

Supporting Information for
One-step Functionalization of Single-Walled Carbon Nanotubes (SWCNTs)
with Cyclopentadienyl Capped Macromolecules via Diels-Alder Chemistry

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Characterization

Size Exclusion chromatography (SEC). SEC measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 μm bead-size guard column (50 \times 7.5 mm) followed by one PLgel 5 μm Mixed E column (300 \times 7.5 mm), three PLgel 5 μm Mixed C columns (300 \times 7.5 mm) and a differential refractive index detector using THF as the eluent at 35°C with a flow rate of 1 mL \cdot min⁻¹. The SEC system was calibrated using linear linear poly(methyl methacrylate) standards ranging from 700 to 2 \cdot 10⁶ g \cdot mol⁻¹. From a 0.1 mg \cdot mL⁻¹ sample solution 100 μL were injected. The molecular weight distribution were corrected with the Mark-Houwink relation with $K = 12.8 \cdot 10^{-5}$ dL \cdot g⁻¹ and $\alpha = 0.69$.¹

Electrospray Ionisation Mass Spectrometry (ESI-MS) Analysis. Spectra were recorded on an LXQ mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the m/z range 195-1822 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 4.5 kV was used and nitrogen at a dimensionless sweep gas flow-rate of 2 (approx. 3 L·min⁻¹) and a dimensionless sheath gas flow-rate of 12 (approx. 1 L·min⁻¹) were applied. The capillary voltage, the tube lens offset voltage and the capillary temperature was set to 60 V, 110 V and 275°C, respectively. From a 0.5 mg·ml⁻¹ solution in THF:MeOH (3:2), the sample was directly injected.

Thermogravimetric Analysis (TGA). Thermogravimetric measurements were carried out on a Q5000 thermogravimetric analyzer from TA-Instruments. Approximately 6 mg of sample was heated at 10 K·min⁻¹ from ambient temperature to 100 °C for 30 minutes, and subsequently at the same heating rate from 100°C to 700°C in a dynamic air atmosphere (*flow rate* = 25 mL·min⁻¹). Samples synthesized in **N-methylpyrrolidone (NMP)** (see synthesis procedures **(2a)** and **(2b)**) were heated under the same conditions, except for the isothermal step conducted at 210°C in order to evaporate potentially adsorbed NMP from the sample. Thermogravimetric profiles obtained under the same conditions (see main text) were derived to deliver the maximal temperature T_m for which the weight loss is maximal and the final temperature T_f of the observed degradation.

Elemental Analysis (EA). Before the determination of the elemental composition, the samples, standards, capsules and chemicals were conditioned as follows: the samples, calibration standards and vanadium pentoxide were allowed to stand for 5 days at ambient temperature in a

desiccator over phosphorous pentoxide. The tin capsules and silver containers were stored at ambient temperature in a drying chamber at 24°C with an humidity of 30%.

For the accurate, simultaneous determination of carbon, hydrogen, nitrogen and sulphur (CHNS) a calibration of the system was conducted with methionine. Methionine was accurately weighed (0.200 to 2.250 mg) into tin containers in duplicate with a microbalance XP26 DR (METTLER TOLEDO, Germany). Vanadium pentoxide (2.5–3.5 mg) was added to the sample. The tin containers were then accurately sealed (air free).

A six point linear calibration curve was generated for each element by combustion of the standard samples and simultaneous gas chromatographic separation of the generated combustion gases N₂, CO₂, H₂O and SO₂. The gases were detected by thermal conductivity detection (TCD). The peak areas were calculated by the software Eager300 (Thermo Scientific). The calculation of the linear function ($y = f(x) = a \cdot x + b$, slope, axis intercept, the coefficient of determination) were performed using MS Excel 2000. The coefficients of determination were 0.9998 for N, C and H, and 0.9999 for S respectively.

The retrieval and accuracy of the method was determined using the standards methionine and 2,5-bis-5-tert-butyl-2-benzoxazolylthiophene (BBOT). 1.000 mg of the standards were weighed six-fold into tin containers, vanadium pentoxide was subsequently added. The containers were sealed and the retrieval of the elements CHNS was determined as described above.

