

# **Tunable thermo-responsive water-dispersed multi walled carbon nanotubes**

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## 1.0 General

### 1.1 *Reagents and materials*

Multiwall carbon nanotubes (Aldrich, OD = 3-10 nm, ID = 1-3 nm, length = 0.1-10  $\mu\text{m}$ , >99%), 1-pyrenemethanol (Aldrich, 98.0%), ethylenediamine (Aldrich, 99.0%) were used as received, poly(ethylene glycol) methyl ether methacrylate (PEGMA, Aldrich, average  $M_n$  ~475) and di(ethylene glycol) methyl ether methacrylate (DEGMA, Aldrich, 95.0%) were stored at 4 °C and used as received. Triethylamine (Fischer, 99.0%) was stored over sodium hydroxide pellets. All other reagents and solvents were obtained at the highest purity available from Aldrich Chemical Company and used without further purification unless stated.

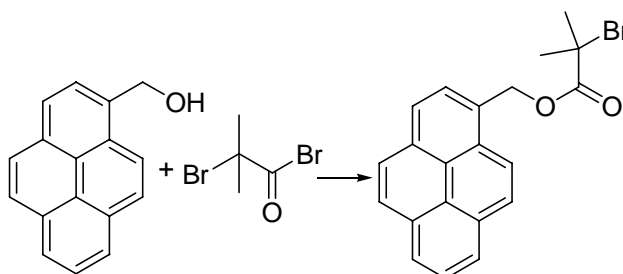
### 1.2 *Analysis and characterization*

All reactions were carried out using standard Schlenk techniques under an inert atmosphere of oxygen-free nitrogen, unless otherwise stated. Molar mass distributions were measured using size exclusion chromatography (SEC), on a system equipped with two PL gel 5 mm mixed C-columns (300  $\times$  7.5 mm) and one PL gel 5 mm guard column (50  $\times$  7.5 mm) (Polymer Laboratories) with differential refractive index detection using THF/triethylamine (95:5) or chloroform/triethylamine (95:5) at 1.0 mL min<sup>-1</sup> as the eluent. Poly(MMA) standards (200 to  $1.5 \times 10^6$  g/mol) and poly(styrene) standards (540 to  $1.64 \times 10^6$  g mol<sup>-1</sup>) were used to calibrate the SEC. The analyzed samples contained (0.2 % vol) toluene as the flow marker. The  $M_n$  reported in the  $M_n$  vs Conversion (%) plots are obtained from SEC data calibrated

with PMMA standards. NMR spectra were obtained on a Bruker DPX300 and Bruker DPX400 spectrometer. All chemical shifts are reported in ppm ( $\delta$ ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances ( $^1\text{H}$  and  $^{13}\text{C}$ ). The following abbreviations were used to explain the multiplicities: s = singlet, m = multiplet. The conversions were calculated by  $^1\text{H}$  NMR by following the decreasing of the integrals of the monomer vinyl signals (5.6 and 6.2 ppm), using the peak of mesitylene (6.9 ppm) as internal standard. Infrared absorption spectra were recorded on a Bruker VECTOR-22 FTIR spectrometer using a Golden Gate diamond attenuated total reflection cell. The thermal gravimetric analysis (TGA) dates were collected on a Perkin Elmer TGA 7, heating from 50 °C to 600 °C at 20 °C min<sup>-1</sup> under nitrogen. The transmission electron microscopy (TEM) was recorded by JEOL 2000 FX TEM with an accelerating voltage of 200 KV. Cloud points (LCSTs) of these polymers were measured using Varian Cary 100 UV-Vis spectrophotometer with temperature controller. The wavelength was set to 670 nm, heated with a rate of 20 °C min<sup>-1</sup>.

## 2.0 Synthesis of pyrene containing initiator and polymers

### 2.1 Synthesis of 2-bromo-2-methyl-propionic acid pyren-1-ylmethyl ester



**Figure S1.** Synthesis of the pyrene initiator employed in this study.

1-Pyrenemethanol, 0.500 g (2.15 mmol), and 0.90 mL (6.4 mmol) triethylamine were dissolved in dry THF (30 mL) in a 250 mL two-neck flask. Then 0.80 mL (6.4 mmol) 2-bromoisobutyryl bromide dissolved in dry THF (10 mL) was added dropwise to the flask under stirring at 0 °C. The mixture was stirred at ambient temperature overnight, then the resulting triethylamine hydrochloride salt was removed by filtration and the volatiles removed under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and washed sequentially with 1.0 M HCl, saturated NaHCO<sub>3</sub> aqueous solution and deionised water. The organic layer was collected and dried over anhydrous MgSO<sub>4</sub> overnight. After filtration and removal of the volatiles under reduced pressure the final 2-bromo-2-methyl-propionic acid pyren-1-ylmethyl ester product was further purified by recrystallisation in methanol (Yield 55%, 0.819g).

