

**Functionalization of Single-Walled Carbon Nanotubes via the Piers-Rubinsztajn
Reaction**

Ryan C. Chadwick, John B. Grande, Michael A. Brook, and Alex Adronov^{*}

Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton,
Ontario, L8S 4M1, Canada

SUPPORTING INFORMATION

Experimental details, characterization, and NMR spectra (¹H-NMR and ¹³C-NMR)

Table of Contents

Experimental Procedures	S2-S5
Thermogravimetric Analysis	S5-S9
UV-Vis-NearIR Spectra.....	S10
Raman Spectra of Controls	S10-11
References	S11

General Experimental:

All experiments were performed on unpurified, as-produced HiPCO SWNTs, NanoIntegris Batch Number R1-901. SWNT masses were based on provided Wet SWNT content of 9.9%. Hydride-terminated PDMS samples (PDMS-H₂) were purchased from Gelest. PTFE filtration membranes (200 nm pore size) were purchased from Sartorius Stedim Biotech. All other reagents were purchased from fine chemical suppliers and used as received. Toluene was dried in a solvent purification system over activated alumina.

Equipment:

Laser Raman spectroscopy was performed on a Renishaw inVia Raman spectrometer at 514 and 785 nm. Thermogravimetric analyses (TGA) were performed using a TA-Q50 instrument and were performed under an argon atmosphere. Samples were held at 100 °C for 15 min, ramped to 500 °C at a rate of 20 °C/min, then held at 500 °C for 45 min. Ultrasonication was performed using a Branson 2510 ultrasonicator bath. UV-Vis-IR spectroscopy was performed on a Cary 5000 instrument.

Procedure for Nanotube Solubility Measurements:

10 mg samples of functionalized SWNTs were sonicated in 10 mL of the desired solvent for 1 h. The suspensions were centrifuged for 1 h at 5000 g, then the supernatant was transferred via pipette, taking care to avoid disturbing any SWNT pellet present. The supernatant was then filtered through cotton and, if necessary, diluted to an appropriate concentration to allow UV-Vis spectroscopy. The specific extinction coefficient at 500 nm ($0.0103 \text{ L mg}^{-1} \text{ cm}^{-1}$)¹ was used to calculate the SWNT concentration.

Procedure for the production of anisole functionalized SWNTs (a-SWNT):²

A 25 mL round bottom flask was charged with a PTFE-coated magnetic stir bar, 6-12 glass beads (6 mm diameter), 20 mg (200 mg wet) of pristine HiPCO SWNTs, and 400 mg p-anisidine. Isoamyl nitrite (800 μ L) was added by pipette and the mixture was stirred for 2 h at 60 °C. The mixture was then diluted with DMF and filtered through a 200 nm PTFE membrane. The filter cake was then washed with DMF until the filtrate was colorless (ca. 100 mL) followed by secondary washing with toluene (100 mL). The filter cake was re-suspended by sonication in an additional 100 mL dry toluene, and again filtered to recover the functionalized a-SWNTs.

a-SWNT samples used for TMDS/PDMS functionalization were kept wet with toluene, and used directly. Samples for TGA were re-suspended in diethyl ether, filtered, and dried at 100 °C under vacuum overnight. a-SWNTs used in PDMS rubber formation were re-suspended in hexanes and filtered once more before use.

General procedure for the silylation of a-SWNTs with PDMS-H₂:

a-SWNT (10 mg nanotube basis), 400 μ L PDMS-H₂ (or TMDS), and 10 mL of dry toluene were placed in a small round bottom flask equipped with a PTFE-coated magnetic stir bar and 6-12 glass beads (6 mm diameter). The mixture was purged with inert gas (N₂ or argon), while under bath sonication. After purging, 50 μ L of 0.1 M (C₆F₅)₃B solution in toluene was added. The mixture was stirred for 2 (TMDS) to 12 (PDMS) hours. After the reaction, the mixture was filtered through a 200 nm PTFE membrane. The filter cake was washed with toluene (100 mL), then air-dried.

If used for solution studies, the filter cake was also rinsed with the suspending solvent. Samples for TGA were re-suspended in diethyl ether, filtered, and dried at 100 °C under vacuum overnight.

Note: Longer stirring times (> 2 h) did not increase graft mass in TDMS samples.