Standard	Composition in <i>wt. %</i> (mean \pm SD; n = 6)			
	N	C	H	S
Methionine (theor.)	9.39	40.25	7.43	21.49
Methionine (determ.)	9.34 \pm 0.12	40.49 \pm 0.44	7.44 \pm 0.09	21.54 \pm 0.19
BBOT (theor.)	6.51	72.53	6.05	7.44
BBOT (determ.)	6.79 \pm 0.06	72.96 \pm 0.48	6.10 \pm 0.04	7.74 \pm 0.07

To determine the CNHS composition of the samples, known amounts (1 to 2 mg) of each sample and vanadium pentoxide were weighed into tin capsules using a microbalance XP26 DR (METTLER TOLEDO, Germany). After sealing the capsules, they were placed inside the MAS 200R auto sampler, and subsequently dropped into an oxidation / reduction reactor kept at 900 °C. The exact amount of oxygen required for the optimum combustion of the sample was delivered into the combustion reactor at a known time. The reaction of oxygen with the tin capsule at elevated temperature generates an exothermic reaction which raises the temperature to 1 800 °C for a few seconds. At this high temperature organic substances are converted into gases.

Reliable oxygen determination is achieved through an oxygen-specific pyrolysis reactor heated at 1 060°C. This allows for a complete pyrolysis of the sample in an oxidant-free environment. A “nickel plated carbon” catalyst ensures a high precision of oxygen determination by generation of carbon monoxide (CO). The formed gas is measured by simultaneous GC-TCD. For the accurate oxygen determination a calibration of the system was performed with methionine. Methionine was accurately weighed (0.200 to 2.250 mg) into silver containers in duplicate with a microbalance XP26 DR (METTLER TOLEDO, Germany). The silver containers

were accurately sealed (air free). A six point linear calibration curve was generated for oxygen by pyrolysis of the standard samples and simultaneous gas chromatographic separation of the generated CO. The gas was determined by TCD. The peak area was calculated by the software Eager300 (Thermo Scientific). The calculation of the linear function ($y = f(x) = a \cdot x + b$, slope, axis intercept, the coefficient of determination) was done using MS Excel 2000. The coefficient of determination was 0.9997 for O.

The retrieval and accuracy of the method was determined using the standards methionine and BBOT. 1.000 mg of the standards was weighed six-fold into silver containers. The containers were sealed and the retrieval of the element O was determined as described above.

Standard	Composition in <i>wt. %</i> (mean \pm SD; n=6)
	O
Methionine (theor.)	21.45
Methionine (determ.)	21.57 \pm 0.16
BBOT (theor.)	7.43
BBOT (determ.)	7.30 \pm 0.1

The determination of the elemental composition CHONS of the samples was carried out as described above. The determination was performed within the calibration range, i.e. the peak areas of the combustion gases (N₂, CO₂, H₂O, SO₂) and the pyrolysis gas (CO) were inside the calibration range. Generally an amount of 1.000 to 2.000 mg of the sample was weighed into tin or silver containers and the composition was determined.

Results

SEC measurements and ESI-MS Analysis of PMMA-Br and PMMA-Cp.

Cyclopentadienyl capped polymer (PMMA-Cp) and its bromine capped precursor (PMMA-Br) were characterized by SEC (see **Figure S1**) to determine the molecular weight distribution of these polymers.

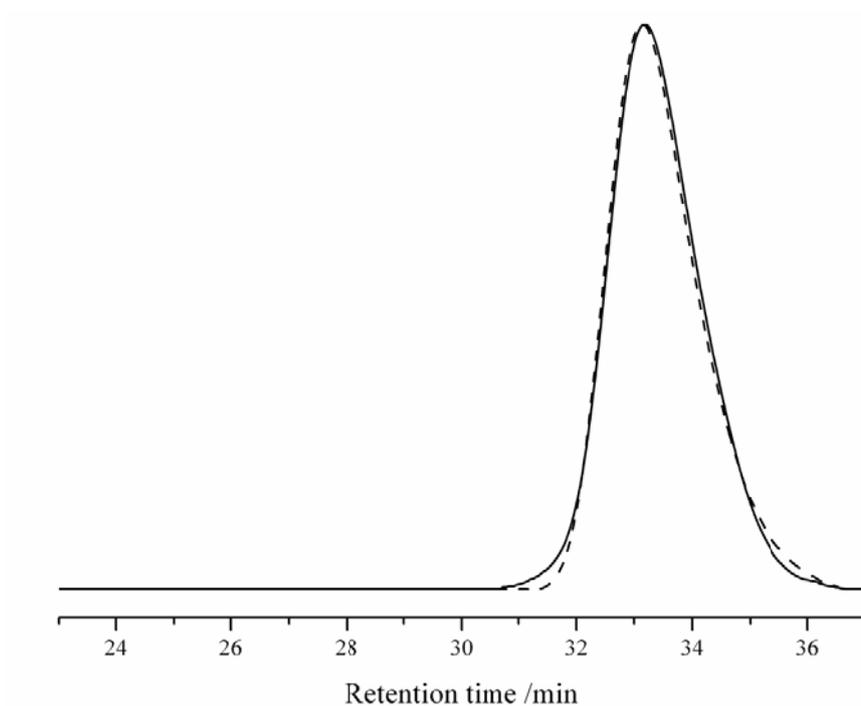


Figure S1. SEC trace of PMMA-Br (dot line) and PMMA-Cp (continuous line).

