

Radical Addition of a Conjugated Polymer to Multilayer Fullerenes (Carbon Nano-onions)

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Multilayer fullerenes (carbon nano-onions, CNOs) represent a largely unexplored carbon allotrope due to their inherent insolubility. Expectations are that the properties of these nano-onions will be unique and potentially useful, as has been the case with the fullerenes and carbon nanotubes (CNTs). CNOs show diminished chemical reactivity; however, the established thermal diradical formation and reactivity of bis-*o*-diynyl arene (BODA) monomers afforded direct functionalization, solution processing, and defunctionalization of CNOs; and the first example of a radical addition of a conjugated polymer to CNOs. The functionalized and soluble CNOs were characterized by TEM, GPC, TGA, Raman spectroscopy, and XPS. A CNO defunctionalization method using oxidative TGA is also presented.

Introduction

While carbon nanotubes (CNTs) have received and continue to receive significant attention due to their many potential applications, the field of multilayer fullerenes (carbon nano-onions, CNOs) still remains in its infancy. Such exotic structures are expected to show interesting and unique properties, in part superimposed with those of fullerenes and carbon nanotubes, with great potential in a wide range of different applications including optical limiting,¹ catalysis,² gas storage,³ additives for aerospace applications,^{4,5} nickel-based composite coatings,⁶ solar cells and light-emitting devices,^{7,8} and fuel-cell electrodes.⁹

CNOs are insoluble in organic and inorganic solvents, similar to single-walled carbon nanotubes (SWNTs). Therefore, to gain access to the fundamental chemical properties of CNOs, their chemical derivatization is desired to enable their solubility and processability. Chemical connection of functional molecules will ultimately lead to new property understanding. After the discovery¹⁰ of CNOs, the lack of

solubility hindered study of their chemical and physical properties for many years, before the first solubilized CNOs were reported.¹¹

Recently, Rettenbacher, Echegoyen, and co-workers reported the first account of functionalized CNOs and laid the foundation for future chemistry on CNOs.¹² Two successful methods for the exohedral functionalization of CNOs are reported therein, including generation and functionalization of defect sites by oxidation and subsequent conversion into derivatives such as amides and PEGylation, and direct chemical functionalization using the 1,3 dipolar cycloaddition of an azomethine ylide.

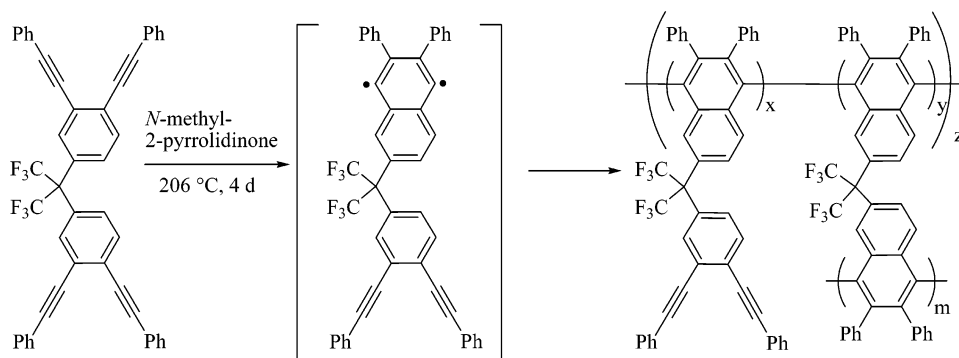
Each of these methods has an analogue in the known chemistry of CNTs. Another direct method, widely used with CNTs, is the addition of aryl radicals formed by the reduction of aryl diazonium salts. Attempts to use the diazonium salt reduction approach (both in solution and solvent-free), which works very well for CNTs,^{13–16} failed for CNOs (see Supporting Information). The reaction of CNOs with in situ generated phenyl radicals (aniline + isoamyl nitrite) yielded, essentially quantitatively, unreacted starting material, with no evidence of CNOs in the soluble fraction of the reaction mixture. Apparently, the radical reaction that works very well with CNTs fails with large-sized CNOs. This may be attributed to a decrease in the chemical reactivity of the CNOs surface as the curvature of the external graphitic sheet decreases, and the stability of the sp² carbon surface increases with CNO size. It has been previously reported¹³ that small-

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Scheme 1. Synthesis of BODA-Derived Oligomer



diameter SWNTs (ca. 0.7 nm)¹⁷ are expected to display enhanced reactivity relative to the larger diameter tubes since the reactivity of C₆₀ has been attributed in part to curvature strain.^{18,19} Another reason why the diazonium chemistry does not work on CNOs but on SWNTs might be the fact that a preceding injection of an electron from the SWNT to the diazonium species is required.²⁰ In that case, CNOs obviously would not be as prone to oxidation as are the SWNTs. To determine whether the failure of the diazonium approach depends upon oxidation/reduction potentials, we attempted the Billups protocol²¹ on our CNOs (see Supporting Information). With this method, free radicals are generated by decomposition of benzoyl peroxide and would not depend at all on the oxidation potential of CNOs. Our results indicated that the CNOs are not reactive using the Billups protocol and only unreacted CNOs were recovered.

