provides convenience and versatility in buildup polymer architectures on CNTs.

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Supporting Information Available: Figures representing the TGA and TGA-GC/MS analytical results on the pristine and modified CNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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