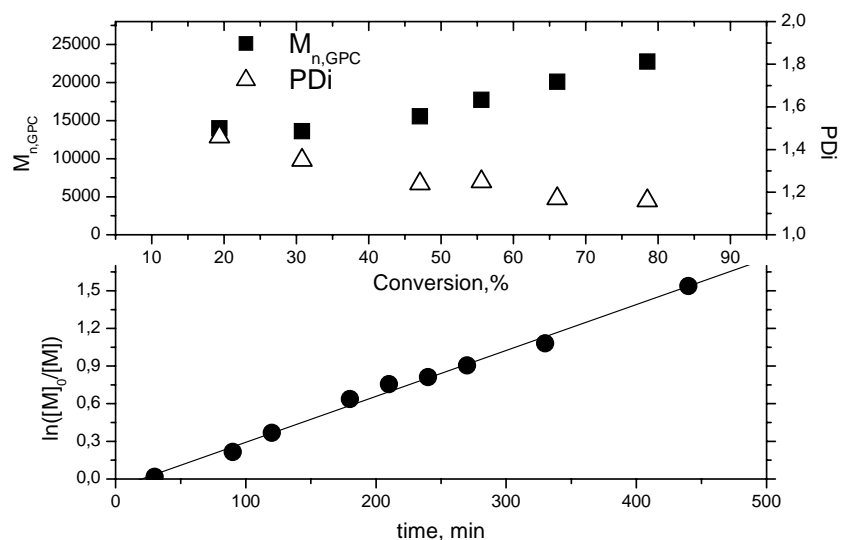
IR (neat):  $\tilde{\nu}$  = 3042, 2970, 1724, 1590, 1458, 1389, 1271, 1154, 1103, 1062, 1009 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 8.27-7.99 (m, 9H, pyrenyl), 5.91 (s, 2H, CH<sub>2</sub>), 1.84-1.81 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100.59 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  = 30.97 (2C, CH<sub>3</sub>), 53.28 (1C, (CH<sub>3</sub>)<sub>2</sub>CBr); 66.65 (1C, CH<sub>2</sub>O), 123.11-128.45 (9C, CH); 125.09-141.09 (7C, C), 171.83 (1C, CO<sub>ester</sub>).

## 2.2 Typical Polymerisation of PEGMA and DEGMA

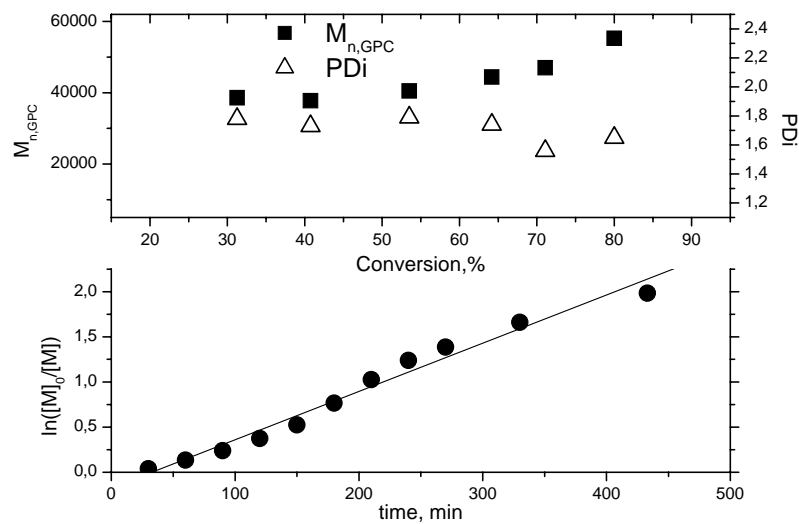
2-bromo-2-methyl-propionic acid pyren-1-ylmethyl ester initiator (0.034 g, 0.090 mmol), PEGMA (0.43 g, 0.90 mmol), DEGMA (1.5 g, 8.1 mmol), Me<sub>6</sub>Tren (0.024 mL, 0.090 mmol) and mesitylene as internal <sup>1</sup>H NMR standard dissolved in toluene (2.4 mL) were poured in a dried Schlenk flask and degassed by four freeze-pump-thaw cycles. The solution was then transferred via cannula to another Schlenk tube

containing Cu(0) powder (0.0058 g, 0.090 mmol) previously evacuated and filled with N<sub>2</sub>. The polymerisation was carried out at 25 °C. Samples were taken periodically using a degassed syringe for molecular weight (SEC) and conversion analysis (<sup>1</sup>H NMR). Once a conversion of 90 % was reached, the polymerisation was quenched by exposing the reaction mixture to air. The final mixture was diluted with toluene and passed through a short neutral alumina column, and the polymer was precipitated from toluene solution into a 10-fold excess of diethyl ether and isolated as pale yellow oil. The polymer was further purified by dialysis in water (nominal molecular weight cutoff (NMWCO) = 6-8 kDa).