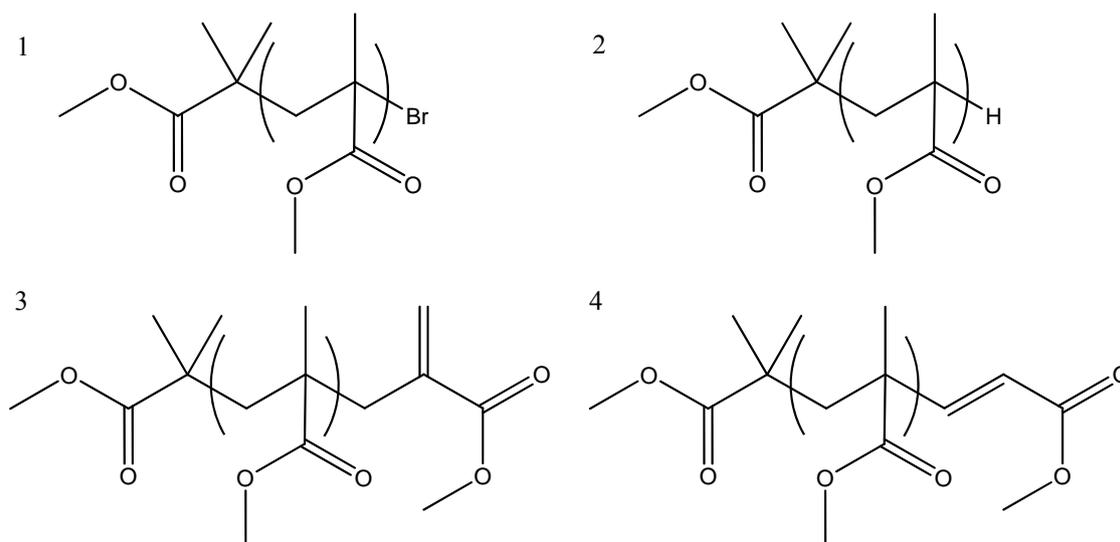
The SEC traces of both species, the molecular weight and the polydispersity index (M_n and PDI , see **Table S1**) are almost identical.

Table S1. SEC characterization of the employed PMMA-Br and PMMA-Cp

	M_n /g·mol ⁻¹	PDI
PMMA-Br	2700	1.18
PMMA-Cp	2900	1.17

Scheme S1 depicts species generated during the **atom transfer radical polymerization (ATRP)** synthesis of PMMA-Br. Bromine capped poly(methylmethacrylate) (PMMA-Br) is the main product (**1**); three minor species (**2**, **3** and **4**) generated by elimination can be identified.²

Scheme S1. Expected species during the ATRP process for the synthesis of PMMA-Br (1), and after elimination of Br (2), HBr (3) and CH₃Br (4)



During the reaction to PMMA-Cp, only PMMA-Br (**1**) reacts to generate the cyclopentadienyl capped polymer (**1**^{*}). Side products are not bromine terminated, hence they remain in the sample and can be still identified in the ESI-MS spectrum of PMMA-Cp at the same *m/z*. Via the transformation and according to the ESI-MS spectra (see **Figure S3**), PMMA-Br is completely transformed to PMMA-Cp, leading to an effective mass change of 13.88 Da. Moreover, the isotopic pattern changed from the PMMA-Br (**1**) peak featuring the characteristic bromine isotopic pattern (⁷⁹Br and ⁸¹Br), to the PMMA-Cp (**1**^{*}) peak with the characteristic carbon isotopic abundance (¹²C and ¹³C).

Peak identification was conducted according to the exact mass of the ATRP starting molecule (2-methyl 2-bromo-2-methylpropanoate, MBMP) and the number of monomer units incorporated in the polymer chain (see **Table S2**). Only sodium adducts were observed and calculation led to the identification of up to three times charged ions for PMMA-Br (**1**) (species **a1-a4** for double charged ions, **b1-b6** for triple times charges ions, see **Table S3**).

In the ESI-MS spectrum of PMMA-Cp, an excellent agreement between the theoretically expected and experimentally observed species is found (see **Table S2**). As for the bromine capped polymer, sodium adducts are observed in the ESI-MS spectrum (species **a1***-**a4*** for the double charged ions, see **Table S4**). The side products **2**, **3** and **4** remain at the same m/z .

