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Graft Polymerization of Styrene from Single-Walled Carbon Nanotube using Atom Transfer Radical Polymerization

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Summary

We grafted polystyrene from the surface of single-walled carbon nanotube (SWNT) via Atom Transfer Radical Polymerization (ATRP). Direct electrophilic addition of chloroform and subsequent hydrolysis introduced hydroxyl groups to the surface of SWNT. ATRP initiators were attached to the SWNT by esterification of 2-chrolopropyl chloride with hydroxyl groups. Subsequent polymerization of styrene with CuCl / N,N,N',N',N''-pentamethyldiethylenetriamine catalyst yielded polystyrene grafted SWNT. Transmission electron microscopy analysis clearly showed that approximately 6 nm-thick polystyrene layer was uniformly formed on 1.2 nm diameter SWNT.

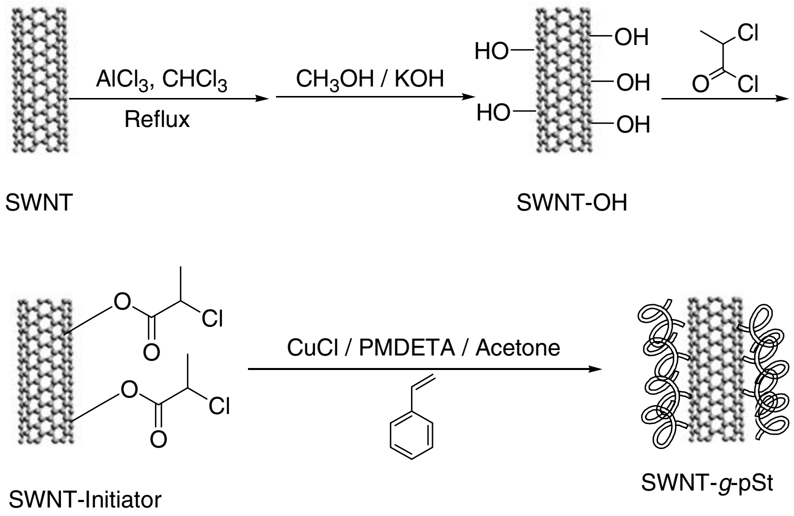
Introduction

SWNT has attracted much attention because of their outstanding electronic, mechanical, and thermal properties and wide range of potential applications including nanoelectronic devices, field emission displays, supercapacitors, sensors, and fillers in composites materials [1-5]. However, the developments of SWNT applications have often been impeded by poor processibility due to low solubility of SWNT in solvents and host matrices.

One approach to overcome this difficulty is the covalent attachment of solubilizing moieties on SWNT [6-9]. In particular, the covalent attachment of polymers on SWNT is an attractive method as the bound polymer can introduce desirable functional groups on SWNT in high density and thus effectively improve the solubility of SWNT with minimum defect formation. There are two approaches to attach polymers on SWNT; graft-onto and graft-from methods. Graft-onto approach describes the attachment of the separately prepared polymer to SWNT [10-12]. Graft-from approach involves the growth of the targeted polymers directly from the surface of SWNT using the attached initiator, via various polymerization intermediates [13-15].

Among various polymerization methods to graft polymers from the surface of carbon nanotube, Atom Transfer Radical Polymerization (ATRP) has several advantages [16, 17]. Firstly, a wide range of polymerizable monomers is available including styrenes, acrylates, methacrylates, and acrylonitriles. Secondly, since ATRP has living polymerization character, further synthesis of complex polymeric architectures including blocks, grafts, and star polymers are possible. Thirdly, the degrees of polymerization can be controlled through adjusting the ratio of feeding monomers to initiators. Several research groups have recently reported successful examples of grafting polymers from the surface of carbon nanotube through ATRP [18-21]. These reports elegantly showed that ATRP is an efficient and versatile method to modify carbon nanotubes.