Procedure for control experiments:

Three control experiments were performed. Each control experiment was performed under the same conditions as used for the silylations in the preceding paragraphs: 1) Pristine HiPCO SWNTs were stirred with 1.1 kDa PDMS-H₂ in the absence of catalyst; 2) Pristine HiPCO SWNTs were stirred with 1.1 kDa PDMS-H₂ and 50 µL of 0.1 M (C₆F₅)₃B solution; and 3) a-SWNTs were stirred with 1.1 kDa PDMS-H₂ in the absence of catalyst.

The mass losses determined by TGA were 6.7, 7.1 and 18.4% for the three controls respectively. In both cases where pristine SWNTs were stirred with PDMS-H₂ the Raman spectra of the products showed no evidence of reaction.

Procedure for the production of a-SWNT foam (1% CNT loading):

20 mg (SWNT basis) a-SWNT and 2 g of 1 kDa PDMS-H₂ were aggressively mixed for 2 min at 10 000 RPM using a variable speed rotary tool (Dremel) with a 1 cm stainless-steel brush attachment. An equal volume of hexanes was added and the suspension was mixed for an additional minute. 200 µL tetraethylorthosilicate (TEOS) was added and the suspension was mixed for 30 s. Then, the mixture was cooled to 10 °C, and 200 µL of 0.05 M (C₆F₅)₃B (in toluene) was added, mixed for 15 s, and poured into a PTFE-lined mold. Gentle heating via cupping in hand or heat gun initiated the

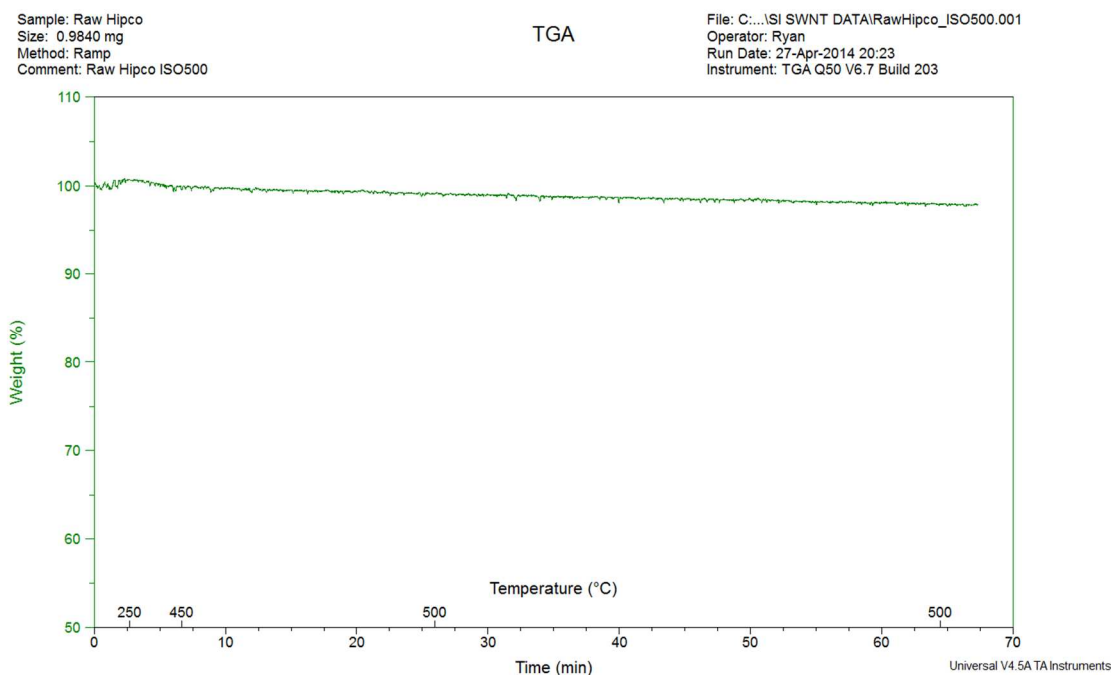
foam formation. The material was allowed to cure for 1 h at room temperature, then the hexanes was evaporated at 50 °C *in vacuo*.

Procedure for the production of a-SWNT rubber (1% CNT loading):

20 mg (SWNT basis) a-SWNT and 2 g of 17 kDa PDMS-H₂ were aggressively mixed for 2 min at 10 000 RPM using a variable speed rotary tool (Dremel) with a 1 cm stainless-steel brush attachment. An equal volume of hexanes was added and the suspension was mixed for an additional minute. 25 µL of TEOS was added and the suspension was mixed for 30 s. Then the mixture was cooled to 10 °C, 200 µL 0.05 M (C₆F₅)₃B (in toluene) was added, mixed for 15 s, and poured into a PTFE-lined mold. The composite was heated for 24 h at 50 °C to cure and remove hexanes.

