Ionomer Covalent Functionalization of Single-Walled Carbon Nanotubes by Radical Polymerization of Zirconium Acrylate

Sellamuthu N. Jaisankar
Dept. of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019

Polymer Division, Central Leather Research Institute, CSIR, Adyar, Chennai 600 020, Tamil Nadu, India

Donna J. Nelson and Ravi Kumar
Dept. of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019

Asit Baran Mandal
Chemical Laboratory, Central Leather Research Institute, CSIR, Adyar, Chennai 600 020, Tamil Nadu, India

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A facile and efficient covalent functionalization of single-walled carbon nanotubes (SWCNTs) via peroxide-mediated free radical covalent attachment and polymerization of zirconium acrylate is reported. The resulting covalently functionalized SWCNTs exhibit improved solubility in organic solvents. The covalently functionalized SWCNTs are characterized by cross polarization magic angle spinning ^{13}C NMR, differential scanning calorimetry, thermogravimetric analysis, x-ray diffraction, Raman, and infrared spectroscopy. Infrared spectroscopy reveals that carboxylate groups of covalently attached ionomers chelate with zirconium ions and the participating carboxylate groups may be from different ionomer chains leading to cross-linking the chains. The SWCNT topology, ionic clustering, and π-electron clouds were explored by transmission electron microscopy. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 820–828, 2014

Keywords: single-walled carbon nanotubes, free radical addition polymerization, covalent functionalization, ionomer, graft copolymer

Introduction

Single-walled carbon nanotubes (SWCNTs) and their functionalized derivatives are important materials in nanotechnology, because of their excellent optical, thermal, mechanical, and electronic properties.[1–9] However, the full advantages of SWCNTs will not be realized until their purity, solubility, and dispersion in organic solvents are resolved.[2,10–17] Most potential applications also require chemical modification of SWCNTs by using specific functionalities.[2,18–22] Chemical modification by covalently functionalizing SWCNTs provides significant changes in their solubility and all other characteristic properties.[2,23,24] Covalent functionalization of SWCNTs is also important to increase their solubility for solution phase processing, manipulation, and obtaining modified electronic structure.[3] SWCNTs have been previously covalently modified for improving lipase activity in reverse micelles,[4] to make thermoresponsive polymeric micelles,[2] to limit their nonspecific interactions,[5] and for composite processing.[7] Making SWCNTs soluble in organic solvents via covalently attaching large polymer which needs smaller number of points of attachment should be very interesting as it will create less defects in SWCNTs. Therefore, synthesizing new functionalized SWCNTs is essential in order to achieve the full advantage of their unique properties.[25–28] The functionalization of SWCNTs by covalently attaching a polymer is a vital and important method of synthesizing nanomaterials. It is also known that specific polymers interact strongly with nanotube surfaces.[29–33] The polymer functionalized SWCNT systems are stable and do not decompose or separate during purification, modification, and application.[26,34,35] The modification of carbon nanotubes, covalently or not, is preferable if the polymer used for functionalizing SWCNTs can be easily removed after application, without destroying the unique properties of the SWCNTs.[36] Covalent functionalization of SWCNTs enhances their solubility,[23,24] so functionalizing SWCNTs covalently with polymers promises to take advantage of their unique properties in polymer applications.[2,23–28,37] There are two main methods of covalent functionalization of SWCNTs by polymers; the "graft from"[26,31,32,38,39] and the "graft to"[26,36,38,40,41] method. SWCNT derivatives with easily modifiable terminal amine,[24] hydroxyl,[35] or carboxyl[24] groups are useful for further modification by graft copolymerization chemistry using either of the above mentioned methods.

Acrylic acids and copolymers have been used to increase the adhesion of polymer films to other substrates like steel,[42] paper,[43] and leather,[36] and they have also been used as adhesion promoters,[44] but not yet in high temperature coating applications. Hence, attaching such an acrylic ionomer to

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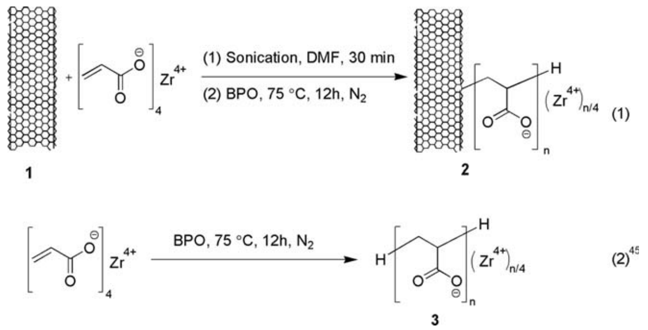
Correspondence concerning this article should be addressed to D. J. Nelson at djnelson@ou.edu; S. N. Jaisankar at snjaio@yahoo.com; A. B. Mandal at abmandal@hotmail.com.