The previous studies mainly employed nitric acid treated carbon nanotube as starting materials [18-21]. Nitric acid oxidizes and shortens carbon nanotube through the formation of carboxyl group on sidewall, mainly on the tips of CNT. Therefore, significant wall damages is expected to occur during the acid treatment, causing detrimental effects on the outstanding properties of CNT [22]. In this work, we introduced the hydroxyl groups and ATRP initiator through the direct electrophilic addition of chloroform onto the sidewall of SWNT to minimize defect formations on CNT [23]. Subsequent attachment of ATRP initiator onto the sidewall of SWNT and the graft polymerization from the surface of SWNT yielded the polystyrene-grafted SWNT.



Scheme 1. Synthesis of Polystyrene-grafted SWNT (SWNT -*g*-pSt).

Experimental

Materials

Styrene (Junsei, 99.5 %) was purified by passing through alumina column under nitrogen. Chloroform (Arlo Erba, Min. 99 %) was distilled over $CaCl_2$. 2-chloropropionyl chloride (Aldrich, 97 %), CuCl (Aldrich, 99.995 %), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99 %), potassium hydroxide (Daia-Kobans), and aluminum chloride (Aldrich, 99 %) were used as received. Methyl alcohol (Hayman, 99.5 %) and pyridine (Kanto, 99.5 %) were used as received. SWNT (Diameter: 0.8-1.2 nm, Length: 2-20 μm, synthesized by Arc-discharge), were purchased from ILJIN Nanotech Co., Ltd.

Measurements

Transmission electron microscopy (TEM) analyses were conducted by a JEOL JEM-3000F TEM system at 200 KV. The Raman spectra were obtained using the FT-Raman spectrometer (Bruker Model IFS100) with the irradiation at 1064 nm after 1024 scans. Fourier-transform infrared (FT-IR) spectra were recorded on JASCO FT/IR-460 plus spectrometer.

Removal of Catalysts from pristine SWNT

Pristine SWNT (255 mg) was grinded with mortar and pestle. The fine black powder and HCl (5 M) were transferred to a round bottom flask and stirred for 40 min. The solution was sonicated for 1 h. Afterwards, the solution was filtered through 0.45 μm Milipore PTFE membrane, and the SWNT was repeatedly washed with distilled water. The filtered black solid was dried in drying oven under vacuum.

Synthesis of SWNT-OH.

HCl-treated SWNT (199.5 mg) and aluminum chloride (1.5469 g) were grinded in the glove box for 20 min. The mixture was transferred to a three-necked round bottom flask filled with dried chloroform and refluxed for 60 h under N_2. After cooling at room temperature, 50 ml of alkaline methanol was slowly added to the reaction mixture through a dropping funnel, and the reaction mixture was stirred at 70 ^{o}C for 20 h. Afterwards, the reaction mixture was filtered through a 0.2 μm PTFE membrane and was repeatedly washed with distilled water, ether, and THF. The obtained black powder was dried under vacuum.

Synthesis of SWNT-Initiator

A round bottom flask was charged with 155 mg of the SWNT-OH, 2-chloropropionyl chloride (20 ml), and 1 ml of pyridine. The reaction mixture was refluxed for 12 h and 2-chloropropionyl chloride was evaporated under reduced pressure. The mixture was cooled to 0 ^{o}C, and 40 ml of water was added. After 1 hour stirring, 40 ml of chloroform was added, followed by 1 h stirring. The chloroform layer was washed with water three times and collected. The product was dried over night under vacuum, yielding SWNT-Initiator.

Synthesis of SWNT-g-pSt

SWNT-Initiator (20 mg) and PMDETA (167 mL, 0.8 mmol) were added to a 20 ml round bottom flask, which was degassed and back-filled with nitrogen three times. Deoxygenated styrene (5 ml) and 0.5 ml of dried acetone were added using syringe, and the reaction mixture was degassed by three freeze-pump-thaw cycles. After addition of CuCl (84.1 mg, 0.8 mmol), the flask was placed in an oil bath at 60 °C. After 96 h, the polymerization was stopped by cooling at room temperature and opening the flask to air. The reaction mixture was diluted with 7 ml of THF, sonicated for 30 min, and passed through alumina for removal of the catalyst. Afterwards, the mixture was precipitated into methanol, filtered and re-dissolved in THF. The solution was filtered through 0.2 μm PTFE membrane. The solid was repeatedly washed with THF and ether to remove the free polymer. The gray solid was obtained after drying under vacuum for 10 h.