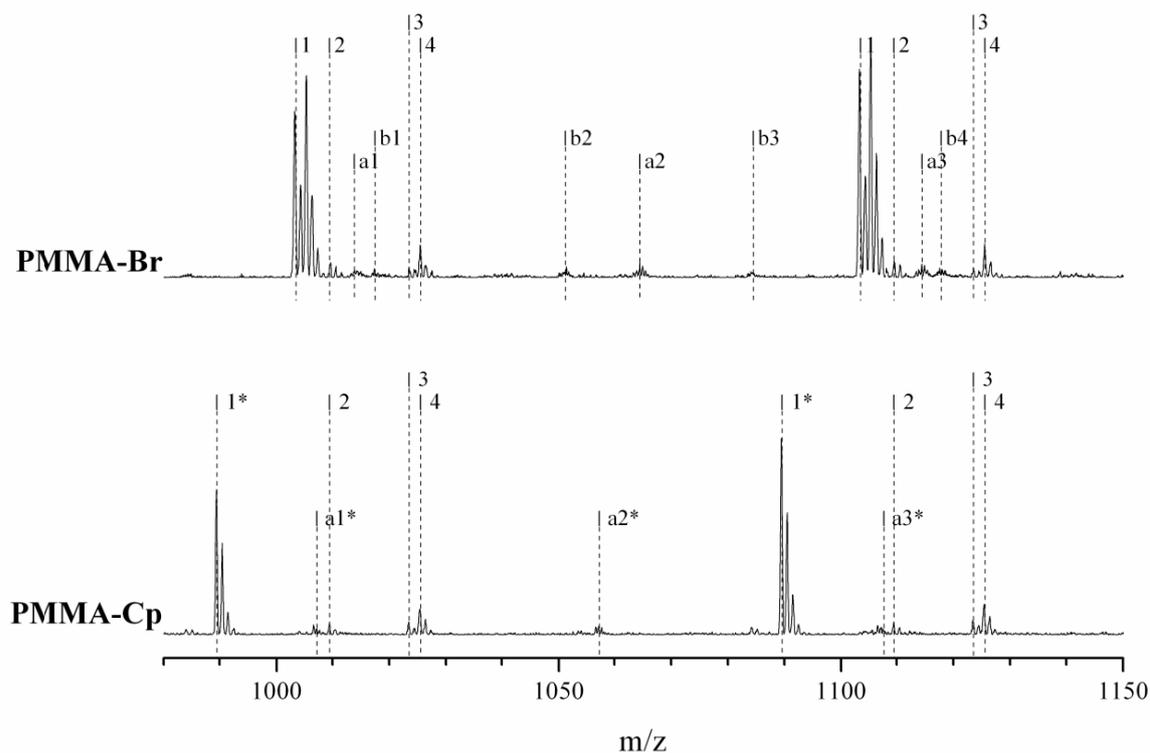


Figure S3. ESI-MS spectra of PMMA-Br and PMMA-Cp polymer obtained via direct source infusion. Signals marked with an asterisk represent polymer chains that have undergone a successful transformation from a -Br to a -Cp terminus.

Table S2. Identification of the single charged species of PMMA-Br and PMMA-Cp polymer

	<i>m/z</i> exp.	<i>m/z</i> th.	$\Delta m/z$	ion assignment	formula
PMMA-Br					
<i>n</i> =8	1003.12	1003.39	0.27	1	[C ₄₅ H ₇₃ O ₁₈ BrNa] ⁺
	1009.68	1009.50	0.18	2	[C ₄₉ H ₇₈ O ₂₀ Na] ⁺
	1023.48	1023.51	0.03	3	[C ₅₀ H ₈₀ O ₂₀ Na] ⁺
	1025.48	1025.53	0.05	4	[C ₅₀ H ₈₂ O ₂₀ Na] ⁺
<i>n</i> =9	1103.24	1103.44	0.20	1	[C ₅₀ H ₈₁ O ₂₀ BrNa] ⁺
	1109.60	1109.55	0.05	2	[C ₅₄ H ₈₆ O ₂₂ Na] ⁺
	1123.60	1123.57	0.03	3	[C ₅₅ H ₈₈ O ₂₂ Na] ⁺
	1125.56	1125.58	0.02	4	[C ₅₅ H ₉₀ O ₂₂ Na] ⁺
<i>n</i> =10	1203.28	1203.49	0.21	1	[C ₅₅ H ₈₉ O ₂₂ BrNa] ⁺
PMMA-Cp					
<i>n</i> =8	989.59	989.51	0.08	1 *	[C ₅₀ H ₇₈ O ₁₈ Na] ⁺
<i>n</i> =9	1089.60	1089.56	0.04	1 *	[C ₅₅ H ₈₆ O ₂₀ Na] ⁺
<i>n</i> =10	1189.64	1189.61	0.03	1 *	[C ₆₀ H ₉₄ O ₂₂ Na] ⁺

The minor side products **2**, **3** and **4** are also found in the ESI-MS spectrum of PMMA-Cp.