Thermogravimetric Analysis Traces:

Raw HiPCO SWNT:

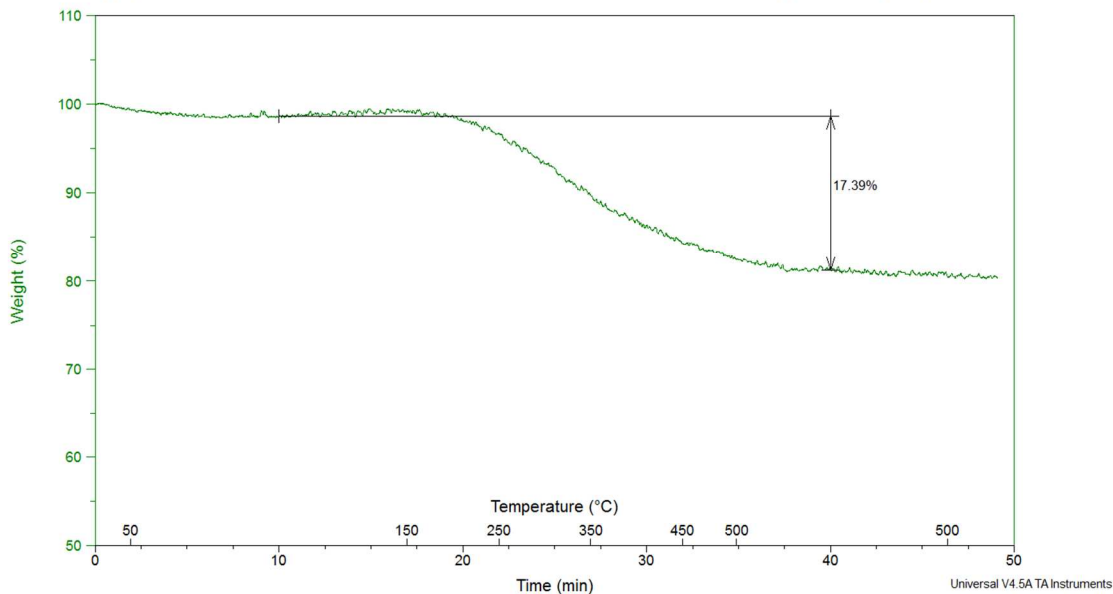


a-SWNT:

Sample: RCC08-32
Size: 2.0660 mg
Method: Ramp
Comment: RCC08-32

TGA

File: C:\...ISI SWNT DATA\RCC08-32.002
Operator: Ryan
Run Date: 29-Apr-2014 16:02
Instrument: TGA Q50 V6.7 Build 203