Scheme 1. ***In situ*** **acryl zirconium ionomer functionalization of SWCNTs (1), which used the procedure similar to previously reported[45] polymerization method.**

SWCNTs would be expected to improve their adhesion properties. Therefore, it was desirable to synthesize SWCNTs covalently functionalized with a polymer of zirconium acrylate (ZA) monomer. So, the method "graft from" by direct addition of organic radicals to the nanotubes in a one-step covalent attachment and polymerization[45] of ZA monomer to SWCNTs was planned. Furthermore, using zirconium (Zr^{4+}) derivatives is environmentally important, due to their nontoxic nature; for example, zirconium compounds have replaced lead and zinc in various products.[46] Accordingly, we report herein the convenient and "green" synthesis of covalently functionalized SWCNTs with ZA ionomer.

Experimental

Materials and methods

SWCNTs and ZA monomer were purchased from Aldrich, and used after purification. The free radical initiator, benzoyl peroxide (BPO), was obtained from SISCO, India, and recrystallized from methanol before use. The 200 nm pore Teflon

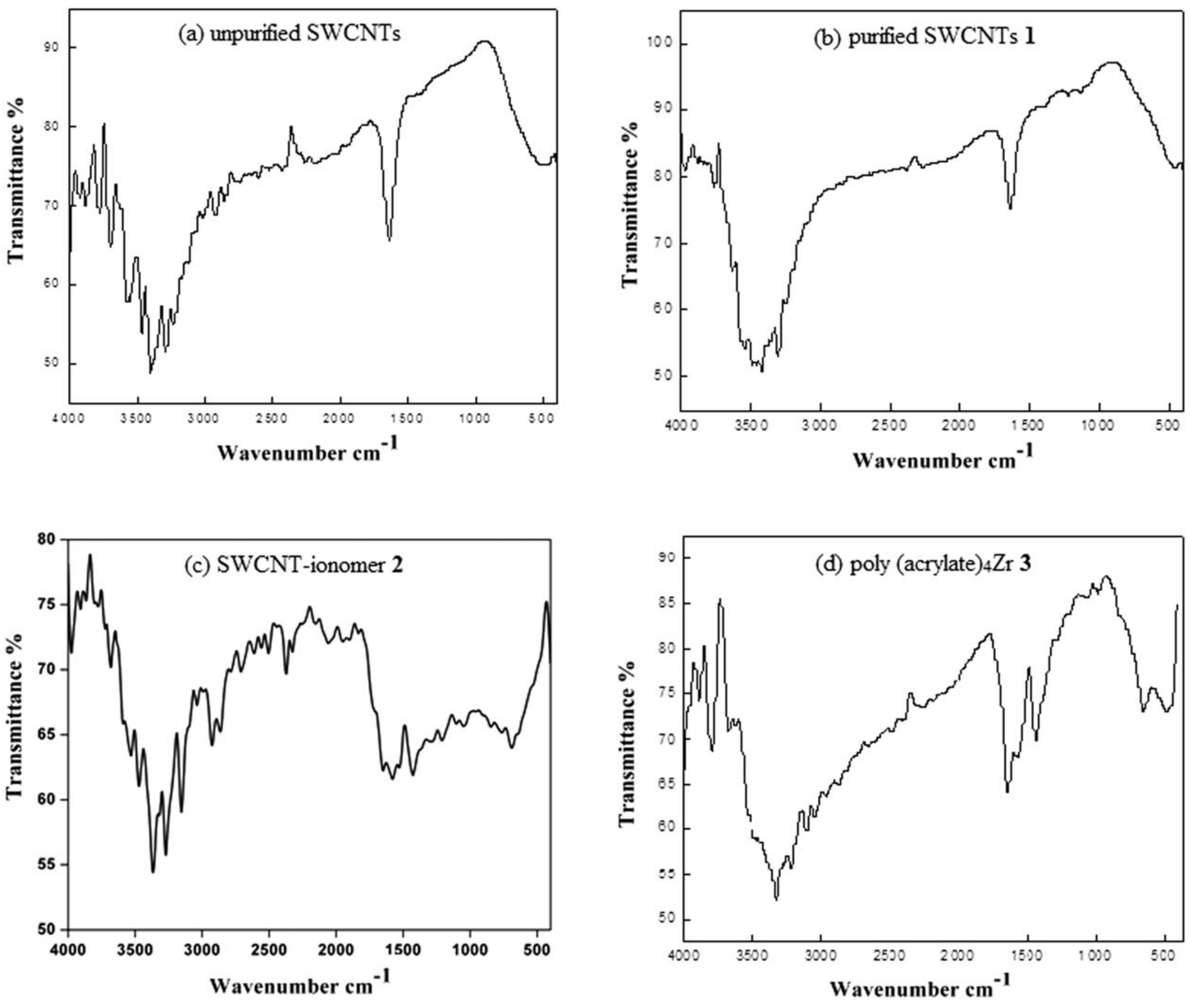
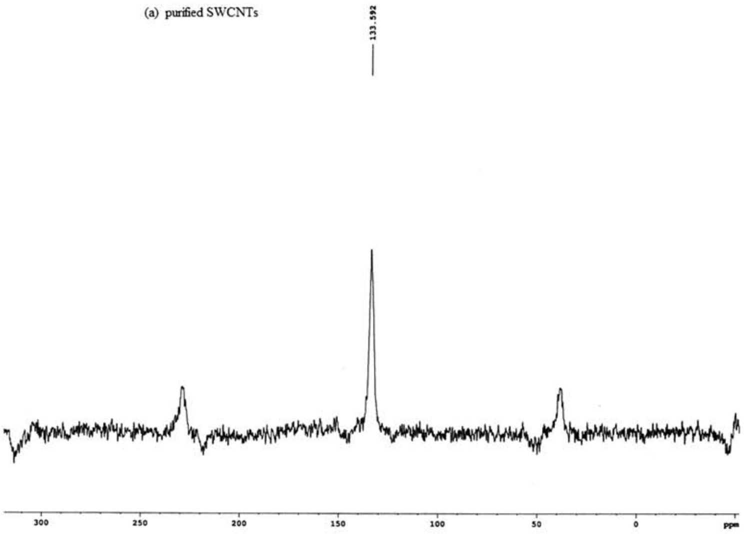
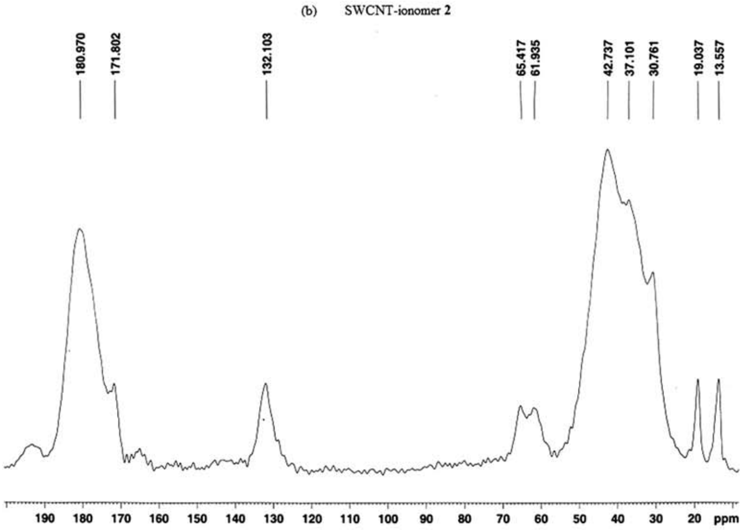


