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Grafting-to approach for the functionalization of carbon nanotubes with polystyrene

Grigoris Mountrichas, Stergios Pispas*, Nikos Tagmatarchis*

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vass. Constantinou Avenue, 11635 Athens, Hellas, Greece

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ABSTRACT

In the present paper we describe the synthesis and the characterization of polystyrene functionalized carbon nanotubes (CNTs). The synthesis is realized through a grafting-to approach of preformed polystyrene chains, synthesized by anionic polymerization high vacuum techniques, onto the surface of a variety of CNTs, i.e. shorted-MWNTs, MWNTs and SWNTs. The functionalized materials are characterized by a variety of complementary techniques including spectroscopy, electron microscopy and thermogravimetric analysis.

1. Introduction

Carbon nanotubes (CNTs) are the basic material for a number of fascinating applications in materials science. The extended π electron structure in combination with the high aspect ratio and the nano-dimensions give some unique properties to the CNTs [1]. CNTs are the strongest known material, while at the same time they have very good thermal stability and electrical conductivity. However, because of extended van der Waals interactions between the sidewalls of CNTs, this material is not soluble in any organic or aqueous media [1]. In order to overcome the aforementioned insolubility, covalent and non-covalent functionalization approaches have been proposed in the literature [2]. Among them, the covalent functionalization of CNTs with polymers is emerging as a very promising method for both the solubilization of CNTs and their straightforward incorporation in polymeric matrices [3].

The covalent functionalization of CNTs with polymers can be realized through grafting-to and grafting-from approaches [3]. In the first case, the polymer chains are synthesized and characterized prior to their connection to CNTs while, in the case of grafting-from approach, the synthesis of the macromolecules is initiated from functional groups that are already attached on CNTs. Whenever well-defined structure, molecular weight and homogeneity of the grafted polymer chains is desired, the grafting-to approach is the method of choice, because the polymers are synthesized prior to the functionalization reaction through controlled polymerization methodologies and can be characterized separately. The covalent attachment of the as prepared polymers onto CNTs can be performed through reaction between functional groups on the polymer and on the CNTs [3].

In the present work we describe the synthesis of polystyrene functionalized CNTs using the grafting-to approach. The synthesis of the polymers has been performed using high vacuum anionic polymerization, in order to ensure both well-defined molecular characteristics of the polymers and the presence of reactive carbanions at the end of the polymer chains. The functionalization reaction is realized by reaction of the anions with the strained carbon atoms onto the sidewalls of CNTs. The current approach based on the high vacuum anionic polymerization methodology gives the best possible control over the molecular characteristics (molecular weight, polydispersity, etc.) of the polymer chains to be grafted on the CNTs, in contrast to controlled radical polymerization approaches. It also presents a straightforward way of attaching PS chains through their reactive $-C^{-}Li^{+}$ ends without the need for other functional groups to be present on the CNTs for this purpose. By the use of vacuum sealed reactors the reactivity of the polymer chain ends is ensured thought out the course of the grafting-to reaction, which, therefore, can last for very long times allowing for the highest possible grafting efficiency. In the grafting-to approach the grafted chains can be isolated before the grafting reaction and be characterized independently, giving valuable information on the characteristics of the final hybrid material. The isolated polystyrene functionalized materials (CNTs-PS) are characterized by thermogravimetric analysis, transmission electron microscopy, ATR-IR, Raman and UV–vis–NIR spectroscopy.

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* Corresponding authors. Tel.: +30 210 7273835; fax: +30 210 7273794.
E-mail address: tagmatar@eie.gr (N. Tagmatarchis).

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2. Experimental

All solvents and reagents were purchased from commercially available sources and used without further purification unless otherwise stated. HiPco SWNT (average diameter 1.1 nm; length > 5 μm) were purchased by Carbon Nanotechnologies Incorporating (CNI). MWNT (with outer diameter 20–30 nm; length > 5 μm) and shorted-MWNTs (with outer diameter 20–30 nm; length ~500 nm) were obtained from Nanostructured & Amorphous Materials, Inc., (www.nanoamor.com).

The synthesis of polystyrenes with an anion end (living polystyrene) was realized by anionic polymerization high vacuum techniques [4]. Monomer, initiator and solvent have been purified in custom made sealed glass apparatus, following standard methods used in this polymerization technique. At the end of polymerization, the desired amount of living polystyrene was isolated in ampoules, under high vacuum, as solution in benzene ($0.1\ \mathrm{g\ mL^{-1}}$). Part of the solution was deactivated and the polymers were isolated for further characterization. The addition reaction of the polystyrene on the surface of the CNTs is preformed in a home made sealed glass apparatus, where an ampoule with the polymer (1 g of polymer) and an ampoule with a pre-dried amount of CNTs (~15 mg) are connected. Alternatively, the addition reaction was performed in the same reactor where the polymerization of styrene was held. In both cases, the addition reaction is preformed in benzene at 40 °C for 3 days under high vacuum. At the beginning of the reaction, 5 min sonication is needed in order to ensure the homogeneous dispersion of the CNTs in the reaction mixture. The reaction is terminated by the addition of degassed methanol, which deactivates the macromolecular anions. The solid reaction product is isolated by evaporation of the solvent. Subsequently, the raw solid material was re-dispersed in toluene and the solution was filtered through a Teflon membrane filter with mean pore size of 200 nm in order to remove the unreacted polymer chains. The polystyrene functionalized CNTs were washed with 100 mL of toluene (2 × 50 mL) and 200 mL of THF (4 × 50 mL) and were left to dry under vacuum.