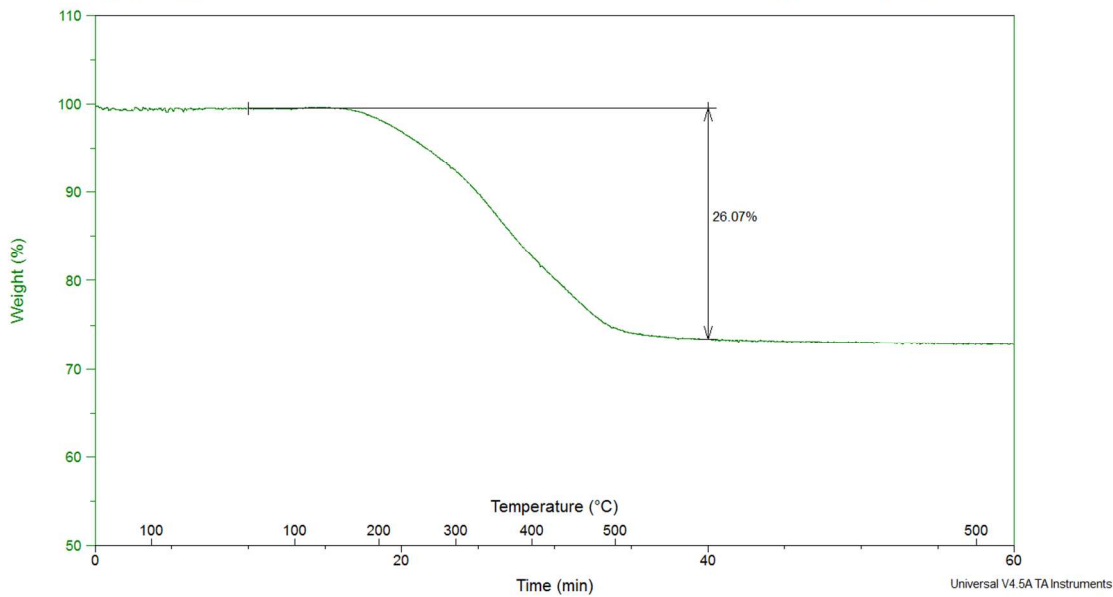


TMDS-SWNT:

Sample: RCC08-33a
Size: 2.5160 mg
Method: Ramp
Comment: RCC08-33a ISO500

TGA

File: C:\...ISI SWNT DATA\RCC08-33a.001
Operator: Ryan
Run Date: 28-Apr-2014 16:40
Instrument: TGA Q50 V6.7 Build 203

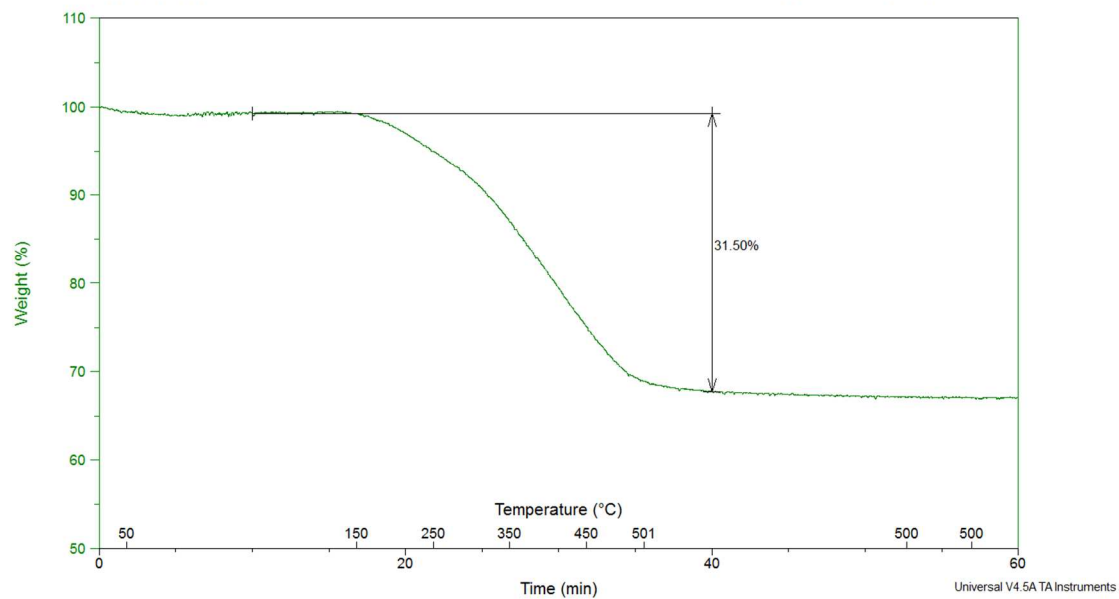


PDMS-SWNT-1k:

Sample: RCC08-33b
Size: 2.8730 mg
Method: Ramp
Comment: RCC08-33b ISO500

TGA

File: C:\SI SWNT DATA\RCC08-33b.001
Operator: Ryan
Run Date: 28-Apr-2014 19:24
Instrument: TGA Q50 V6.7 Build 203

