

Covalent Functionalization of Carbon Nanotubes using Atom Transfer Radical Polymerization

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Introduction

Both single-walled and multi-walled carbon nanotubes (CNTs) have attracted much attention owing to their outstanding electronic, mechanical, and thermal properties.^{1,2} However, the developments of CNT applications have often been impeded by lack of chemical functionalities on the surface of CNTs, resulting in low compatibility with other materials. One approach to overcome this challenge is the covalent attachment of functional moieties on the surface of CNTs.³⁻⁵ In particular, the covalent modification of CNTs with polymers is an attractive method as the bound polymer can introduce desirable functional groups on CNTs in high density and thus effectively alter the surface properties of CNTs with minimum defect formation.

Among various polymerization methods to graft polymers on the surface of CNTs, Atom Transfer Radical Polymerization (ATRP) has several advantages,^{6,7} such as a wide range of polymerizable monomers and superb control in molecular structure and weights. Several research groups including us have showed that ATRP is an efficient and versatile method to modify the surface of CNTs.⁸⁻¹¹ Here, we will discuss two independent approaches for the covalent attachment of polymers based on ATRP graft-from and graft-onto methods.

Experimental

Grafting-from Method

Removal of Catalysis from SWNT. Pristine SWNT was grinded and then stirred with HCl for 40min. The solution was sonicated for 1hour. The solution was filtered through 0.45μm membrane, and the SWNT was repeatedly washed with distilled water. The filtered black solid was dried.

Synthesis of SWNT-OH. HCl-treated SWNT and aluminum chloride were grinded in the glove box. The mixture was transferred to round bottom flask filled with dried chloroform and refluxed for 60hours under N₂. After cooling at room temperature, alkaline methanol was slowly added to the reaction mixture through a dropping funnel, and the reaction mixture was stirred at 70°C for 20hours. Afterwards, the reaction mixture was filtered through a 0.2μm membrane and was repeatedly washed with distilled water, ether, and THF. The obtained hydroxyl SWNT (SWNT-OH) was dried under vacuum.

Synthesis of SWNT-Initiator. A round bottom flask was charged with the SWNT-OH, 2-chloropropionyl chloride, and pyridine. The reaction mixture was refluxed for 12hours and 2-chloropropionyl chloride was evaporated under reduced pressure. The mixture was cooled to 0°C, and water was added. After 1hour stirring, chloroform was added, followed by 1hour stirring. The chloroform layer was washed with water and collected. The product was dried under vacuum, yielding SWNT-Initiator.

Synthesis of SWNT-g-pSt. SWNT-Initiator and PMDETA were added to a round bottom flask, which was degassed and back-filled with nitrogen. Deoxygenated styrene and acetone were added using syringe, and the reaction mixture was degassed by three freeze-pump-thaw cycles. After addition of CuCl, the flask was placed in an oil bath at 60°C. After 96hours, the polymerization was stopped by cooling. The mixture was diluted with THF, sonicated, and passed through alumina for removal of the catalyst. Afterwards, the mixture was precipitated into methanol, filtered and redissolved in THF. The solution was filtered through 0.2μm 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 hours.

Grafting-onto Method

Synthesis of p(tBA). CuBr and tBA were added to a Schlenk flask. After degassing by freeze-pump-thaw, PMDETA and 2-EBriB were added and the mixture was stirred at 60°C. After 2hour 20min, the polymerization was stopped by cooling to room temperature and opening the flask to air. The mixture was dissolved in THF, passed

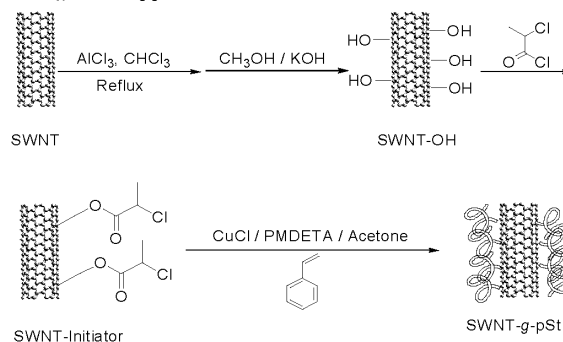
through a neural alumina column and precipitated into methanol. After filtration and vacuum-drying, poly(t-butyl acrylate) was collected.

Oxidizing and Shortening of MWNTs. The chemical oxidation and shortening of the MWNTs were carried out in a mixture of concentrated H₂SO₄ and HNO₃ (3:1) under sonication for 24hours. The excess acid was removed by centrifugation and dilution with distilled water. Nanotubes were further polished in a mixture of H₂SO₄ and H₂O₂ (4:1) by sonication. Remaining mixture was washed with water, acetone and hexane.

Synthesis of MWNT-g-p(tBA). A flask was charged with obtained MWNTs, CuBr and anisole. After three freeze-pump-thaw cycles, PMDETA and p(tBA) were added. The reaction mixture was heated at 60°C for 72 hours. The product was diluted in THF and filtered through 0.2μm membrane with repeated washing with methanol and THF. A black powder was collected after vacuum drying at 65°C for 24hours.

Results and discussion

Grafting-from Approach



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

Introduction of hydroxyl groups on the surface of SWNT was achieved by following the reported procedure.¹² 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°C with CuCl/PMDETA as catalyst and SWNT-initiator as macro-initiator.

Figure 1 shows TEM images of obtained SWNT after the graft polymerization of styrene. While the original SWNT aggregated in bundles, 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 6nm-thick polystyrene layer on 1.2nm SWNT as shown as bright gray center line.

The products were characterized by FT-IR spectroscopy. The characteristic stretching bands for SWNT-Initiator appear at 1762cm⁻¹(C=O) and 1138cm⁻¹(C-O). Also, the C-Cl stretching is observed at 752cm⁻¹. In the case of SWNT-OH, C-O stretching at 1119cm⁻¹, indicates the successfully introduction of OH group onto the SWNT.

The covalent functionalization of the side wall of SWNT after electrophilic addition of chloroform and subsequent hydrolysis was confirmed by the FT-Raman spectra. The disordered mode (at ~1270cm⁻¹) appeared to be enhanced significantly for the SWNT-OH. 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.⁶ The characteristics of radial ring breathing mode (at ~170cm⁻¹) and tangential (at ~1590cm⁻¹) mode still remained, indicating that the structure of SWNT remained basically intact.