However, the diradical formation and reactivity of bis-*o*-diynyl arene (BODA) monomers and growing oligomers, currently under study within our laboratories,^{22–24} present an excellent opportunity to directly functionalize the less reactive large-sized CNOs. Aryl radicals are known to have a very short lifetime;²⁵ however, BODA-derived aryl radicals have been shown to have remarkably long lifetimes by EPR.²² BODA monomers are a class of enediyne compounds which undergo Bergman cyclization²⁶ (see Scheme 1) when heated to form naphthyl diradical species,²² which then react with other monomers to propagate polymerization.

BODA monomers have variable functionality at both the bridging group (e.g., C(CF₃)₂) and the alkyne terminal groups (e.g., Ph). The polymer has a large processability window compared to other enediyne-based polymers^{22–24} due to the solubilizing effect of branched intermediate oligomers containing unreacted enediynes. The polymer remains fully conjugated both as an oligomer and as a complete polymer network, and the conjugation length may be tuned based on reaction temperature and time.^{22,24} BODA-derived polymers are wide band absorbers of light depending on molecular weight and appear deep red to brown at higher molecular weights. Therefore, BODA-derived polymers may be potentially good donors for photovoltaic applications.

Experimental Section

Materials. All chemicals were analytical grade and used as received without further purification unless otherwise specified. BODA monomers were prepared as previously described in detail elsewhere.^{22,24} Synthesis and purification of carbon nano-onions (CNOs) were described in detail elsewhere.¹² The copper grids for TEM were purchased from SPI Supplies (300 mesh Cu grid, lacey carbon coated).

Transmission Electron Microscopy (TEM). The size and morphology of the products were observed using an Hitachi Model NANO H9500 transmission electron microscope for high-resolution images (HRTEM, 300 kV) and an Hitachi Model 7600 transmission electron microscope for low-resolution images (LRTEM, 120 kV). The specimens were prepared from solution or dispersion by placing a drop onto a Cu grid. Prior to TEM experiments, the grids were dried at 100 °C under high vacuum and stored in a desiccator.

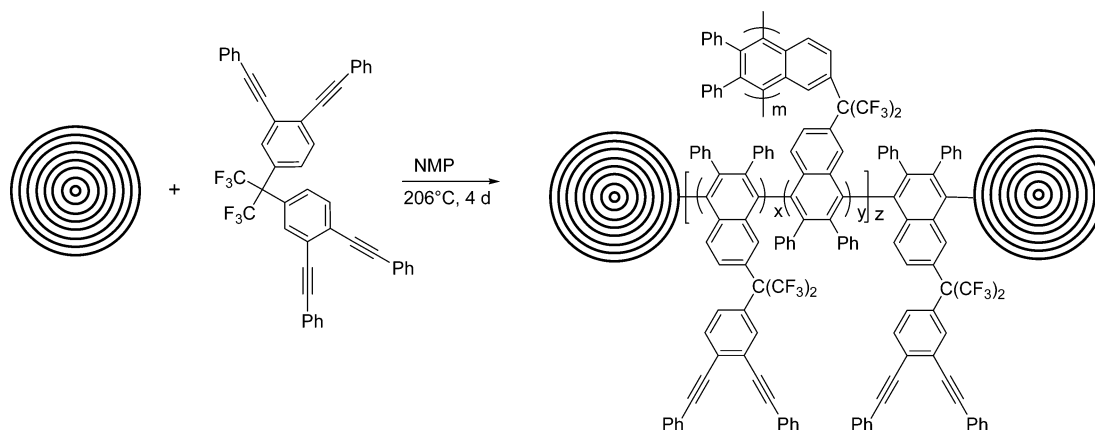
Gel Permeation Chromatography (GPC). GPC was carried out using a Waters Alliance system equipped with Refractive Index and UV/Vis Photodiode Array detectors. Columns used consist of PLGel 5 μm Mixed-D and Mixed-E from Polymer Laboratories connected in series. The columns were calibrated against ten narrow polystyrene standards (MW = 377400–580) from Polymer Laboratories.

Thermal Gravimetric Analysis (TGA) Scans. TGA of the samples were conducted on a Mettler TGA/SDTA851^c. In a typical experiment, a functionalized CNO sample (typically around 10 mg) was loaded into an alumina pan under constant nitrogen (air) flow (50 mL/min). The temperature ceiling was set at 1100 °C, with a relatively slow scanning rate (3 °C/min) to ensure a complete thermal defunctionalization.

Raman Spectroscopy. The Raman spectra were recorded using a Renishaw 1000 Raman spectrometer with the 785 nm emission line of a near-infrared laser as the excitation source. In all cases, a small amount of the solid compound was placed onto a glass slide

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Scheme 2. Synthesis of BODA–CNO Copolymer



and placed beneath the laser beam. All spectra were recorded under the same conditions (objective lens $\times 50$, detector gain on high, time 30 s, laser power 25, number of accumulations 3).

X-ray Photoelectron Spectroscopy (XPS). XPS analyses were performed with a Kratos model Axis 185 spectrometer using focused (diameter of the irradiated area, 300 μm) monochromatic Al K α radiation (12 kV, 6 mA). The residual pressure inside the analysis chamber was 2×10^{-8} Pa.