Figure 1. FT-IR spectra of (a) unpurified SWCNTs, (b) purified SWCNTs 1, (c) SWCNT-ionomer 2, and (d) poly (acrylate)$_4$Zr 3.





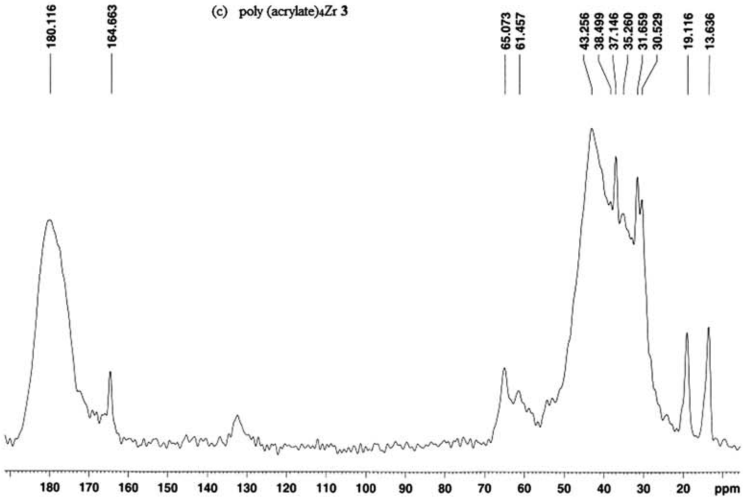


Figure 2. (a) Solid-state CP MAS ^{13}C NMR spectrum of purified SWCNTs 1.

(b) Solid-state CP MAS ^{13}C NMR spectrum of SWCNT-ionomer 2. (c) Solid-state CP MAS ^{13}C NMR spectrum of poly (acrylate)$_4$Zr 3.

(Millipore) membrane filter was purchased from Millipore Chemicals and used for filtration. All solvents (High-Performance Liquid Chromatography grade) were purchased from Aldrich, and used as such. The Fourier Transform Infrared (FT-IR) spectra of the samples in KBr pellets were recorded on a Perkin Elmer FT-IR spectrophotometer. The spectra were scanned from 4000 to 400 cm^{-1}, with a 4 cm^{-1} resolution over 100 scans. Raman spectra were taken by using an

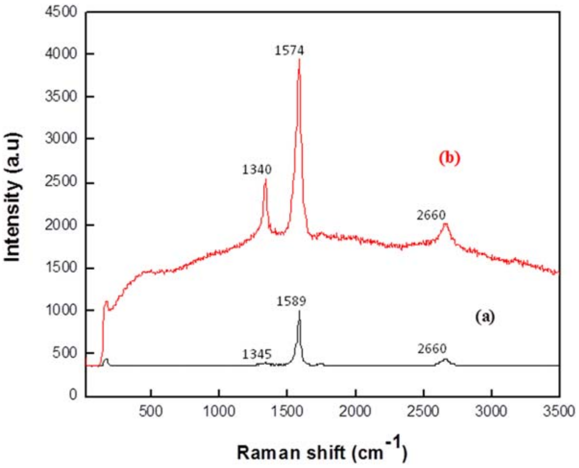


Figure 3. Raman spectra of (a) purified SWCNTs 1 and (b) SWCNT-ionomer 2.