Table S3. Identification of double and triple charged species in the ESI-MS spectra of the PMMA-Br polymer

<i>n</i>	<i>m/z</i> exp.	<i>m/z</i> th.	$\Delta m/z$	ion assignment	formula
18	1013.92	1013.87	0.05	a1	$[\text{C}_{95}\text{H}_{153}\text{O}_{38}\text{BrNa}_2]^{2+}$
19	1064.44	1064.48	0.04	a2	$[\text{C}_{100}\text{H}_{161}\text{O}_{40}\text{BrNa}_2]^{2+}$
20	1114.44	1114.51	0.07	a3	$[\text{C}_{105}\text{H}_{169}\text{O}_{42}\text{BrNa}_2]^{2+}$
21	1164.44	1164.53	0.09	a4	$[\text{C}_{110}\text{H}_{177}\text{O}_{44}\text{BrNa}_2]^{2+}$
<i>n</i>	<i>m/z</i> exp.	<i>m/z</i> th.	$\Delta m/z$	ion assignment	formula
28	1017.36	1017.48	0.12	b1	$[\text{C}_{145}\text{H}_{233}\text{O}_{58}\text{BrNa}_3]^{3+}$
29	1051.36	1051.16	0.20	b2	$[\text{C}_{150}\text{H}_{241}\text{O}_{60}\text{BrNa}_3]^{3+}$
30	1084.08	1084.51	0.43	b3	$[\text{C}_{155}\text{H}_{249}\text{O}_{62}\text{BrNa}_3]^{3+}$
31	1117.48	1117.86	0.38	b4	$[\text{C}_{160}\text{H}_{257}\text{O}_{64}\text{BrNa}_3]^{3+}$
32	1151.12	1151.21	0.09	b5	$[\text{C}_{165}\text{H}_{265}\text{O}_{66}\text{BrNa}_3]^{3+}$
33	1184.48	1184.57	0.09	b6	$[\text{C}_{170}\text{H}_{273}\text{O}_{68}\text{BrNa}_3]^{3+}$

The species **a4**, **b5** and **b6** are not represented in the zoom section ESI-MS spectrum shown in **Figure S3**.

Table S4. Identification of double and triple charged species in the ESI-MS spectra of the PMMA-Cp polymer

<i>n</i>	<i>m/z</i> exp.	<i>m/z</i> th.	$\Delta m/z$	ion assignment	formula
18	1007.08	1007.01	0.07	a1 *	[C ₁₀₀ H ₁₅₈ O ₃₈ Na ₂] ²⁺
19	1057.04	1057.12	0.08	a2 *	[C ₁₀₅ H ₁₆₆ O ₄₀ Na ₂] ²⁺
20	1107.57	1107.57	0.00	a3 *	[C ₁₁₀ H ₁₇₄ O ₄₂ Na ₂] ²⁺
21	1157.60	1157.59	0.01	a4 *	[C ₁₁₅ H ₁₈₂ O ₄₄ Na ₂] ²⁺
<i>n</i>	<i>m/z</i> exp.	<i>m/z</i> th.	$\Delta m/z$	ion assignment	formula
28	1013.18	1013.12	0.06	b1 *	[C ₁₅₀ H ₂₃₈ O ₅₈ Na ₃] ³⁺
29	1046.68	1046.54	0.14	b2 *	[C ₁₅₅ H ₂₄₆ O ₆₀ Na ₃] ³⁺
30	1079.84	1079.89	0.05	b3 *	[C ₁₆₀ H ₂₅₄ O ₆₂ Na ₃] ³⁺
31	1113.24	1113.23	0.01	b4 *	[C ₁₆₅ H ₂₆₂ O ₆₄ Na ₃] ³⁺
32	1146.32	1146.58	0.26	b5 *	[C ₁₇₀ H ₂₇₀ O ₆₆ Na ₃] ³⁺
33	1179.68	1179.94	0.26	b6 *	[C ₁₇₅ H ₂₇₈ O ₆₈ Na ₃] ³⁺

The species **a4*** are not represented in the zoom section ESI-MS spectrum shown in **Figure S3**.

The triple charged ions **b1***-**b6*** were not observable.