Synthesis of BODA Oligomers. BODA monomer (101.3 mg) was dissolved in *N*-methyl-2-pyrrolidinone (NMP, 1 mL) and refluxed for 4 days in a pressure vessel immersed in a sand bath heated to 240 °C. After cooling to room temperature, the resulting transparent deep orange solution was evaporated to dryness at 100 °C under high vacuum. The remaining orange residue was extracted 5 times with ether, so the final washing remained colorless. After drying at 150 °C under high vacuum overnight, 39.4 mg of an orange black solid was obtained. The compound is freely soluble in organic solvents like CHCl_3 or THF. Thin-layer chromatography (silica, NMP/ $\text{CH}_2\text{Cl}_2 = 1/1$) shows a single yellow spot at $R_f = 0.95$.

Synthesis of BODA–CNO Copolymers. In a typical experiment, a suspension of an annealed (1 h, 400 °C), nitric acid-treated (3 M, 48 h reflux), again annealed (1 h, 400 °C), and supercritical water-treated sample of CNOs (20.0 mg) with 4,4'-(perfluoropropane-2,2-diyl)bis(1,2-bis(phenylethynyl)benzene) (BODA 6F Ph, 40.0 mg) in NMP (1 mL) was ultrasonicated for 30 min and thereafter refluxed for 4 days in a pressure vessel immersed in a sand bath heated to 240 °C. After the mixture was cooled to room temperature, the resulting black-green suspension was centrifuged for 18 h, the clear greenish supernatant decanted, and the remaining black residue sonicated with 3 mL of NMP for 5 min. After four additional centrifuging/decanting steps (until the supernatant NMP solution remained colorless), the remaining black residue was treated twice with ether (3 mL each) to ensure the complete removal of the high boiling NMP. After drying in the vacuum oven at 200 °C until the weight became constant, 12.8 mg (64%) of unreacted CNOs (*solid 1*) were recovered.

The collected dark-colored NMP solutions of BODA-functionalized CNOs were evaporated to dryness under high vacuum at 100 °C. The black residue was treated (sonication, centrifugation) with ether (2 mL) until the supernatant remained colorless (three cycles were needed therefore). The pale yellow ether washings did not show any CNOs by TEM and consisted mainly of unreacted BODA monomer.

The same procedure was repeated with CHCl_3 (four cycles of 2 mL treatments were needed). The deep red solutions were collected and filtered (0.45 μm dp PP WHATMAN) before evaporating to dryness. To ensure the total removal of the high boiling NMP, the

resulting black residue was suspended in 5 mL of ether, sonicated for 30 min, and centrifuged, the colorless supernatant decanted, and the dark residue dried at 150 °C under high vacuum for 48 h. This procedure yielded 25.8 mg of black *solid 4*. The solubility of *solid 4* was determined to be 259 mg/mL in CHCl_3 (Supporting Information). Thin-layer chromatography (silica, NMP/ $\text{CH}_2\text{Cl}_2 = 1/1$) showed a single dark spot at $R_f = 0.00$. Free polymer ($R_f = 0.95$) could be removed by excessive ether washings (the free polymer was only slightly soluble in ether) or by washings in a mix of ether/ CHCl_3 9/1.

To ensure that the black residue obtained after the chloroform washings (*solid 3*) was still soluble, it was sonicated in 10 mL of NMP, filtered (0.45 μm dp PP WHATMAN), and centrifuged for 48 h. After evaporation of the deep black solution (no residue could be found after the centrifugation) to dryness under high vacuum at 100 °C and one treatment with ether (2 mL), 4.7 mg of a black powder *solid 3* was obtained after drying at 150 °C under high vacuum. The solubility of *solid 3* was determined to be 0 mg/mL in CHCl_3 and 6 mg/mL in NMP (Supporting Information). Thin-layer chromatography (silica, NMP/ $\text{CH}_2\text{Cl}_2 = 1/1$) showed a single dark spot at $R_f = 0.00$.

Results and Discussion

Synthesis of BODA–CNO Copolymer. A twofold excess of BODA monomer to CNOs in refluxing *N*-methyl-2-pyrrolidinone (NMP, bp = 206 °C) and long reaction times (4 days) gave the best results for preparation of BODA–CNOs copolymer (Scheme 2). Under these conditions, BODA–CNOs copolymer yields did not improve after 3–4 days. At higher temperatures the BODA oligomers prematurely cross-link and the solubility of the resulting BODA–CNOs network reduces to zero. Lower temperatures slow the reaction excessively, due to the lower free radical concentration. Workup of the reaction mixture as illustrated in Figure 1 led to three different solid compounds: Unreacted CNOs starting material *solid 1*, partially BODA-functionalized CNOs *solid 3* (soluble in NMP only), and highly BODA-functionalized CNOs *solid 4* (soluble in both NMP and CHCl_3). In all cases, the copolymer products can be liberated from unreacted BODA monomer and BODA-derived polymer simply by applying different solvents as outlined in the Experimental Section. To ensure the conjugated polymer is indeed bound to the CNOs through a covalent linkage, a control mixture of CNOs and free polymer were mixed and sonicated and resulted only in

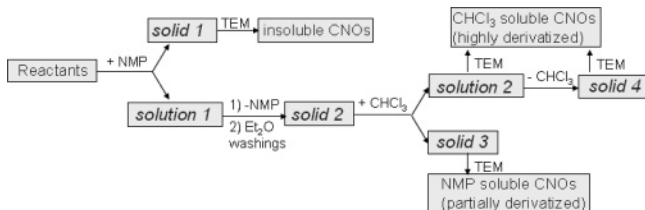


Figure 1. Process flow chart for 40.0 mg of BODA monomer and 20.0 mg of CNOs in 1 mL of NMP, resulting in 12.8 mg of *solid 1*, 4.7 mg of *solid 3*, and 25.8 mg of *solid 4*.

