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Grafting Living Polymers onto Carbon Nanohorns

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Abstract: In the present paper we describe a new way for the covalent functionalization of carbon nanohorns by means of anionic polymerization with the “grafting to” approach. Polyisoprene homopolymers, as well as polyisoprene-*b*-polystyrene block copolymers have been attached on the surface of carbon nanohorns. The functionalized carbon nanostructures have been fully characterized by means of complementary spectroscopic techniques, electron microscopy, thermogravimetric analysis, and light scattering.

Keywords: block copolymers · carbon · nanohorns · polymerization

Introduction

Recently, living/controlled polymerization methodologies, including anionic polymerization,[1] atom-transfer radical polymerization,[2] and reversible addition–fragmentation chain transfer,[3] have received considerable attention for the modification of carbon nanotubes (CNTs). Blending of polymers with CNTs is expected to substantially increase not only the mechanical strength, but also the electrical and thermal conductivity of the polymeric material.[4] However, the significant content of metallic nanoparticles, remaining as impurity during CNTs production, together with the low miscibility of CNTs with polymeric matrices, hinder potential applications of CNT-based composite materials.

A new nanostructured material, namely carbon nanohorns (CNHs), within the family of fullerenes and CNTs, has lately been produced in bulk with high yield and purity.[5] Free from any transition-metal contaminants, CNHs self-aggregate forming a secondary spherical superstructure.[6] However, similar to CNTs, the insolubility of CNHs in all solvents has to be overcome before considering practical technological applications. Recently, in this context, substantial progress has been made towards solubilization of CNHs, based on the covalent functionalization of their skeleton[7] and highly strained cone-ends,[8] as well as by means of supramolecular π–π stacking interactions[9] with pyrenes and porphyrins. Nevertheless, the functionalization of carbon nanohorns with polymers has not yet been reported.

Living anionic polymerization is a unique synthetic methodology that allows the preparation of a plethora of novel polymeric materials through the controlled manipulation of macromolecular characteristics like molecular weight and architecture. Herein, we present the covalent functionalization of CNHs with a homopolymer and a well-defined diblock copolymer (Scheme 1). For the first time, living anionic polymerization is applied in the “grafting-to” approach for the covalent immobilization of pre-formed polymers onto the framework of CNHs,[10] although a functionalization methodology involving reactions between butyl lithium and CNTs has been reported.[11,12]

The aim of our work is to explore a new strategy for the polymer functionalization of CNHs that will complement the already existing ones. For the benefit of simplicity and to avoid redundancy, data presented throughout the manuscript are based on CNHs functionalized with the diblock copolymer of polystyrene-*b*-polyisoprene (abbreviated as CNH-SI), while data regarding CNHs functionalized with polyisoprene homopolymer (abbreviated as CNH-PI) are presented in the Supporting Information section.

Results and Discussion

The living polymers used in this work, namely, polyisoprenyl lithium and polystyrene-*b*-polyisoprenyl lithium were synthesized by anionic polymerization high vacuum techniques.[13] Briefly, sequential polymerization of styrene and isoprene (or only isoprene in the case of homopolymer) was

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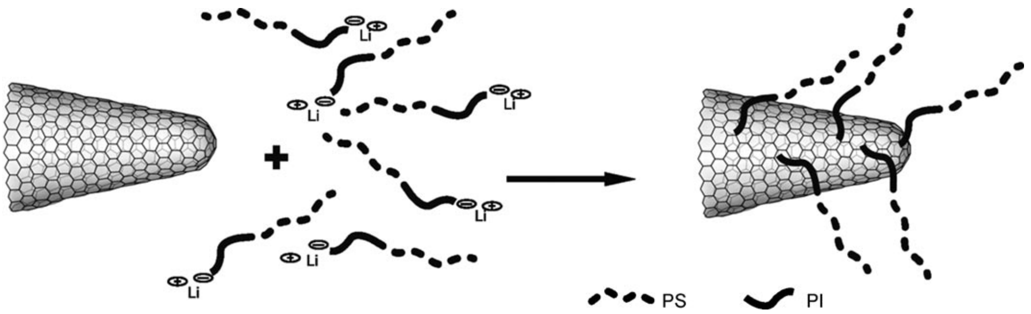