Thermogravimetric analysis (TGA). The maximal temperature T_m for which the weight loss is maximal and the final temperature T_f of the observed degradation were determined for each samples studied, i.e. non-modified **single-walled carbon nanotubes (SWCNTs)**, the polymer

PMMA-Cp (**1**), the PMMA-Cp SWCNTs modified at ambient temperature (**2a**) and at 80°C (**2b**) as well as the blind sample (**3**). T_m and T_f were obtained graphically from the first derivative of the thermogravimetric profile of the samples.

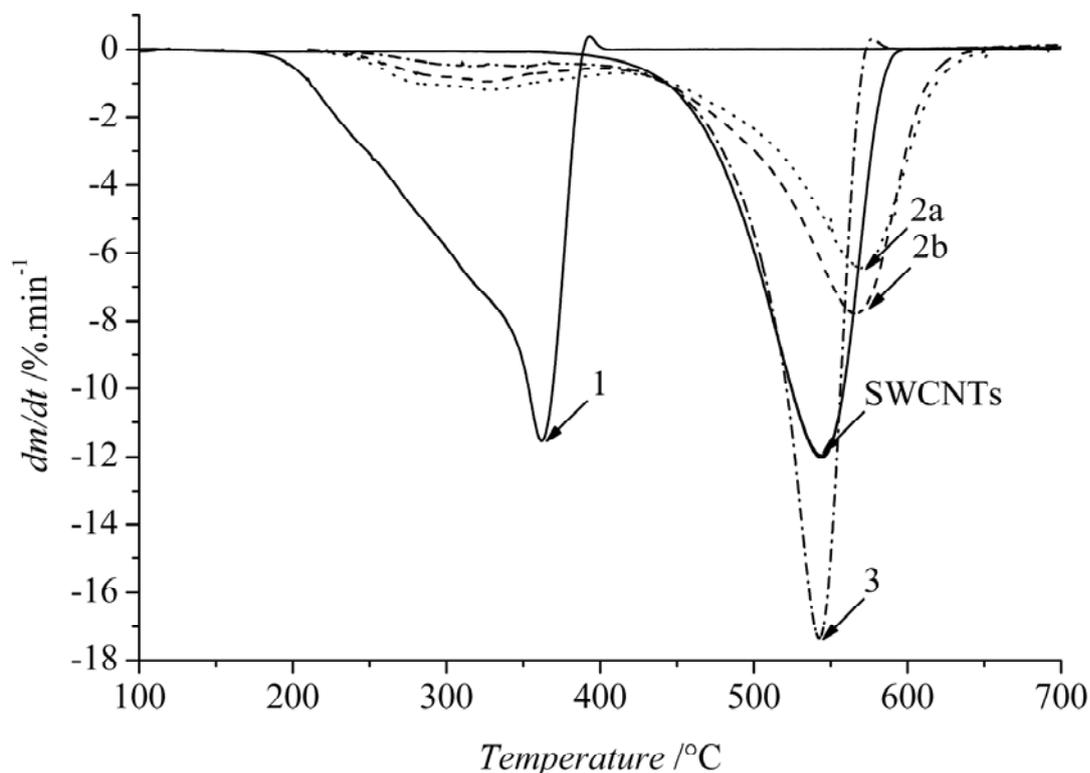


Figure S4. Derivatives of thermogravimetric profile in air atmosphere, with a heat flow of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ for non-modified SWCNTs, (**1**) PMMA-Cp, (**2a**) SWCNTs modified with PMMA-Cp at ambient temperature, (**2b**) SWCNTs modified with PMMA-Cp at 80°C, (**3**) SWCNTs mixed with PMMA-Br at ambient temperature. Once the temperature reached 100°C, the sample was equilibrated for 30 minutes at 100°C for SWCNTs and (**1**) as well as at 210°C for (**2a**), (**2b**) and (**3**) to evaporate residual solvent (NMP).

After the estimation of the amount of degraded polymer after the first reaction finishing at T_f ($x_{\text{polymer at } T_f}$ in wt. %) and of the amount of residue at 700°C ($x_{\text{residue at } 700^{\circ}\text{C}}$ in wt. %), the grafting density (σ_1) in $\text{mol}\cdot\text{g}^{-1}$ was calculated based on the weight loss at T_f , the polymer chain

molecular weight M_n and by assuming the rest of the samples is constituted purely of carbon. Based on the above procedure, the grafting density (σ_2) in chains·m⁻² was calculated according to the polymer chain molecular weight M_n and the theoretical specific surface of the SWCNTs (1315 m²·g⁻¹).³ The third calculable parameter is the grafting density expressed as periodicity (σ_3) for which the number of polymer chains (also based on the molecular weight M_n) is reported relative to the area of one graphene hexagon ($A_{\text{hexagon}} = 5.25 \text{ \AA}^2$),⁴ delivering the number of carbon atoms covered by one polymer chain (since one hexagon is constituted by two carbon atoms, according to the structure of graphene). In summary, the different grafting densities are given by the **Equation S1-S3**.