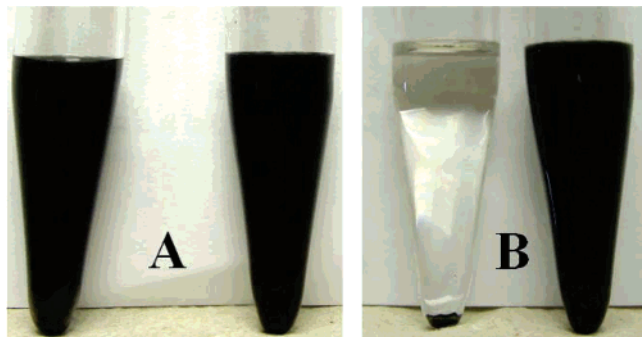


Figure 2. (A) Left vial: CNO starting material suspended in NMP (0.67 mg/mL); right vial: BODA-functionalized CNOs solubilized in NMP (0.67 mg/mL). (B) Left vial: CNO starting material suspended in NMP (0.67 mg/mL) after 2 h of centrifugation; right vial: BODA-functionalized CNOs solubilized in NMP (0.67 mg/mL) after 48 h of centrifugation.

insoluble CNOs (see Supporting Information). Each of these compounds was examined by GPC, TEM, TGA, XPS, and Raman spectroscopy. To compare the data obtained from BODA-functionalized CNOs with pure oligomeric BODA, a BODA monomer/oligomer control was submitted to the same reaction and workup conditions (Scheme 1).

Characterization Using TEM. A first proof of successful functionalization was the solubility test (Figure 2) in combination with TEM. The CNOs starting material (*solid 1*) is completely insoluble in NMP, whereas the BODA-CNOs (*solid 3*) remain soluble after long centrifugation times. The same holds true for the CHCl_3 -soluble BODA-functionalized CNOs (*solid 4*). Solutions of *solid 4* in CHCl_3 are deep orange in color, while solutions of *solid 3* in NMP are green black. Low-resolution TEM images of dilute solutions of *solid 3* (in NMP) and *solid 4* (in CHCl_3) are shown in Figures 3 and 4, respectively. Figure 5 depicts a high-resolution TEM image of *solid 4*; the BODA-functionalized CNO is round-shaped, vicinal to, and partially overlapped with other CNOs. The rings of the CNOs are clearly resolved and about 20 shells can be counted. This shows unequivocally that the radical addition reaction of the BODA oligomers is able to solubilize the CNOs and demonstrates the first radical addition to multilayer fullerenes in general.

Characterization Using Gel Permeation Chromatography. GPC chromatograms for the BODA oligomer control and BODA-CNO copolymer are shown in Figure 6. The BODA oligomer control (Figure 6 top) exhibits a higher average molecular weight relative to polystyrene and much broader polydispersity, due to branching, than does the copolymer as expected. The GPC data for the BODA-CNO copolymer (11 wt % CNO, see Table 1) indicated that monomer homopolymerization is limited due to the compet-

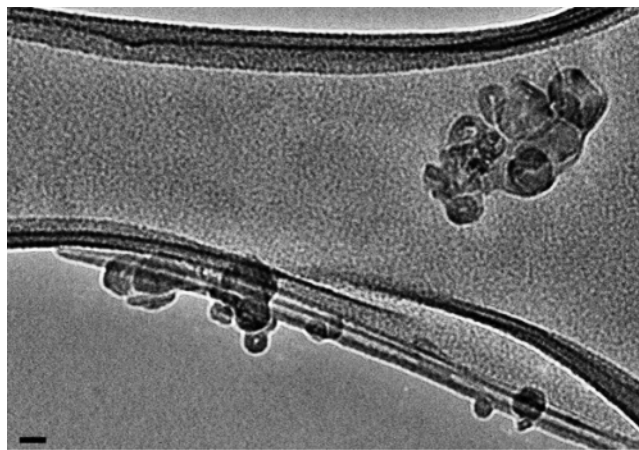


Figure 3. LRTEM (120 keV) image of *solid 3*; scale bar represents 20 nm.

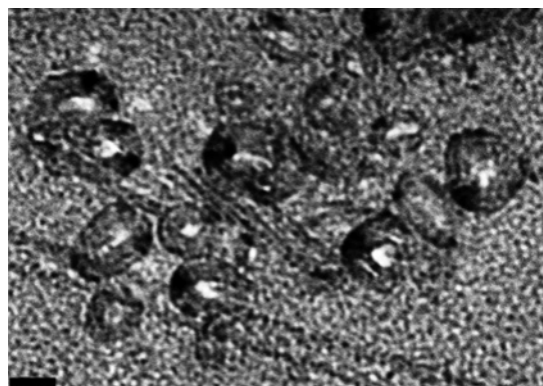


Figure 4. LRTEM (120 keV) image of *solid 4*; scale bar represents 20 nm.