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ALPHA-SNOM CRM 200 instrument with a tunable Argon-ion laser and a 40-mW power laser output at 514-nm modes in the system. Scanning electron microscopy (SEM) used to study the topology and surface coverage of the ionomers was performed via a HITACHI V500 instrument equipped with an energy dispersive x-ray (EDX) analyzer to obtain the elemental values. Specimens for transmission electron microscopy (TEM) measurements were prepared by dispersing suspensions of the functionalized nanotubes, applying a few drops of the sample solution (with nanotubes concentration on the order of 0.1–0.5 mg/mL) onto a carbon coated copper grid, and then evaporating the solvent. These samples produced a film in which it was possible to discern embedded SWCNTs. The ^{13}C NMR spectrum was obtained at room temperature by using a 300MHz FT-NMR spectrometer (Brucker MSL 300P). The spectrum resulting from the cross polarization/magic angle spinning (CP/MAS) experiment was recorded by spinning the sample at the magic angle of 54.74° with respect to the external magnetic field and with a spinning frequency of 7.0 kHz, in order to avoid overlapping the spinning side bands of other resonance lines. Differential scanning calorimetry (DSC) measurements were performed by using a TA DSC V500 series with a heating rate of 15°C/min. Thermo gravimetric analysis (TGA) was carried out on TA TGA Q50 V20.6 Build 31 Universal analysis at a heating rate of 15°C/min from room temperature to 800°C. 10 mg of sample was used for each measurement for both DSC and TGA. X-ray diffraction (XRD) measurements were recorded by using a Seifert JSO Debye flex (30 mA and 40 kV) with CuK$_\alpha$ radiation. The scanning rate was 0.02°/s and the samples were powdered well and placed over Mylar foil.

Purification of SWCNTS

Unpurified SWCNTs were purified as reported previously[29–33,38] by refluxing with nitric acid, followed by subsequent oxidation and annealing, and verified by Raman spectra and TGA. A small amount (50 mg) of unpurified carbon nanotubes was taken in a 100-mL round bottom flask fitted with condenser, and 60 mL of 3 M nitric acid was added. The acid mixture was refluxed for 15 h. Then, the reaction mixture was centrifuged at 10,000 rpm for 2 h, and the supernatant liquid was discarded. The sediments were filtered, and collected by using polycarbonate membrane. The sediments were then air-dried at room temperature and kept in a furnace for air oxidation at 300°C for 1 h, in order to remove the traces of acid and amorphous carbon in the sample. The air-oxidized samples were further annealed at 800°C for 6 h to obtain purified SWCNTs and were used for ionomer functionalization.

In situ ionomer functionalization of SWCNTs

The *in situ* ionomer functionalization of purified SWCNTs (Eq. 1) was carried out by using a procedure similar to the previously reported addition polymerization technique[45] shown in Eq. 2, Scheme 1. Purified SWCNTs (20 mg) and 30-mL DMF were placed in a 100-mL polymerization tube and sonicated for 30 min. The ZA monomer (3.7 g) and initiator BPO (0.04 g) were added to the polymerization tube in order to initiate an *in situ* covalent bond formation between the monomer and SWCNT.[25–28,45,47,48] The polymerization mixture was heated to 75°C for 12 h under a nitrogen atmosphere (Scheme 1).[48–51] The resulting SWCNT-ionomer **2** solution was filtered and washed with distilled water using a 200 nm pore Teflon (Millipore) membrane, and the homopolymer was separated using Soxhlet extraction for 18 h in ethanol. The homopolymer of ZA **3** was also obtained separately, in absence of SWCNTs, via the above experimental procedure for comparison purposes. The SWCNT-acrylic ionomer was separated as a solid, washed with distilled water to remove the unreacted monomer, dried at room temperature, and used for further analysis.

Results and Discussion

The SWCNT-acrylic ionomer **2** was analyzed by examining the spectral, morphological, and thermal properties in order to determine ionomer functionalization. The FTIR spectrum of unpurified SWCNTs shows a peak at 1633 cm^{-1}, corresponding to the SWCNT C=C bond (Figure 1). The corresponding peak for purified SWCNTs **1** is lower in intensity compared to unpurified SWCNTs[38,52,53] (Figures 1b vs. 1a). The FT-IR spectrum of SWCNT-ionomer **2** is shown in Figure 1c, and the appearance of two broad intense bands in the C—O stretching region at 1566 and 1435 cm^{-1} support the presence of carboxylate groups in **2**. No such bands appear in unpurified and purified SWCNTs (Figures 1a, b), but analogous bands do appear in **3** (Figure 1d). These bands may be assigned to the asymmetric and symmetric C—O stretches of chelating bidentate or bridging bidentate carboxylate groups of ionomer.[54] This is supported by the appearance of C—O stretch bands in the same region in the spectra fatty acids on zirconia.[55] So, zirconium cations may be chelated by carboxylate groups from the different ionomer chains and may serve to ionically crosslink the ionomer chains.