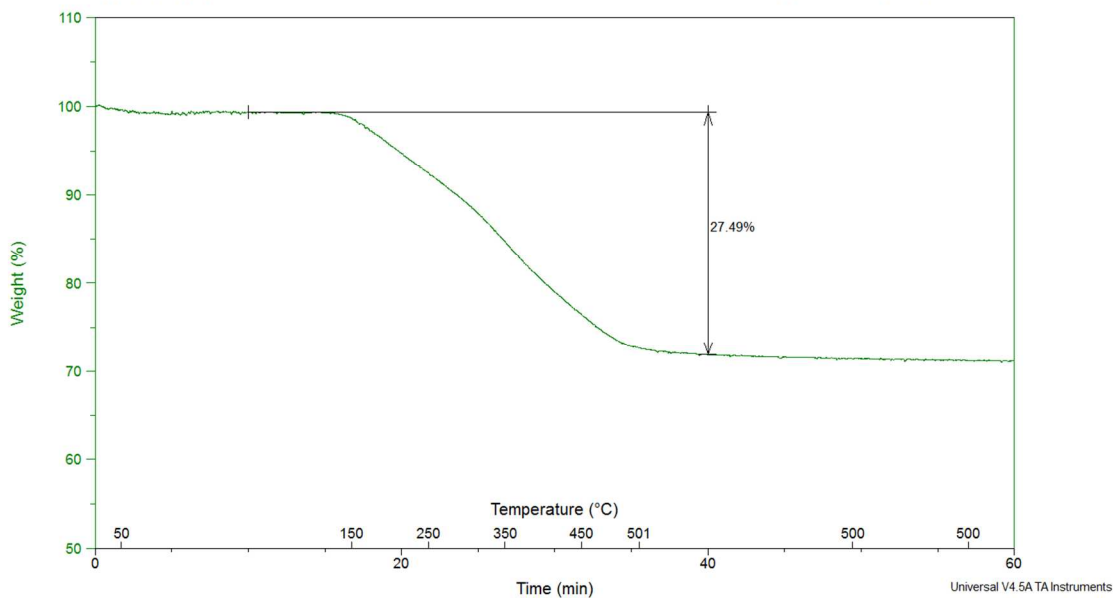


PDMS-SWNT-6k:

Sample: RCC08-33c
Size: 3.3330 mg
Method: Ramp
Comment: RCC08-33c ISO500

TGA

File: C:\...ISI SWNT DATA\RCC08-33c.001
Operator: Ryan
Run Date: 28-Apr-2014 14:34
Instrument: TGA Q50 V6.7 Build 203

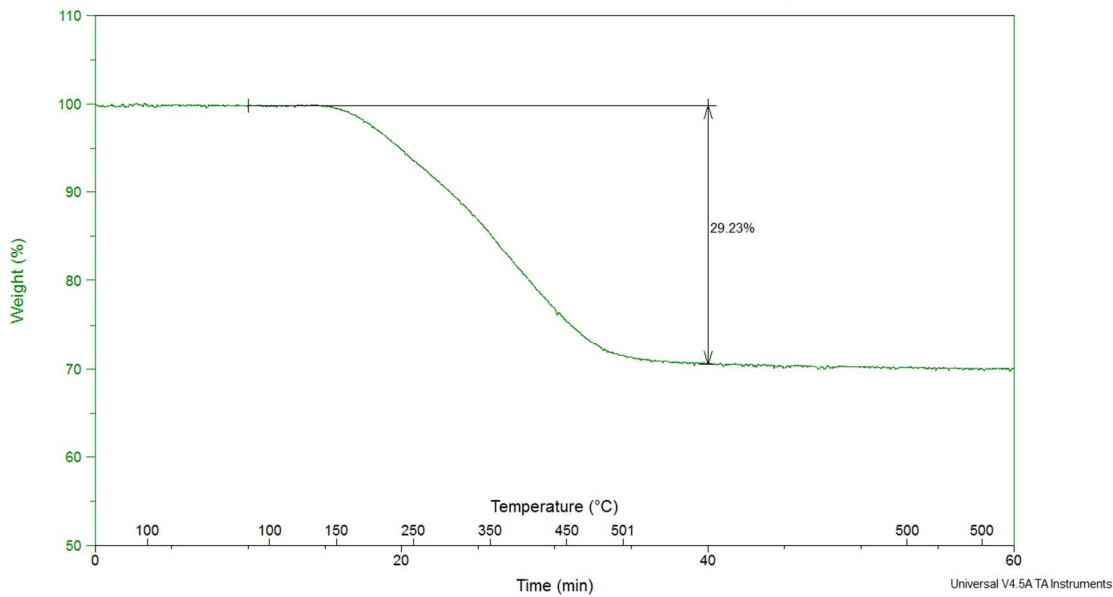


PDMS-SWNT-17k:

Sample: RCC08-33d
Size: 3.0140 mg
Method: Ramp
Comment: RCC08-33d ISO500

TGA

File: C:\...ISI SWNT DATA\RCC08-33d.001
Operator: Ryan
Run Date: 28-Apr-2014 21:26
Instrument: TGA Q50 V6.7 Build 203

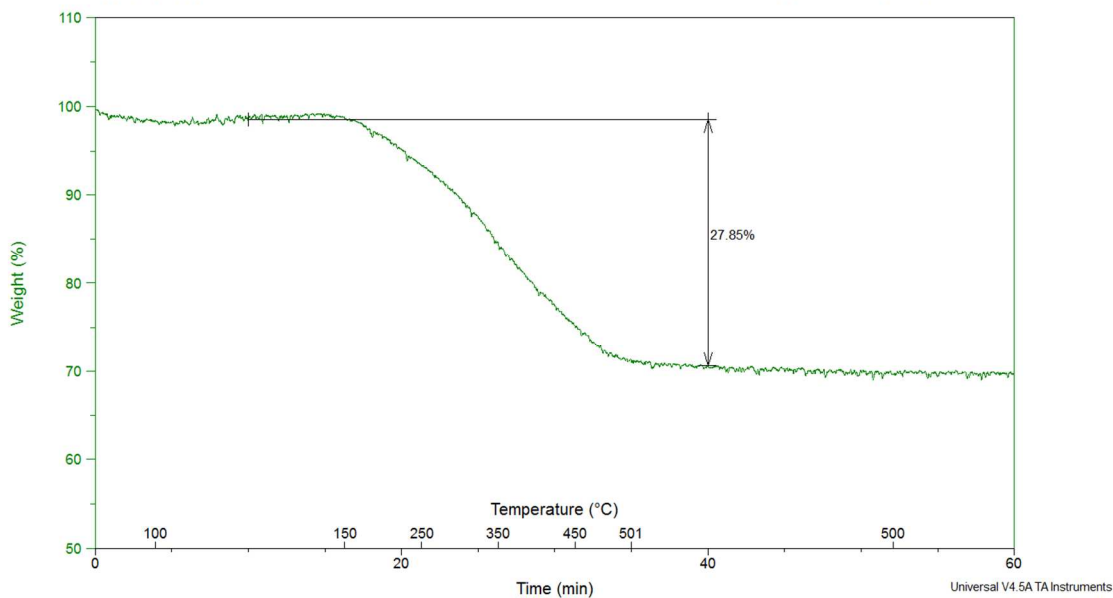


PDMS-SWNT-28k:

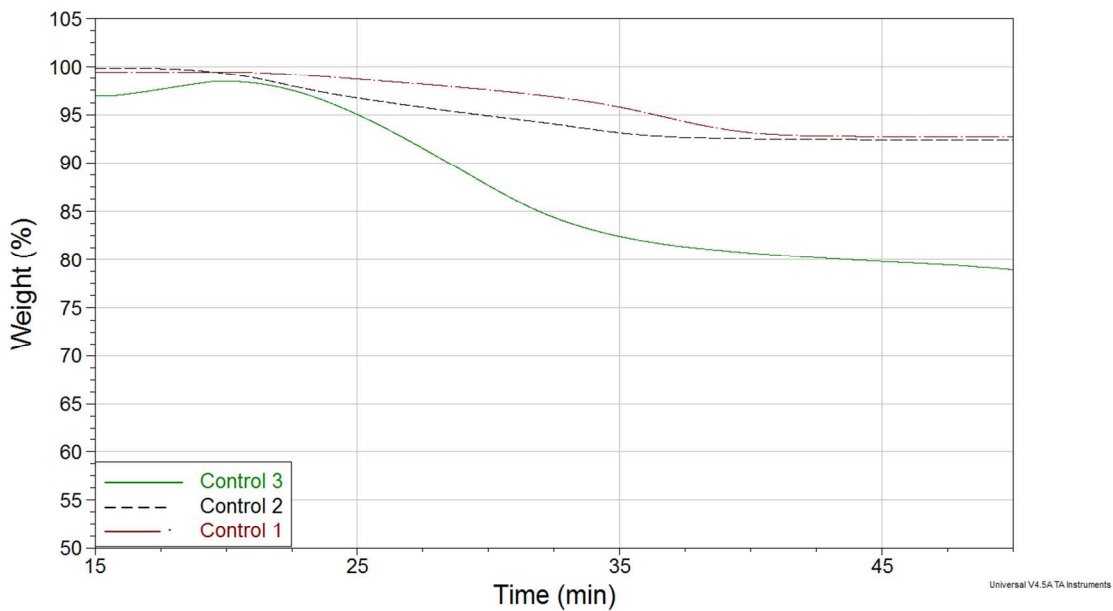
Sample: RCC08-33e
Size: 1.4900 mg
Method: Ramp
Comment: RCC08-33e ISO500