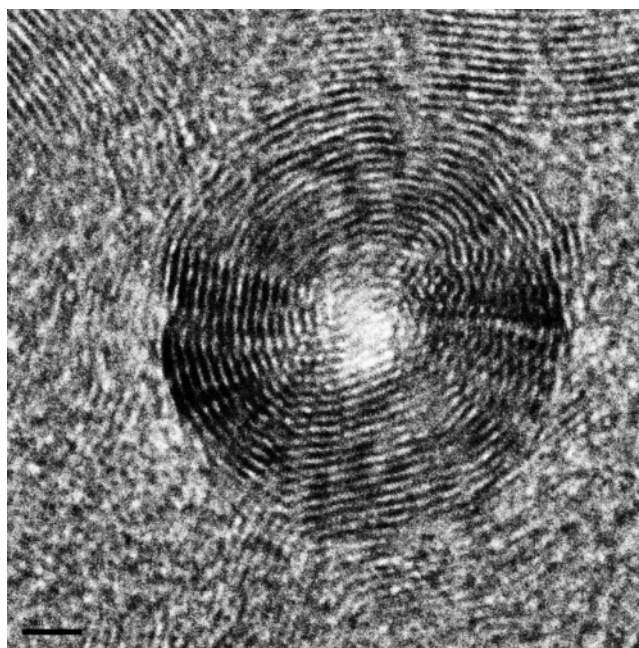


Figure 5. HRTEM (300 keV) image of BODA-CNO copolymer *solid 4* (CHCl_3 solution); scale bar represents 2 nm.

ing reaction with the CNOs. The polydispersity for the co-reaction is lower and the CNOs serve as an effective chain transfer agent (Figure 6 bottom). These two polymerizations were both performed under identical conditions and concentrations. Enchainment of the large CNO molecules does

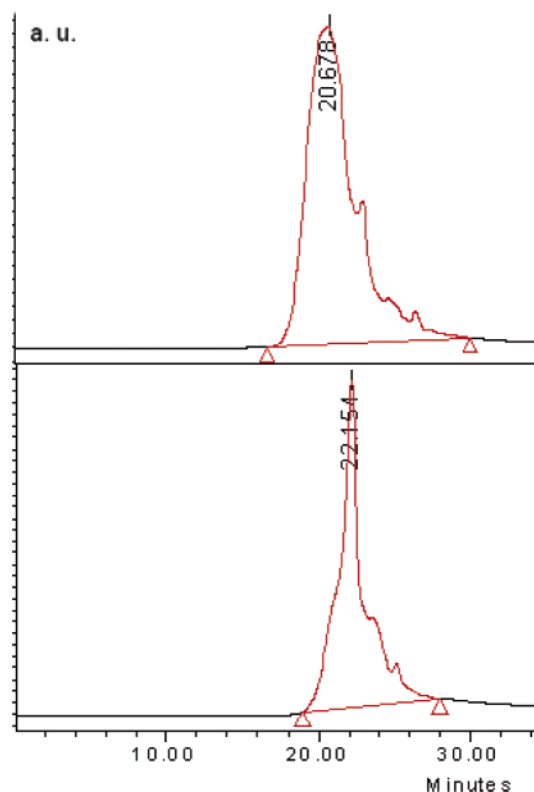


Figure 6. GPC data for BODA oligomer control (top) and BODA–CNO copolymer *solid 4* (bottom); CHCl_3 solutions (1 mg/mL) on Polymer Laboratories PLGel 5 μm Mixed-D and Mixed-E Columns at 1 mL/min.

Table 1. Mass Balance of BODA-Functionalized CNOs; Percentages Given Can Be Obtained from the Corresponding TGA Data

compound	[mg]
BODA monomer (starting material)	40.0
CNOs (starting material)	20.0
CNOs in 12.8 mg of <i>solid 1</i> (100%)	12.8
CNOs in 4.7 mg of <i>solid 3</i> (79%)	3.7
CNOs in 25.8 mg of <i>solid 4</i> (11%)	2.9
total sum of CNOs recovered	19.4
BODA oligomer in 12.8 mg of <i>solid 1</i> (0%)	0.0
BODA oligomer in 4.7 mg of <i>solid 3</i> (21%)	1.0
BODA oligomer in 25.8 mg of <i>solid 4</i> (89%)	22.9
total sum of BODA oligomers	23.9

not increase the GPC relative molecular weight dramatically as might be expected. We have observed that the effective hydrodynamic volumes (vs polystyrene) of multilayer fullerene derivatives¹² are compact and exhibit long retention times by GPC, and therefore appear to have lower molecular weights when compared to less compact standards of solvated linear polymers, such as the polystyrene used here.

UV–vis data as extracted from the photodiode array detector of GPC-separated BODA control are shown in Figure S2 (Supporting Information) at several retention times. As the polymer is formed, the absorbance λ_{max} settles at 243–244 nm. The BODA copolymer retains the absorbance λ_{max} at 242 nm, but has a distinct λ_{max} at 265–273 nm (Figure S3, Supporting Information).

Characterization Using TGA and Raman Spectroscopy.