Results and Discussion

Introduction of hydroxyl groups on the surface of SWNT was achieved by following the reported procedure [23]. Electrophilic addition of chloroform to SWNT was followed by hydrolysis to result in hydroxyl group to the surface of the SWNT in one pot, two step reactions as shown in Scheme 1. Subsequent esterification of SWNT-OH with 2-chloropropionyl chloride introduced ATRP initiators onto the sidewall of SWNT. ATRP of styrene was carried out at 60 ^{o}C with CuCl / PMDETA as catalyst and SWNT-initiator as macroinitiator.

Figure 1 shows TEM images of obtained SWNT after the graft polymerization of styrene. The specimen for TEM measurements was prepared by depositing a drop of THF solution of SWNT-*g*-pSt onto a carbon-coated copper grid, followed by the evaporation of the solvent. While the original SWNT aggregated in bundles,

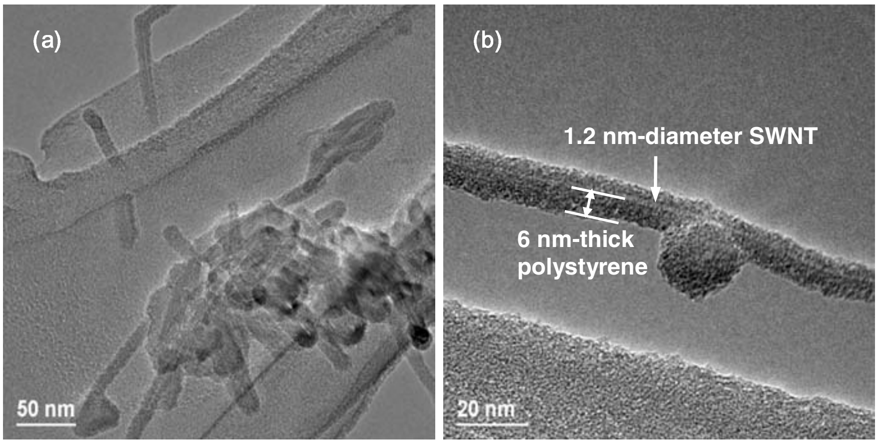


Fig. 1. Transmission electron microscopy of polystyrene-grafted SWNT (a) and (b) in different magnifications.

approximately in the order of 10 nm, the polystyrene-grafted SWNT were unbundled and existed as individual SWNT as shown in Figure 1(a). The average diameter of polystyrene-grafted SWNT was 11.7 nm. A zoomed image in Figure 1 (b) clearly revealed the uniform formation of 6 nm-thick polystyrene layer on 1.2 nm SWNT as shown as bright gray center line. Compared with pristine SWNT, the obtained polystyrene-grafted SWNT showed improved solubility in organic solvents such as chloroform.

The covalent functionalization of the side wall of SWNT after electrophilic addition of chloroform and subsequent hydrolysis was confirmed by the FT-Raman spectra. (Figure 2) The disordered mode (at ~1270 cm^{-1}) appeared to be enhanced significantly for the SWNT-OH (Fig 2(b)). As the disordered mode is the diagnostic of the disruption in the hexagonal framework of the SWNT, the increase of the relative intensity of this peak provided direct evidence of covalent modification.[24] The characteristics of radial ring breathing mode (at ~170 cm^{-1}) and tangential (at ~1590 cm^{-1}) mode still remained, indicating that the structure of SWNT remained basically intact. We have not found any (additional or perturbed) Raman peaks after introducing the initiator group and polymerized moieties, presumably due to their large fluorescence.