Characterization of the polymers grafted on the CNTs in terms of the molecular weight and polydispersity was performed independently by size exclusion chromatography (SEC), after withdrawing a sample from the polymerization solution. In particular, the SEC analysis has been performed by using a Waters system consisting of a Waters 1515 pump, three μ-styragel separation columns with a continuous porosity of 10^2–10^5 Å and a Waters 2414 differential refractive index detector. The solvent was tetrahydrofuran and the flow rate was 1 mL/min. The calibration of the instrument was performed using polystyrene standards (M_w varying from 2500 to 900,000). The molecular characteristics of synthesized polystyrenes are given in Table 1.

Mid-infrared spectra in the region 500–$4000\ \mathrm{cm^{-1}}$ were obtained on a Fourier transform IR spectrometer (Equinox 55 from Bruker Optics), equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). One drop of polystyrene functionalized CNTs solution in THF was placed on the diamond element and the solvent was removed under a steam of nitrogen in order to produce a thin film of the material on the surface of the reflection element. Typically, 100 scans were acquired at $4\ \mathrm{cm^{-1}}$ resolution. UV–vis absorption spectra were recorded on a PerkinElmer (Lamda 19) spectrophotometer in the range 200–500 nm. Raman spectra were measured on a Fourier transform instrument (RFS 100 by Bruker Optics) employing ca. 250 mW of the Nd:YAG 1064 line in a back scattering geometry. The spectra were measured at $2\ \mathrm{cm^{-1}}$ resolution and typically represent averages of 3600 scans (9 sets of 400 scans). TEM imaging was carried out using a JEOL model JEM100C electron microscope, operated at 80KV accelerating voltage and under bright field conditions. The thermogravimetric analysis has been performed using a TGA Q500 V20.2 Build 27 instrument by TA Instruments in an inert atmosphere of nitrogen. In a typical experiment 1 mg of the material was placed in the sample pan and the temperature was equilibrated at 60 °C. Subsequently, the temperature was increased to 600 °C with a rate of 10 °C/min and the weight changes were recorded as a function of temperature.

Table 1
Influence of PS molecular weight and of CNTs type on the degree of polymer attachment on the nanotubes

Sample	M_w of PS	CNTs	%wt PS
CNT-PS-1	500	s-MWNTs	16
CNT-PS-2	3.000	s-MWNTs	35
CNT-PS-3	33.000	MWNTs	82
CNT-PS-4	3.000	SWNTs	30

3. Results and discussion

The synthesis of polystyrene functionalized CNTs has been performed through grafting-to approach of living polystyrene chains onto CNTs. The work of Viswanathan et al. has previously indicated that carbanions could react with the sidewall of carbon nanotubes [5]. However, it is well known that carbanions are very reactive and could be easily deactivated from the oxygen and the humidity of the atmosphere [4]. In order to take advantage of the ability of anion to react with CNTs and to ensure the stability of anions at the one end of polystyrene chains during the functionalization reaction, the whole procedure was performed under high vacuum. In particular, polystyrenes of different molecular weights were synthesized using standard techniques of anionic polymerization. The absence of the termination step in the aforementioned polymerization offers the ability of using the living polystyrene anions in the reaction with CNTs. Additionally, the custom made, sealed under high vacuum, glass apparatus, which have been used in all steps, ensure that the anions will not be deactivated during the functionalization reaction. Besides, similar procedures have already been demonstrated in another work where carbon nanohorns and polyisoprenyl lithium have been used [6]. The functionalization reaction took place by mixing the as prepared active macromolecules with CNTs, Fig. 1. The molecular characteristics of the used polystyrene chains are given in Table 1. The functionalization reaction has been performed in many different carbon nanotubes types. In particular shorted-MWNT (i.e. nanotubes with lengths not exceeding 500 nm), MWNT and SWNT have been used in the present study in order to ensure that this grafting-to approach is a general method for the effective functionalization of CNTs. The type of CNTs which have been used in any

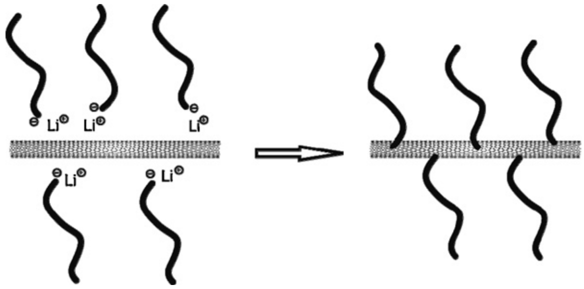

Fig. 1. Schematic illustration of the attachment of polystyrene on CNTs. Polymer chains and CNTs are not drawn in scale.