$$\sigma_1 = \frac{x_{\text{polymer at } T_f}}{M_n \cdot \left(100 - x_{\text{polymer at } T_f} - x_{\text{residue at } 700^\circ\text{C}}\right)} \text{ (mol} \cdot \text{g}^{-1}) \quad \text{Eq. S1}$$

$$\sigma_2 = \frac{\sigma_1 \cdot N_A}{1315} \text{ (chain} \cdot \text{m}^{-2}) \quad \text{Eq. S2}$$

$$\sigma_3 = \frac{2}{A_{\text{hexagon}} \cdot \sigma_2} \text{ (carbon atoms)} \quad \text{Eq. S3}$$

Equation S1-S3 determining the grafting density from the thermogravimetric analysis. N_A represents Avogadro's number.

Elemental analysis (EA). The variable grafting densities (σ_1 , σ_2 and σ_3) were determined by the same procedure as described above for the thermogravimetric analysis. It should be noted that the key data for the grafting density calculation are the carbon and oxygen contents in **(2a)** and **(2b)**. Therefore the calculated carbon ($C\%$) and oxygen ($O\%$) contents (excluding the nitrogen, sulphur and hydrogen contents) from non-modified SWCNTs and polymer PMMA-Cp were employed to calculate the grafting density (σ_{CO}) in wt. %. According to the following

Equation S4, the results provide a slightly underestimated grafting density (σ_{CO}) for **(2a)** and **(2b)**, since the oxygen content ($O\%$) from non-modified SWCNTs was directly used and not recalculated according to the composition of the sample. This leads to an error of close to 1% for (σ_{CO}).

$$\sigma_{CO} = \frac{O\%_{Sample} - O\%_{SWCNTs}}{O\%_{PMMA-Cp}} \cdot 100 \text{ (wt. \%)} \quad \text{Eq. S4}$$

Equation S4 for determining the grafting density from elemental analysis.

As the hydrogen content remains very low, the hydrogen contribution was estimated from the amount of polymer (based on the stoichiometry of the methyl methacrylate monomer unit) according to (σ_{CO}). Taking into account the carbon, oxygen and theoretical hydrogen contents, a second value for the grafting density is subsequently delivered. From this value, the other grafting densities (σ_1 , σ_2 and σ_3) can then be expressed using the **Equation S1-S3**.

X-ray photo-electron spectroscopy (XPS). A detailed overview of the deconvolution of the C 1s signal is represented in **Figure S5**.