CP/MAS solid-state ^{13}C NMR has also been used to characterize the covalently modified SWCNTs,[56–61] and ionomer-functionalized SWCNTs **2** and polymer **3** were also characterized by same technique. ZA ionomer is a linear polymer that contains polar carboxylate groups attached to the hydrophobic C—H polymer backbone. This type of polymer having polar groups on hydrophobic backbone has also been characterized by ^{13}C NMR and is reported to solubilize SWCNTs by wrapping around them, creating a stable dispersion.[56] Purified SWCNTs **1** show a ^{13}C NMR signal at 133 ppm (Figure 2a) and this signal for SWCNT-ionomer **2**

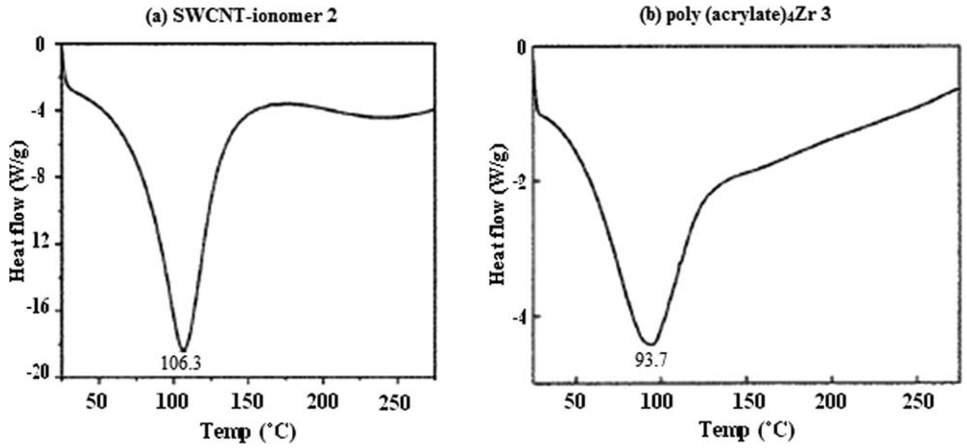
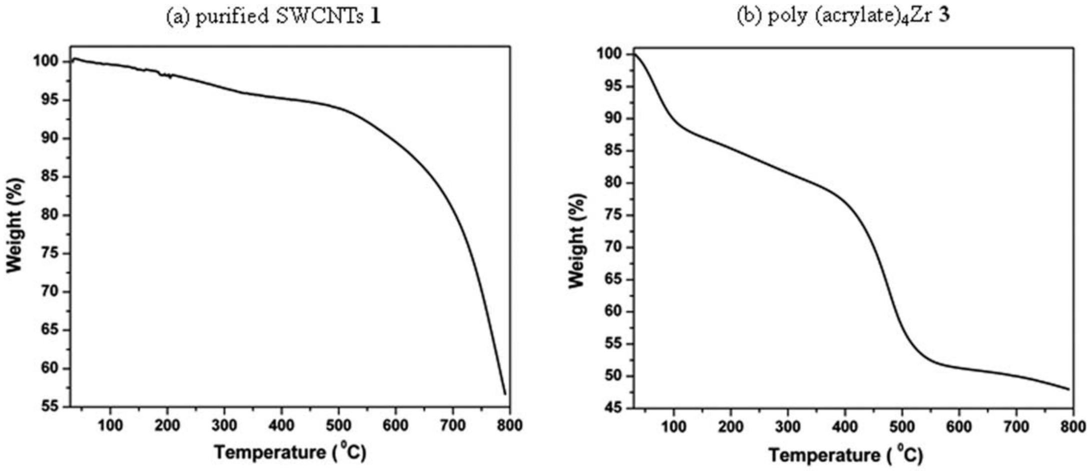


Figure 4. DSC thermograms of (a) SWCNT-ionomer 2 and (b) poly (acrylate)$_4$Zr 3.

appears at 132 ppm (Figure 2b). Although there is a very small signal in the ^{13}C NMR spectrum of **3** around 130–135 ppm (Figure 2c), upon covalent functionalization of SWCNTs with ZA polymer, the signal at 132 ppm grows to a much higher intensity.