Scheme 1. Illustration of the addition of the diblock copolymer on the CNHs.

performed in benzene with *s*-butyl lithium as initiator. Subsequently, the anionic site of the polymer reacted directly with pre-dried CNHs resulting in the solubilization of the CNH-based conjugates. The polymer–nanohorn conjugates, namely CNH-SI and CNH-PI, were soluble in a variety of solvents depending on the polymer's solubility. In this context, CNH-SI was soluble in $CHCl_3$, THF, toluene, acetonitrile, ethyl acetate, and DMF, while CNH-PI only in $CHCl_3$, THF, and toluene. Importantly, in blank experiments, in which pristine CNHs and deactivated polystyrene-*b*-polyisoprene block copolymer or polyisoprene homopolymer were mixed together and treated under exactly the same experimental conditions as in the functionalization reaction (i.e., glass apparatus sealed under high vacuum, concentration, sonication time and power, reaction time, filtration process), precipitation of CNHs was observed within two days of preparation (Figure 1). This result directly confirms the covalent attachment of the living polymer onto the surface of CNHs and the stability of the hybrid nanomaterial.

The formation of the polymer-grafted CNH conjugates was followed by ATR-IR spectroscopy.[14] In this context, the characteristic peaks of the polymers, that is, at 2915 and at around 1400 cm^{-1} attributed to polyisoprene and at 696 cm^{-1} attributed to the polystyrene block, are observed in the spectrum of CNH-SI (Figure 2) and CNH-PI (see Supporting Information section, Figure S1) conjugates.

Figure 1. Photographical proof of soluble CNHs covalently functionalized with living polystyrene-*b*-polyisoprene block copolymer (right, after standing for one month) as compared with the insoluble CNHs (left) from the blank experiment, after standing for one month.

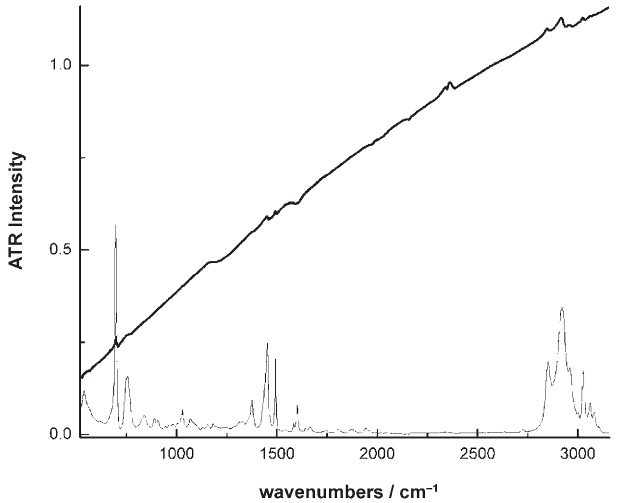

Figure 2. ATR-IR spectrum of CNH-SI (black) and diblock copolymer SI (gray).

Raman vibrational spectroscopy of the polymer-functionalized CNHs revealed the presence of the D- and G-bands, at 1272 and 1598 cm^{-1}, respectively (Figure 3). The G-band is assigned to the vibrations of the sp^2-hybridized carbons, while the D-band is associated not only with defect sites generated onto the network of CNHs upon the polymer grafting-to functionalization procedure, but also to the loss of the basal plane lattice periodicity of CNHs[15] and to sp^3 single-bonding carbon atoms existing within CNHs aggregates.[16] The small increase in the intensity of the D-band is assigned to the destruction of the fine nanohorn structure, due to the covalent attachment of the polymer chains. It has to be noted that the small increase in the D-band intensity is not directly connected with the amount of the polymer grafted on the CNHs. The aforementioned observation is a consequence of the high molecular weight of the polymer, that is, a large amount of polymeric material is attached on the nanohorn surface with only one covalent bond between the CNHs and the polymer chain end.

