Cyclopentadienyl End-capped Polymers for a One-step Functionalization of Carbon Nanotubes

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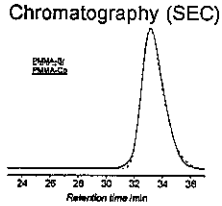
Abstract: Single-Walled Carbon Nanotubes (SWCNTs) were functionalized via **an ambient temperature Diels-Alder reaction** with narrow dispersity polymer strands. The SWCNTs react as dienophiles with cyclopentadienyl end-capped polymers, without any preliminary treatment. The grafting density of the polymers on the surface of the SWCNTs was determined by three quantitative methods (Thermogravimetric Analysis TGA, Elemental Analysis EA, X-Ray Photoelectron Spectroscopy XPS). In addition, High Resolution Transmission Electron Microscopy (HRTEM) indicates the functionalization of the SWCNTs with a polymer layer.

Synthesis

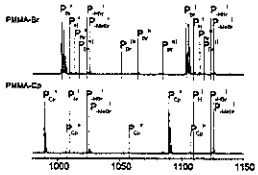
Polymer end-group functionalization and characterization

Size-Exclusion Chromatography (SEC)



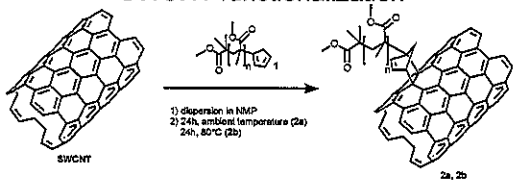
SEC traces of PMMA-Br and PMMA-Cp (M_n = 2900 g·mol^{-1}, PDI = 1.2), calibration with PMMA standards in THF.

Electrospray Ionization Mass-Spectrometry (ESI-MS)



ESI-MS spectra of PMMA-Br and PMMA-Cp. P_n^x and P_{Cp}^x represent the polymers with different charges (single, double or triple charged), P_H the termination product, P_{-HBr} and P_{Abstr} the elimination products.

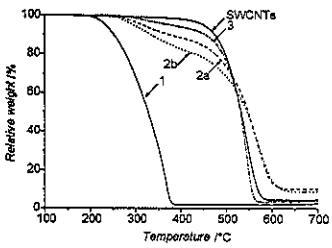
SWCNT functionalization



Cyclopentadienyl end-capped PMMA-Cp **(1)** is synthetized[1] from PMMA-Br obtained via ATRP, after the complete conversion of bromine end-group (*see ESI-MS spectra*). SEC displays a narrow dispersity of the polymer. The SWCNT are firstly dispersed in N-methylpyrrolidone (NMP) (SWCNT:NMP weight ratio of 1:5). PMMA-Cp is subsequently added (SWCNT:PMMA-Cp weight ratio of 1:10). The solution is stirred for 24h at ambient temperature **(2a)**, and at 80°C **(2b)**, then filtered and washed with THF.

Characterization of the SWCNTs

Thermogravimetric Analysis (TGA)

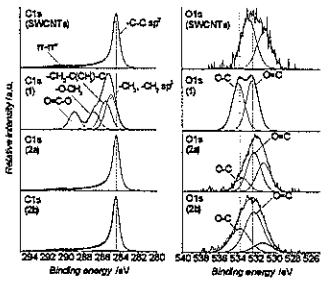


Quantitative analysis

Elemental Analysis (EA)

	wt. %			
	C	H	N	O
SWCNTs	85.4	1.7	0.8	2.2
(1)	58.3	7.7	1.0	30.2
(2a)	74.6	1.8	1.8	7.0
(2b)	73.6	1.9	2.2	7.7

X-Ray Photoelectron Spectroscopy (XPS)



Summary

		wt. % of polymer	Grafting ratio: mmol·g^{-1}	chains·nm^{-2} a	Periodicity b
(2a)	TGA	12.3	0.055	0.025	1523
	EA	19.2	0.082	0.038	1015
	XPS	13.0	0.052	0.024	1615
	Average	14.8	0.064	0.029	1369
(2b)	TGA	18.2	0.088	0.040	968
	EA	22.1	0.098	0.045	850
	XPS	17.9	0.075	0.034	1108
	Average	20.1	0.065	0.039	975

a assuming the SWCNT specific surface area of 1315 g·m^{-2}
b number of C atoms covered by one polymer chain

TGA traces (left), EA results (middle) and XPS spectra (right) of non-modified SWCNTs, PMMA-Cp (1), SWCNTs modified with PMMA-Cp at ambient temperature (2a) and at 80°C (2b). TGA profiles under air atmosphere (*heating flow* = 10 K·min^{-1}). The reference (3) is obtained from the mixture of PMMA-Br and SWCNTs, at the same conditions as for (2a).

Conclusions

The present work has demonstrated that cyclopentadienyl terminal polymer strands can readily react with SWCNTs in a Diels-Alder reaction under very mild conditions[2]. Three analytical methods enable the quantification of the achieved grafting densities in good agreement with each other. The presented facile SWCNT modification process opens the door for the effective dispersion of CNTs in solid polymer matrices via reactive extrusion processes to achieve composites with enhanced material properties.

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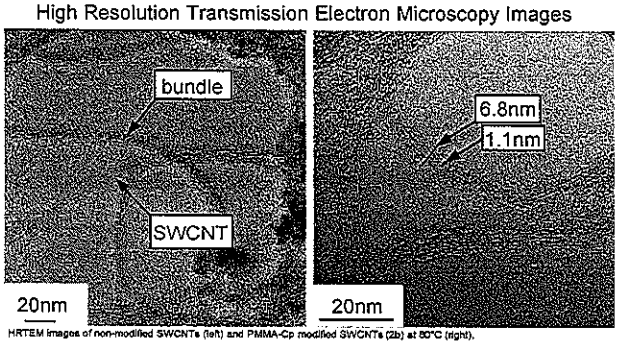
References

[1] Inglis, A. J.; Paulöhrl, T.; Barner-Kowollik, C. *Macromolecules* **2010**, *43*, 33–36.

[2] Zydziak, N.; Hübner, C.; Bruns, M.; Barner-Kowollik, C. *Macromolecules* **2011**, *44*, 3374–3380.

Observation at the nm-scale

High Resolution Transmission Electron Microscopy Images



HRTEM images of non-modified SWCNTs (left) and PMMA-Cp modified SWCNTs (2b) at 80°C (right).