TGA

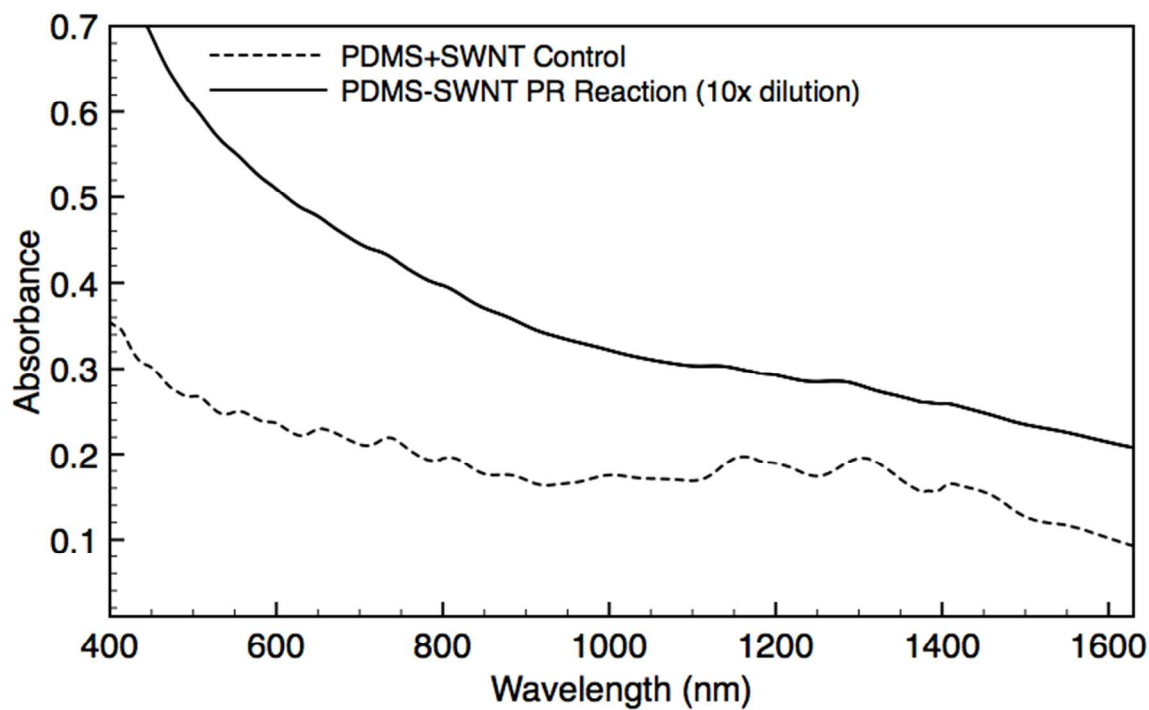
File: C:\...ISI SWNT DATA\RCC08-33e.001
Operator: Ryan
Run Date: 28-Apr-2014 23:35
Instrument: TGA Q50 V6.7 Build 203