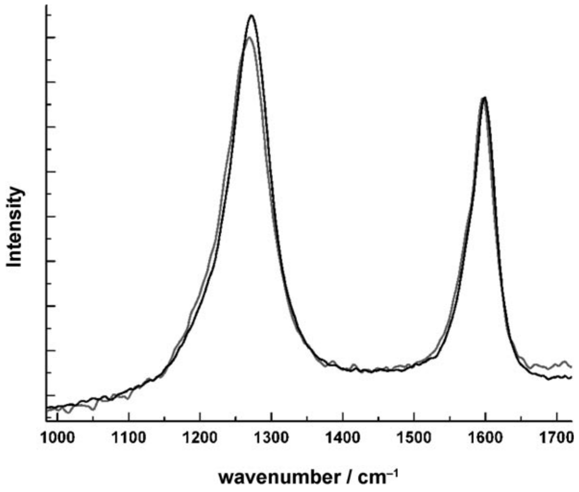

Figure 3. Raman spectra of pristine CNHs (gray) and CNH-SI (black). The intensity of pristine CNHs spectrum was normalized to the one of the functionalized CNHs.

The UV/Vis spectra of pristine CNHs and functionalized CNH-SI, recorded in acetonitrile (an organic solvent without significant absorbance in the whole UV/Vis region, even at wavelength lower than 300 nm) displayed differences in addition to the characteristic continuous absorbance of CNHs in the Vis region (see Supporting Information, Figure S2). In particular, the two discrete absorption peaks at 258 and 290 nm related to the pristine CNHs are not observed in the spectrum of the diblock functionalized material CNH-SI; instead, a new absorption at 265 nm and an upturn after 215 nm are discernable and attributed to the characteristic absorbances of the polystyrene block. It should be noted that polyisoprene-functionalized CNHs are not soluble in acetonitrile, because this solvent is not a thermodynamically good solvent for the polyisoprene.

High-resolution transmission electron microscopy (HR-TEM) and dynamic light-scattering (DLS) measurements were used to probe the morphological characteristics and particle size distributions of the CNH-based polymer conjugate material. Images of the polymer-functionalized CNHs obtained from transmission electron microscopy, reveal that the unique morphological features of CNHs are retained, that is, conical tips and dahlia flower-like assemblies with average diameters in the order of 80–130 nm (Figure 4 and Supporting Information, Figure S3). Although direct comparison of TEM images obtained between pristine and functionalized CNHs demonstrates similar morphologies, the polymer grafted CNHs are very soluble, in contrast to the insoluble pristine ones.

The apparent hydrodynamic radii of the polymer-functionalized CNHs determined by DLS measurements in various organic solvents, by using cumulant analysis, are presented in Table 1. Near monodisperse particles with a hydrodynamic radius of about 110 nm are identified in chloroform, THF, and toluene. However, when ethyl acetate or DMF were utilized for dissolving the block copolymer composite, larger particles were observed. The above observation is rationalized in terms of a secondary aggregation that occurs between the polymer-functionalized CNHs, due to PI's insolubility in these solvents. The above observation gives further proof for the creation of covalent bond between CNHs and polymers. In particular, in ethyl acetate, which is a good solvent for the polystyrene outer block, but a poor solvent for the polyisoprene inner block, the aggregates with a mean radius of about 180 nm are attributed to a secondary self-assembly process, due to the presence of the PI insoluble part in the composite material.