Another method to prove the existence of CNOs in the soluble samples is by thermal defunctionalization under inert gas, which has been described with PEGylated carbon SWNTs²⁷ and CNOs.¹² This of course requires that the temperature necessary for the removal of the carbon onion-

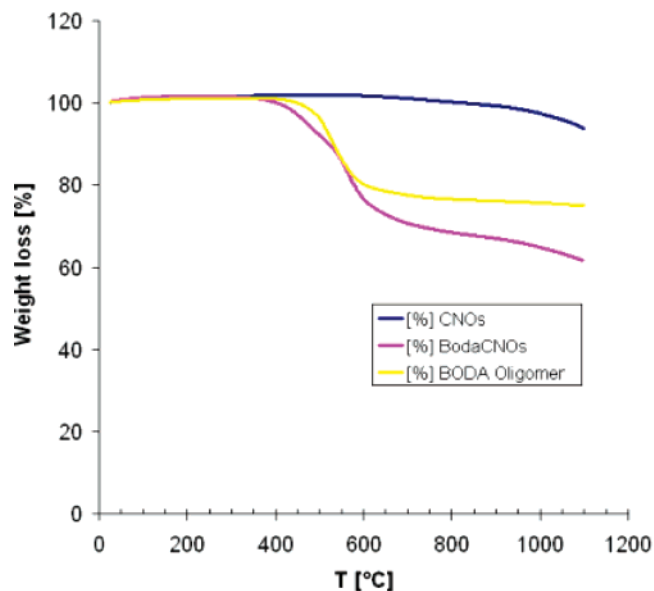


Figure 7. TGA (3 °C/min) of BODA–CNO copolymer (red line), compared to TGA of CNOs (blue line) and oligomeric BODA (yellow line).

bound functional groups (oligomeric BODA) is suitably lower than the decomposition temperature of the CNOs to enable the selective removal of the functional groups in a thermal gravimetric analysis (TGA) scan. Figure 7 shows a TGA scan under N_2 for the BODA-functionalized CNOs *solid 4* in comparison to pure CNOs starting material and oligomeric BODA. Oligomeric BODA alone loses ca. 20% of its original weight under N_2 , starting at about 410 °C. On continued heating, a minimal loss is observed, implying further carbonization and/or graphitization as previously reported.²² Obviously, even if the functionalized CNOs were fully defunctionalized under these conditions, the final mixture obtained after the TGA experiment will most likely be dominated by glassy carbon—the end product of the pyrolysis of BODA polymers.

This can be seen by comparing the Raman spectra of CNOs starting material with the residues of oligomeric BODA and BODA-functionalized CNOs after a TGA experiment to 1100 °C in N_2 (Figure 8). Glassy carbon dominates the Raman spectrum of the pyrolyzed copolymer (Figure 8, bottom). Magnification of the wavenumber range around 2600 cm^{-1} shows the CNOs still to be present in the thermolyzed BODA CNOs sample (inset Figure 8 bottom) which are dominated by the much stronger BODA-derived carbon bands. The maximum of 2616 cm^{-1} matches well with the one found for *solid 4* (Figure 11 top). A detailed description for the D and G bands occurring in CNOs and graphitic materials is given elsewhere.¹²

In contrast, heating the same samples in air provides a better defunctionalization method (Figure 9). CNOs show an onset degradation temperature of 470 °C in air, whereas BODA networks show an onset of weight loss at 390 °C in the oxidative atmosphere. This difference of 80 °C was sufficient to separate and isolate the pure CNO starting material from the BODA network. At 490 °C (see the vertical

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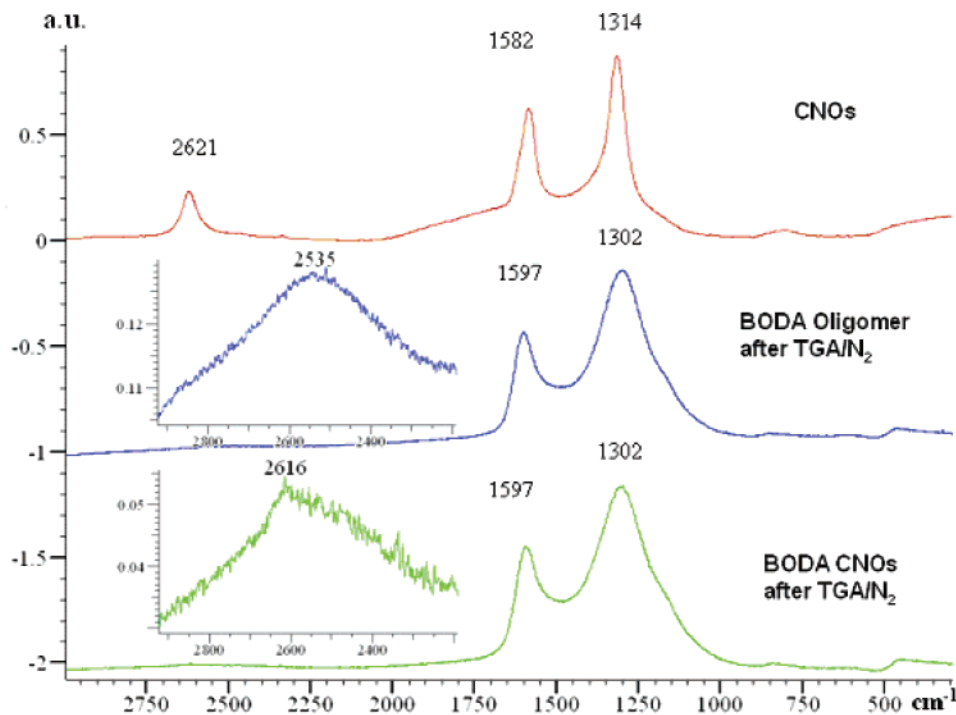


Figure 8. Raman of CNO starting material (top), oligomeric BODA after a TGA/N₂ (middle), and BODA–CNO copolymer after a TGA/N₂ (bottom). The insets show a magnification of the range around 2600 cm⁻¹.