Raman spectroscopy has been extensively used to detect sidewall functionalization.[25–28] The Raman spectrum (Figure 3a) of **1** shows a prominent tangential G-band vibration mode at 1589 cm^{-1}, which is due to sp^2 C=C bond stretching vibrations.[62,63] The spectrum of **2** (Figure 3b) shows a significant G-band shift to 1574 cm^{-1}. The low intensity M band, which is present in SWCNTs, disappeared due to the covalent attachment and polymerization of ZA onto the SWCNT surface. The characteristic G-band shift and M-band disappearance confirm the covalent bond formation. In addition to this, the D (disorder) band in **1** (Figure 3a) is also shifted to a lower frequency by 5 cm^{-1} at 1340 cm^{-1}in **2**, but the intensity of D-band in **2** is higher than **1**(Figure 3b).[62–64] The disorder mode corresponds to the conversion of an sp^2-hybridized (trigonal) carbon to an sp^3-hybridized carbon on the



(c) SWCNT-ionomer 2

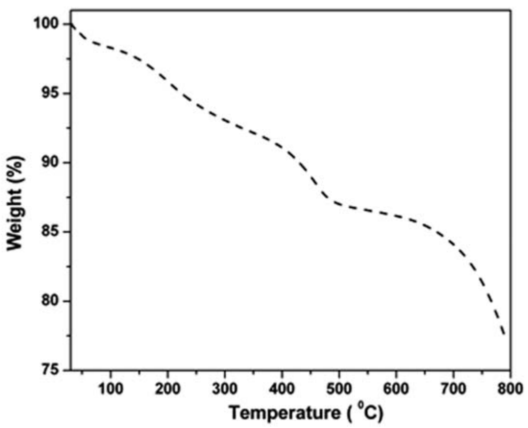
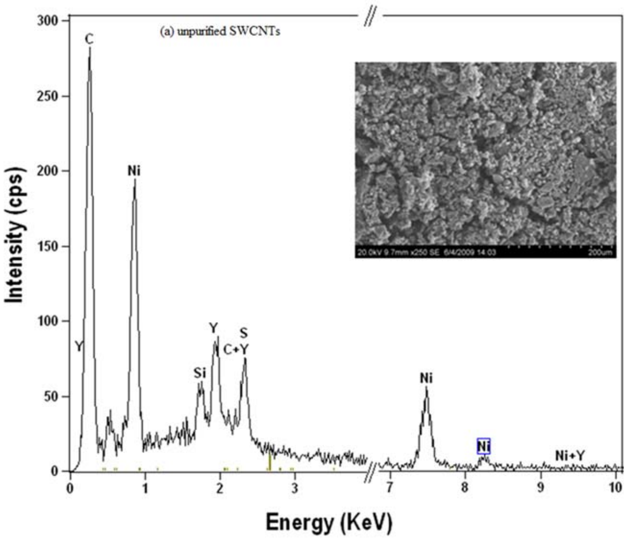


Figure 5. TGA thermogram of (a) purified SWCNTs 1, (b) poly (acrylate)$_4$Zr 3, and (c) SWCNT-ionomer 2.



(b) SWCNT-ionomer 2

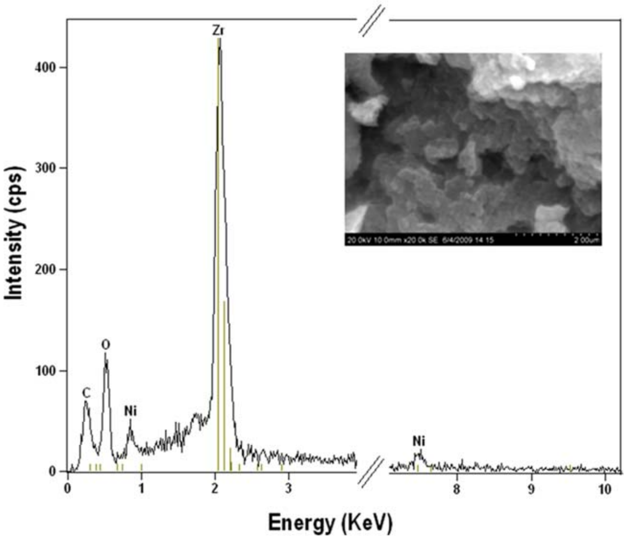


Figure 6. (a)SEM/EDX spectrum of unpurified SWCNTs.

(b) SEM/EDX spectrum of SWCNT-ionomer 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface of SWCNTs, as a result of covalent bond formation between acrylic ionomer and SWCNT. The area under the D bands measures the extent of covalent sidewall functionalization of SWCNTs and indicates the presence of a small amount of sp^3-hybridized carbon atom formation as result. The I_G/I_D ratio for purified SWCNTs is 10.35 and is reduced to 4.17 for the SWCNT-ionomer **2** supporting that upon functionalization some carbons of SWCNTs are converted from sp^2 to sp^3 hybridization. These characteristic G- and D-band shifts support a significant sidewall functionalization of SWCNTs with the acrylic ionomer.[62–64] The combination of IR, Raman, and ^{13}C NMR spectroscopic data indicate a covalent attachment of ionomer to SWCNT.

Thermal transition temperatures of **2** and **3** were determined by DSC (Figure 4) and TGA (Figure 5). The thermogram of compound **2** shows an endothermic peak at 106.3°C, whereas that of **3** exhibits a broad endothermic peak at 93.7°C in the DSC.[37] Thus, a shift of about 13°C in the thermal transition temperature was observed. This is also supported by a previous report,[37] of covalent polymer attachment to carbon nanotube sidewalls, resulting in a 6°C increase in the transition temperature over the pure styrene polymer. Hence, increase in transition temperature for **2** as compared to **3**, supports the ionomer functionalization of SWCNTs.