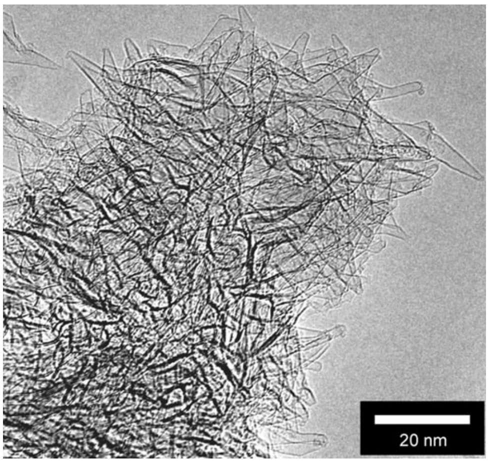

Figure 4. HR-TEM image of CNH-SI.

Table 1. Light-scattering data of CNH-PI and CNH-SI in different solvents using cumulants analysis.

	CNHs-PI		CNHs-SI	
	R_h [nm][a]	PD.I.[b]	R_h [nm][a]	PD.I.[b]
$CHCl_3$	104	0.045	109	0.199
THF	115	0.147	108	0.188
toluene	113	0.161	110	0.324[c]
ethyl acetate	insoluble	–	182.65	0.342
DMF	insoluble	–	124.20	0.217

[a] r_h = Apparent hydrodynamic radius. [b] PD.I. = polydispersity index. [c] The increased value of the PD.I. is attributed to an aggregation of the sample leading to a population at ≈950 nm. The population of these aggregates is considerably decreased upon further sonication as has been revealed by CONTIN analysis.

Furthermore, in the case of DMF (a strongly selective solvent for the polystyrene block and at the same time a very good dispersing agent for the CNHs), cumulant analysis gives a mean radius of about 125 nm. This value is also larger than in the case of good solvents for both of the blocks and is similar to the case of ethyl acetate. CONTIN analysis indicates the existence of supramolecular structures with radii ranging from 100 to almost 1000 nm in DMF (see Supporting Information, Figure S4). The above results are related to the complex interactions between the solvent, the diblock copolymer, and the CNHs and further indicate the covalent functionalization of the carbon nanostructures with polymer. It has to be mentioned that the polyisoprene-functionalized CNHs are not soluble in ethyl acetate and DMF, because PI itself is not soluble in the above solvents. Finally, DLS results and TEM images indicate particles with almost the same dimensions.

The amount of the polymer grafted onto the skeleton of CNHs was evaluated by themogravimetric analysis (TGA). CNHs show very good thermal stability up to 600 °C under an inert argon atmosphere, while the presence of the grafted polymer onto CNHs is verified by the decomposition occurring in this temperature range (Figure 5). TGA measurements demonstrated that approximately 25 wt % of the CNH-SI conjugates is due to the block copolymer.[17] However, it should be noted that given an overall molecular weight of the polymer equal to 50000, the functionalization percentage of the CNHs with polymer is calculated to be approximately 8×10^{-3} %. The above results are in agreement with the small increase observed in the D-band of the Raman spectrum.

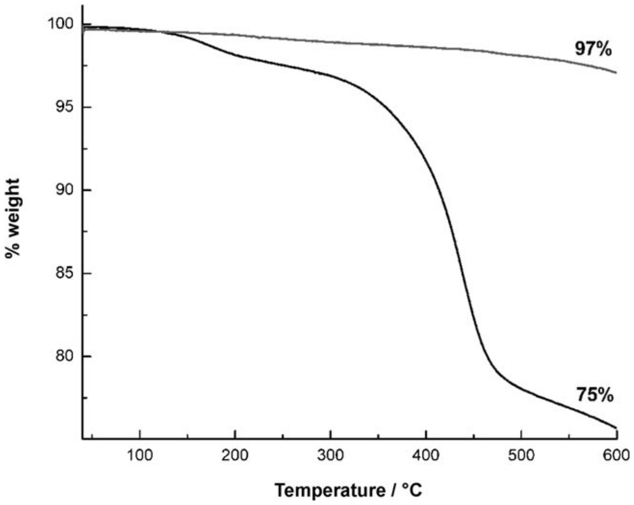

Figure 5. Thermogravimetric analysis graph of CNH-SI (black) and pristine CNHs (gray).