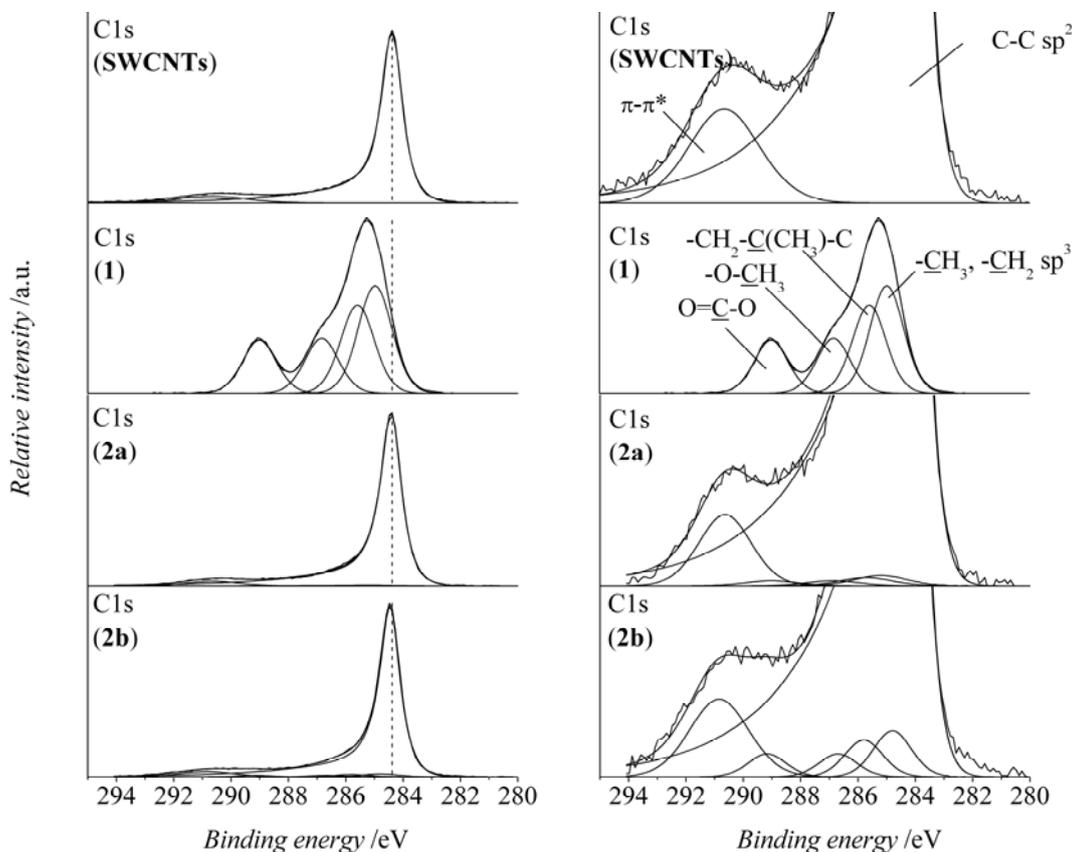


Figure S5. XPS spectra of non-modified SWCNTs, (1) PMMA-Cp, (2a) SWCNTs modified with PMMA-Cp at ambient temperature, (2b) SWCNTs modified with PMMA-Cp at 80°C. The C 1s signal from modified SWCNTs (C-C sp² at 284.4 eV) is represented.

The grafting densities (σ_1 , σ_2 and σ_3) were determined by the same procedure as employed for the thermogravimetric results. As for the elemental analysis, the grafting density (σ) was firstly expressed in *mol. %* and subsequently converted into *wt. %*. The different signals for oxygen and for carbon were respectively summed up to deliver the atomic content in oxygen and in carbon to be treated separately according to the signal assignment. The result was subsequently converted into *wt. %* after adding the contribution of hydrogen from the polymer based on the

stoichiometry of the methyl methacrylate monomer unit and the oxygen signals of the samples identical to PMMA-Cp reference spectrum. Based on the grafting density (σ) in *wt. %*, the other grafting densities (σ_1 , σ_2 and σ_3) can be expressed using the **Equation S1-S3**.

Estimation of the theoretical grafting density. The maximum theoretical grafting density can be calculated after the complete reaction of all unsaturated carbon double bonds with a PMMA-Cp polymer chain. In this model, one polymer chain is covalently linked with two carbon atoms, and – according to the graphene structure of the SWCNTs – the occupied surface can be approximated by a hexagon. By definition, the periodicity $\sigma_3 = 2$ leads to the **Equation S5** and **S6** using the same notation:

$$\sigma_1 = \frac{1315}{N_A \cdot A_{hexagon}} \text{ (mol} \cdot \text{g}^{-1}) \quad \text{Eq. S5}$$

$$\sigma_2 = \frac{1}{A_{hexagon}} \text{ (chain} \cdot \text{m}^{-2}) \quad \text{Eq. S6}$$

Equation S5-S6. determining the maximum theoretical grafting density for one polymer chain linked with one single carbon double bond. The employed terms refer to **Equation S1-S3**.

For a more realistic estimation of the theoretical grafting density, the PMMA-Cp chain length was approximated according to an ideal polymer chain model, i.e. the equivalent of an attached chain free to move. The Kuhn length b (17Å) and the Flory coefficient C_∞ (9.0) were taken from literature⁵ and applied for PMMA-Cp using the same formalism. The resulting approximation leads to a value of N monomers by 5.71 units. The mean-square radius of gyration and the radius of the corresponding disk are calculated according to **Equation S6 and S7**:

$$\langle R_g^2 \rangle = \frac{N \cdot b^2}{6} \quad \text{Eq. S7}$$

$$R_{disk}^2 = 2 \cdot \langle R_g^2 \rangle \quad \text{Eq. S8}$$

Equation S6-S7 (polymer equivalent freely jointed chain with interactions model) to determine a theoretical length of the PMMA-Cp polymer chain.

The surface of this disk for one polymer chain corresponds to the grafting density σ_2 (in chains·nm⁻²). The value of σ_1 and σ_3 were determined employing **Equation S9** and **S10**:

$$\sigma_1 = \frac{1315}{N_A \cdot \pi \cdot R_{disk}^2} \text{ (mol} \cdot \text{g}^{-1}) \quad \text{Eq. S9}$$

$$\sigma_3 = \frac{2 \cdot \pi \cdot R_{disk}^2}{A_{hexagon}} \text{ (carbon atoms)} \quad \text{Eq. S10}$$

Equation S9-S10 determining the grafting density of an ideal polymer chain onto SWCNTs. The employed terms refer to **Equation S1-S3**.

References and Notes

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