The TGA curve of **3** (Figure 5b) shows two weight losses at 96.4 and 419°C. The first stage decomposition at 96.4°C, with 10% weight loss, may be due to the elimination of surface water molecules from the ionomer. The second stage decomposition observed at 419°C, with 31% weight loss, may be due to the loss or decomposition of its organic functional groups. SWCNT-ionomer **2** (Figure 5c) shows decomposition at 429.8°C, with a weight loss of only 10%. Similar to the effects observed in DSC, an upward shift of 13°C in the decomposition temperature was observed for **2,** compared to **3** in TGA (Figures 5b vs. 5c). In addition, the higher thermal stability of **2** at 429.8°C relative to **3,** gives evidence for covalent attachment of the ionomer to SWCNTs.[65,66] This may be due to the more labile nature of acrylic ionomer bonds, which results in lower decomposition temperatures (T_d),[65,66] whereas the covalent bonding to SWCNTs in **2** leads to a higher T_d.

Although SEM has not yet been very successful in characterizing carbon nanotubes, which are covalently functionalized with organic moieties,[67–69] SEM/EDX spectroscopy is widely used to study the topology and surface coverage of the ionomers, as well as the elemental composition of the material (Figure 6). The EDX elemental analysis spectra (Figure 6b) shows the presence of Zr in **2**, which originated from the ionomer, while no peak corresponding to Zr is observed in the unpurified SWCNT spectrum (Figure 6a). The presence of Zr in **2** also supports that SWCNTs are functionalized with an ionomer of ZA.

The structural characteristics of ionomer functionalized carbon nanotubes such as spatial correlations between atoms within a single layer, the nature of interlayer correlations were identified by x-ray diffraction. The x-ray diffractogram of **1** shows a broad peak at $2\theta = 11.6°$ and coincides with hexagonal graphite (002) (JCPDS card no: 41–1487) and confirms the crystalline nature of the nanotubes (Figure 7a).[67–69] Peaks at $2\theta = 11.6°$ and 12.40° reveal the crystallinity of acrylic ionomer **3** (Figure 7b). Compound **2** exhibits characteristic XRD peaks at $2\theta = 11°$ and 12° in Figure 7c, giving evidence for SWCNT-ionomer functionalization and indicating that the nature of the nanotubes was disturbed by that functionalization.[70] The region from 10° to 15° has been expanded in the right part of Figure 7 and it shows a $2\theta = 0.6°$ shift for the functionalized SWNTs, due to carbon nanotube incorporation, indicating that the crystalline nature of the nanotubes was slightly disturbed by the ionomer functionalization. This indicates that the crystallinity of these ionomer functionalized nanotubes was slightly increased, due to the interface between SWCNTs and the zirconium ionomer, producing Ohmic contact formation. Similar results for interactions between Ti and carbon nanotubes have been reported.[71]

More direct evidence for the production of acrylic ionomer functionalized carbon nanotubes was provided by transmission electron microscopy (TEM) imaging. The TEM images suggest that the functionalized nanotubes are well dispersed in tetrahydrofuran. At higher magnification, the TEM image shows acrylic ionomers attached to the SWCNT sidewalls and that each nanotube is sheathed by regions of