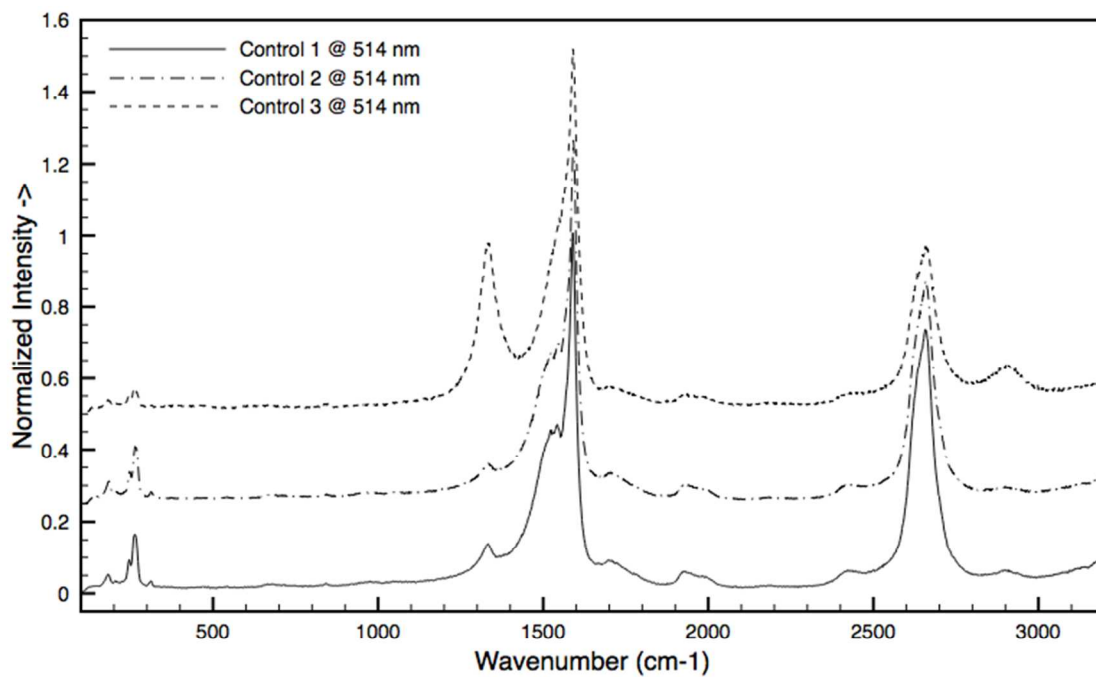
Control Experiments

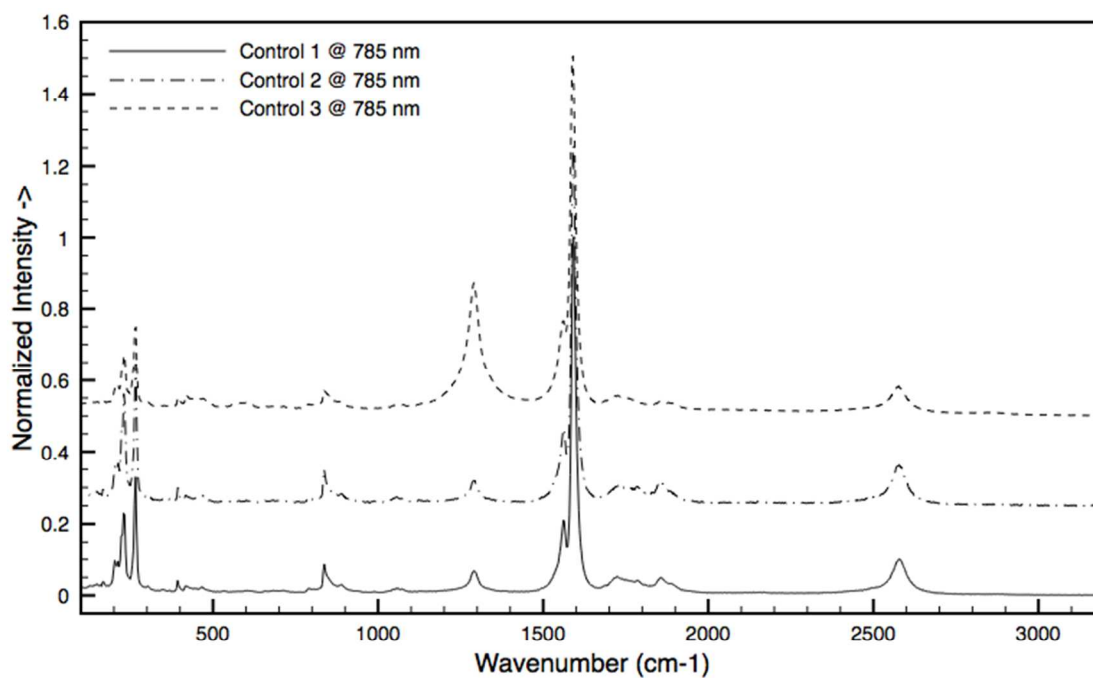


Representative UV-Vis-NearIR Spectra:



Raman Spectra of Control Experiments:





References:

- (1) Li, H.; Cheng, F.; Duft, A. M.; Adronov, A. *J. Am. Chem. Soc.* **2005**, *127*, 14518–14524.
- (2) Dyke, C. A.; Tour, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 1156–1157.