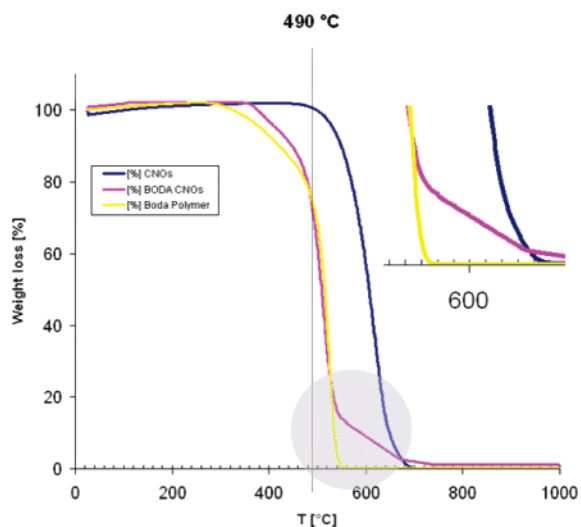


Figure 9. TGA (3 °C/min, 50 mL air/min) of BODA–CNO copolymer (red line), compared to TGA of CNOs (blue line) and oligomeric BODA (yellow line).

line and inset in Figure 9) the oligomeric BODA starts to burn off quickly, whereas the CNOs oxidize much slower. Therefore, isothermal heating for 1 h at 490 °C in air of the BODA–CNO copolymer *solid 4* allowed for isolation of the CNOs (Figure 10). The constant mass remains of *solid 4* (11%) were obtained as a black powder which was not soluble in any organic solvent.

A Raman spectrum of the recovered black powder compared to those of CNOs starting material and the original BODA–CNO copolymer *solid 4* revealed the success of the functionalization process as well as the subsequent oxidative thermal defunctionalization. Figure 11 clearly shows that, after heating, the BODA network was eliminated. The BODA–CNO copolymer sample *solid 4* yields a broad continuum (Figure 11 middle) in contrast to the visible

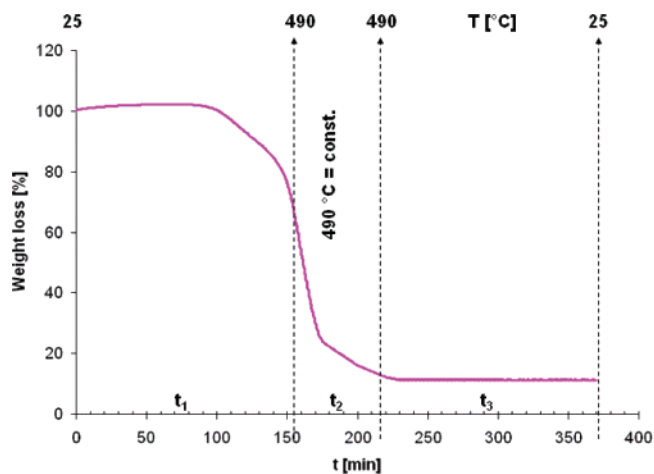


Figure 10. TGA (3 °C/min, 50 mL air/min) of BODA–CNO copolymer *solid 4*: $t_1 = 0$ –155 min (25 °C to 490 °C, 3 °C/min); $t_2 = 156$ –216 min (490 °C = constant for 60 min); $t_3 = 217$ –372 min (490 °C to 25 °C, –3 °C/min).

discrete peaks from the unfunctionalized CNOs (Figure 11 bottom). The same effect can be seen and was described in the Raman spectra of PEGylated CNOs¹² and nanotubes.²⁷

Figure 1 shows there is one part (*solid 3*) of the BODA–CNOs which exhibits different solubility than the other part (*solid 4*). *Solid 3* is soluble only in the highly polar NMP and is composed of partially functionalized CNOs. *Solid 4* is also soluble in the less polar CHCl₃ and represents highly functionalized CNOs. Evidence for this can be seen in the Raman spectrum of *solid 3* (Figure 12 middle), compared to the Raman spectra of *solid 4* (Figure 11 middle) and CNOs starting material (Figure 12 bottom). Where the CNOs are more highly functionalized, the broad continuum of the BODA oligomers dominates the weaker Raman bands of the CNO cage (Figure 11 middle). The less functionalized the CNOs are (as in *solid 3*), the more likely the weaker Raman

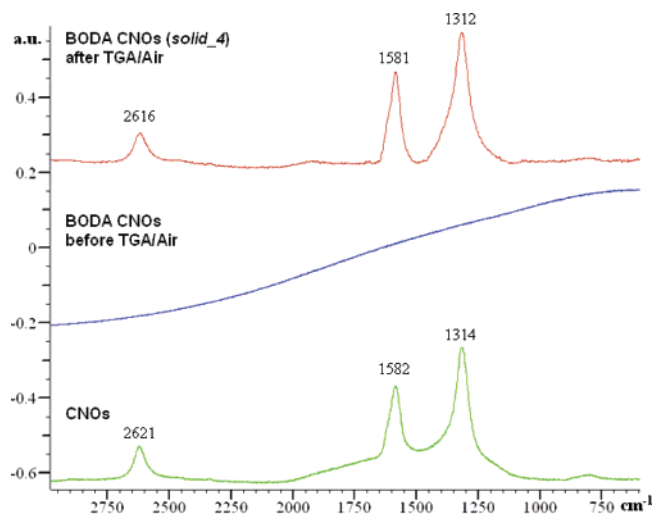


Figure 11. Raman of CNOs starting material (bottom), BODA–CNO copolymer *solid 4* before TGA/air experiment (middle), and BODA–CNO copolymer *solid 4* after TGA/air (top).