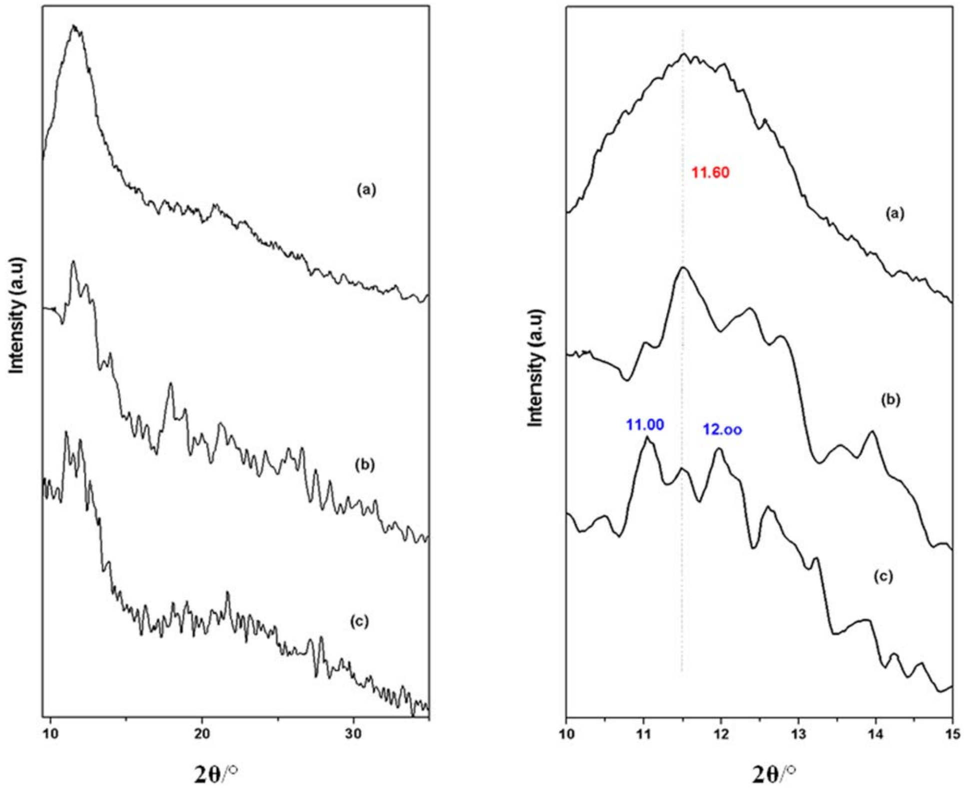


Figure 7. Powder XRD spectra of (a) purified SWCNTs 1, (b) poly (acrylate)$_4$Zr 3, and (c) SWCNT-ionomer 2.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ionomer, presumably corresponding to the poly (acrylate)$_4$Zr. In Figures 8a–c, (see arrows), large nanotube bundles of **2** are separated into individual tubes due to ionomer functionalization,[56–61] possibly as a result of steric repulsion between ionomeric groups.[65,66] Formation of a large network of nanotubes that are interconnected by Zr cations, chelated by carboxylate groups which ionically crosslink the ionomer chains is also possible.[72,73]

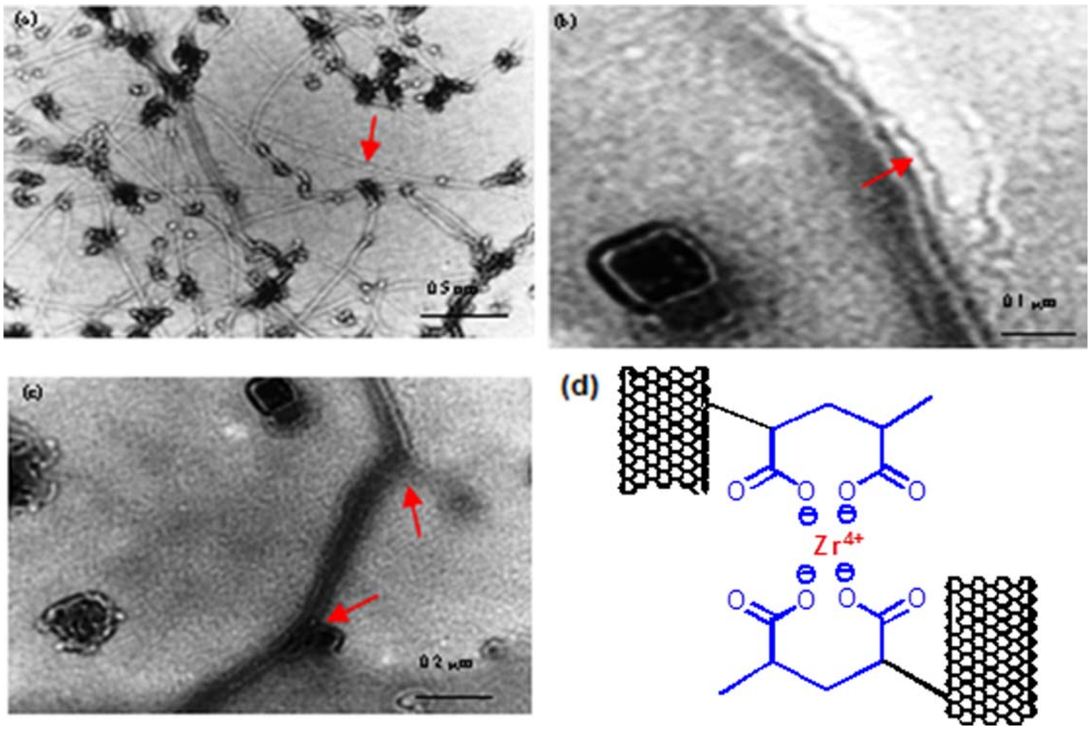


Figure 8. TEM images of SWCNT-ionomer 2.

Arrows show where separation into individual tubes due to ionomer functionalization is visible. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conclusions

In conclusion, a simple, efficient, and cost-effective one-step method has been developed for covalently functionalizing SWCNTs by covalently attaching and polymerizing ZA onto the surface by an *in situ* polymerization technique. The functionalized SWCNTs (SWCNT-ionomer) are characterized by using FT-IR, solid-state ^{13}C NMR, Raman, DSC, TGA, SEM/EDX, XRD, and TEM. IR results indicate that the carboxylate groups of the synthesized ionomer chelate with zirconium ions, and the participating carboxylate groups may be from different ionomer chains leading to cross-linking. Possible advantages of the synthetic procedure are that it may (a) generate a high molecular weight acrylic ionomer chain, (b) exhibit better film formation, and (c) provide thermal stability, which may have great potential in industrial coating applications.

Acknowledgments

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