Conclusion

In conclusion, a methodology for the surface functionalization of CNHs based on the grafting-to approach has been achieved through addition of living anionic (co)polymer chains. The success of functionalization was demonstrated by ATR-IR, UV/Vis, and Raman spectroscopy, as well as TGA, while the secondary spherical superstructure of CNHs was imaged by HR-TEM. The CNH conjugates obtained show enhanced solubility in common organic solvents, which allowed their investigation by DLS. Further work utilizing specially designed multiblock copolymers for the functionalization of CNHs is underway, targeting at the generation of smart CNH-based nanomaterials suitable for technological applications.

Experimental Section

The synthesis of the living polymers was performed in an all-glass homemade apparatus. All reagents were purified following standard methods used in the anionic polymerization high-vacuum technique.[12] In the case of the living diblock, sequential polymerization of the styrene monomer followed by the polymerization of isoprene took place. At the end of polymerization, the desired amount of living block copolymer in benzene was isolated in ampoules, under high vacuum, as a solution in benzene (0.1 g mL^{-1}). The addition reaction of the polymer on the surface of the CNHs was preformed in another all-glass apparatus, in which an ampoule with the polymer (1 g of polymer) and an ampoule with a pre-dried amount of CNH (16.4 mg) were connected. The reaction was preformed in benzene at 40 °C for 1 day under high vacuum. At the beginning of the reaction 5 min sonication was needed in order to ensure the homogeneous dispersion of the CNHs. The reaction was terminated by the addition of degassed methanol. The solid reaction products were 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 100 nm in order to remove unreacted polymer chains. The polymer-functionalized CNHs were washed with toluene (2×50 mL) and THF (4×50 mL) and were left to dry under vacuum.

Characterization of the polymers, that is, determination of the molecular weight, polydispersity, and composition of the deactivated living polymers, were performed by size exclusion chromatography (SEC) and NMR spectroscopy. In particular, the SEC analysis was 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^{-1}. The calibration of the instrument was performed using polystyrene standards (M_w varying from 2500 to 900000). Moreover, ^{1}H NMR (300 MHz) spectra of the diblock SI were recorded on a Bruker AC300 instrument at 25 °C by using $CDCl_3$ as the solvent. The molecular characteristics of the samples are a) SI diblock copolymer: $M_w=50.000$, $M_w/M_n=1.03$, 68 wt % polystyrene and b) PI homopolymer: $M_w=23.000$, $M_w/M_n=1.03$.

Mid-infrared spectra in the region 500–4000 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 polymer-functionalized CNH solution in THF was placed on the diamond element and the solvent was removed under a steam of nitrogen in order to have a thin film of the material on the surface of the reflection element. Typically, 100 scans were acquired at 4 cm^{-1} resolution. Raman spectra were measured on a Fourier transform instrument (RFS 100 by Bruker Optics) employing about 250 mW of the Nd:YAG 1064 line in a back scattering geometry. The spectra were measured at 2 cm^{-1} resolution and typically represent averages of 3600 scans (9 sets of 400 scans). UV/Vis absorption spectra were recorded on a Perkin Elmer (Lamda 19) spectrophotometer in the range 200–500 nm. HR-TEM imaging was carried out using a 002B Topcon electron microscope operated at an accelerating voltage of 120 kV. Light-scattering experiments were performed on a ALV/CGS-3 Compact Goniometer System (ALV GmbH, Germany), using a JDS Uniphase 22 mW He-Ne laser, operating at 632.8 nm, interfaced with a ALV-5000/EPP multi-tau digital correlator with 288 channels and a ALV/LSE-5003 light scattering electronics unit for stepper motor drive and limit switch control. The raw data were analyzed by the Contin and the cumulants algorithms. Apparent hydrodynamic radii, R_h at different solvents were calculated by using the Stokes-Einstein equation. The thermogravimetric analysis has been performed using a TGA Q500 V20.2 Build 27 instrument by TA 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^{-1} and the weight changes were recorded as a function of temperature.

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