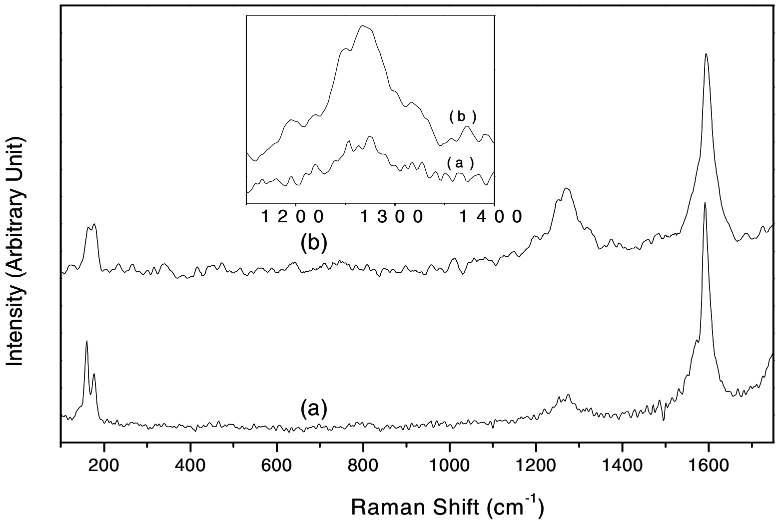


Fig. 2. Raman spectra of (a) pristine SWNT and (b) SWNT-OH.

The products were also characterized by FT-IR spectroscopy. Figure 3 shows the FT-IR spectra of the functionalized nanotube before and after the esterification, respectively. As clearly evident, the characteristic stretching bands for SWNT-Initiator (Fig 3(c)) appear at 1762 cm^{-1}(C=O) and 1138 cm^{-1}(C-O). Also, the C-Cl stretching is observed at 752 cm^{-1}. In the case of SWNT-OH (Fig 3(b)), C-O stretching at 1119 cm^{-1}, indicates the successfully introduction of OH group onto the SWNT.

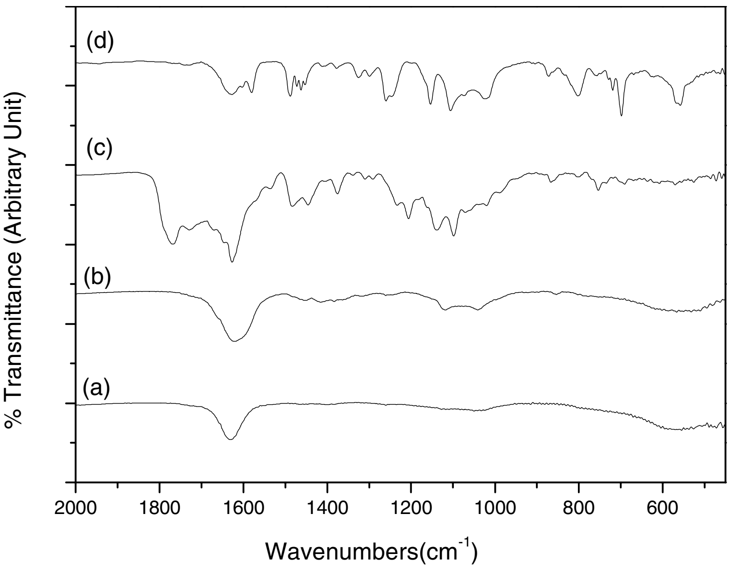


Fig. 3. FT-IR spectra of (a) pristine SWNT, (b) SWNT-OH, (c) SWNT-Initiator and (d) SWNT-*g*-pSt.

Conclusion

We prepared polystyrene-grafted SWNT using Atom Transfer Radical Polymerization. This method utilized direct side wall functionalization which may have advantages in conserving original structure and properties of SWNT. The obtained SWNT-*g*-pSt was unbundled into individual SWNT with uniform coating with polystyrene and showed improved solubility in organic solvents such as chloroform.

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