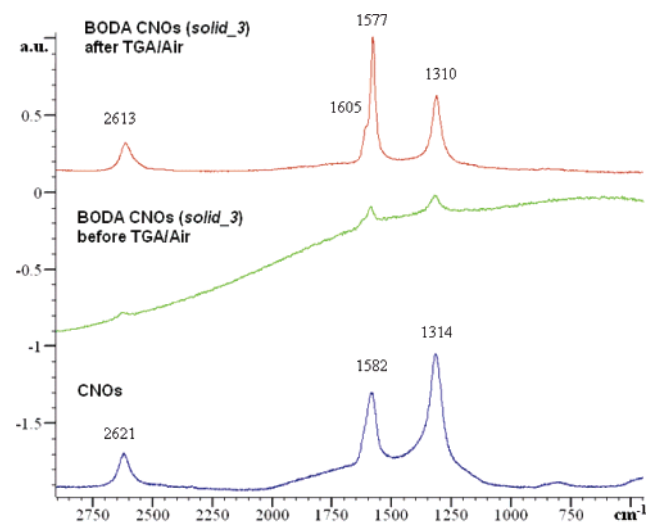


Figure 12. Raman of CNOs starting material (bottom), BODA–CNO copolymer *solid 3* before TGA/air (middle), and BODA–CNO copolymer *solid 3* after TGA/air (top).

bands for the CNOs cage can be seen (Figure 12 middle).

The same procedure that has been used before for *solid 4* (TGA in air, holding at 490 °C for 1 h) was applied to *solid 3* (Supporting Information, Figure S4). This time 79% of the original sample of BODA CNOs *solid 3* was obtained as a black powder, which again was not soluble in any organic solvent. This implies that only 21% w/w of *solid 3* can be attributed to the BODA network, compared to 89% w/w of *solid 4*. This is consistent with the Raman spectrum of *solid 3* (Figure 12 middle) compared with the broad continuum in the Raman spectrum of *solid 4* (Figure 11 middle). A Raman spectrum of the remaining 79% of *solid 3* after the TGA/air experiment (Figure 12 top) compared to CNOs starting material (Figure 12 bottom) and *solid 3* before the TGA/air experiment (Figure 12 middle) revealed the success of the total oxidative thermal defunctionalization.

Table 1 gives the mass balance for the process shown in Figure 1 and subsequent methods described. This procedure found that 19.4 mg of pure CNOs out of 20.0 mg CNO

starting material could be recovered as unreacted CNOs *solid 1* and defunctionalized CNOs from *solid 3* and *solid 4*. Likewise, 23.9 mg out of 40.0 mg of BODA monomer reacted with the CNOs, whereas the rest could be easily removed by washing the BODA–CNO copolymers with ether. This proves that a BODA monomer/CNOs ratio of 2/1 should be sufficient to achieve functionalization, processing, and isolation via this method.

Characterization Using XPS. To gain further proof of functionalization, we checked for the presence of fluorine by XPS (Figure S5, Supporting Information). Comparing the XPS spectra of pristine CNOs (Figure S5 bottom) and neat BODA (Figure S5 middle) to the XPS spectrum of BODA–CNO copolymer *solid 4* (Figure S5 top) shows the absence of fluorine in CNOs starting material but it can be found in pristine BODA (binding energy of main F 1s peak at 685.6 eV) as well as in the copolymer *solid 4* (binding energy of main F 1s peak at 685.7 eV). The O 1s signals in the CNO-containing samples arise from the carboxy groups attached to the outer shell; they have been introduced in the purification process of CNOs.¹²

Conclusions

In summary, the methods to functionalize CNOs and their related chemistry still represents a largely unexplored field. With this report, we introduce the very first example of a radical addition of a conjugated polymer to CNOs. Exploiting the thermal reactivity, tunable conjugation length, and functional group content of the BODA strategy, processing, and fabrication of novel CNO composites may now be possible for a variety of applications. The functionalized and soluble CNOs were characterized by transmission electron microscopy, thermal gravimetric analysis, Raman spectroscopy, gel permeation chromatography, and X-ray photoelectron spectroscopy (XPS).

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Supporting Information Available: The experimental details are given for the attempted synthesis of functionalized CNOs using in situ generated diazonium compounds as well as using free radicals generated by decomposition of benzoyl peroxide; the control experiment where free polymer has been mixed with CNOs; solubility of *solid 4* and *solid 3* in CHCl₃ and NMP; Figure S1 showing the Raman spectrum of *solid 1* compared to that of CNOs starting material; Figures S2 and S3 showing UV–vis data as extracted from the photodiode array detector of GPC-separated BODA oligomer control and BODA–CNO copolymer *solid 4*, respectively; Figure S4 showing TGA of copolymer *solid 3*; Figure S5 comparing XPS data of neat CNOs and neat BODA and BODA–CNOs copolymer *solid 4*. This material is available free of charge via the Internet at <http://pubs.acs.org>.