The kinetic plots of the homo-polymerisation of DEGMA and PEGMA in the presence of the pyrene initiator are shown in Figures s1 and s2, respectively. They both gave good first order kinetic plots, although an induction period was observed in both cases, which may be due to the heterogenous nature of the catalyst. The molecular weights increased with conversion in both cases, although the PDI of the polymers was found to be relatively high, ~ 1.3 for poly(DEGMA) and ~ 1.7 for poly(PEGMA).



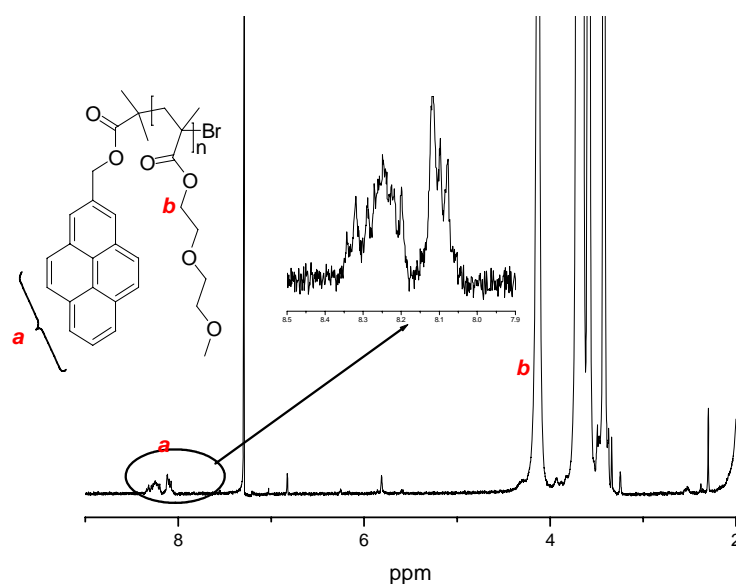
**Figure S2.** First order kinetic plot and  $M_n$ , PDI vs. conversion plot for the polymerisation of DEGMA. Reaction conditions:  $[DEGMA]_0 : [I]_0 : [Cu(0)]_0 : [L]_0 = 100 : 1 : 1 : 1$ , 25 °C.



**Figure S3.** First order kinetic plot and  $M_n$ , PDI vs. conversion plot for the polymerisation of PEGMA. Reaction conditions:  $[PEGMA]_0 : [I]_0 : [Cu(0)]_0 : [L]_0 = 100 : 1 : 1 : 2$ , 25 °C.

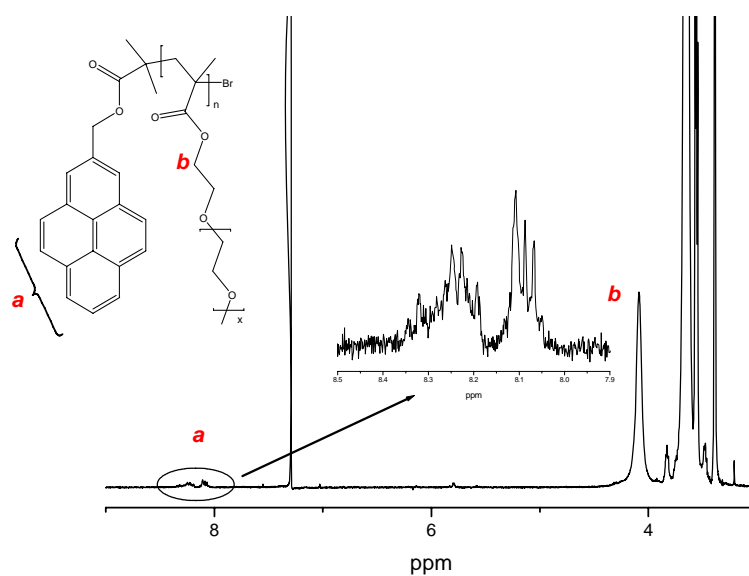
### 2.3 <sup>1</sup>H NMR analysis of the pyrene-terminal polymers.

The <sup>1</sup>H NMR spectra of the homo-polymer and copolymers of DEGMA and PEGMA with a pyrene ester moiety as chain-end (Polymer **1**, **2**, **3**) are shown in (Figure S4, Figure S5 and Figure S6). The peaks at approximately 8 ppm (peak *a*) corresponds to the protons on the pyrene ring, the peak at 4.1 ppm (peak *b*) is the -OCH<sub>2</sub> of the PEGMA or/and DEGMA chain. The degree of polymerisation (DP) for the polymers studied in this work was calculated according to the formula the ratio of  $DP = (4 \times I_{4.0}) / (2 \times I_{2.8})$ , where  $I_{4.0}$  and  $I_{2.8}$  are the integral relative to the peaks at approximately 4 and 2.8 ppm respectively.



Integration Attempt	Peak A Integral	Peak B Integral	Dp Calculated
1	9	219	109
2	9	223	111.5
3	9	223	111.5

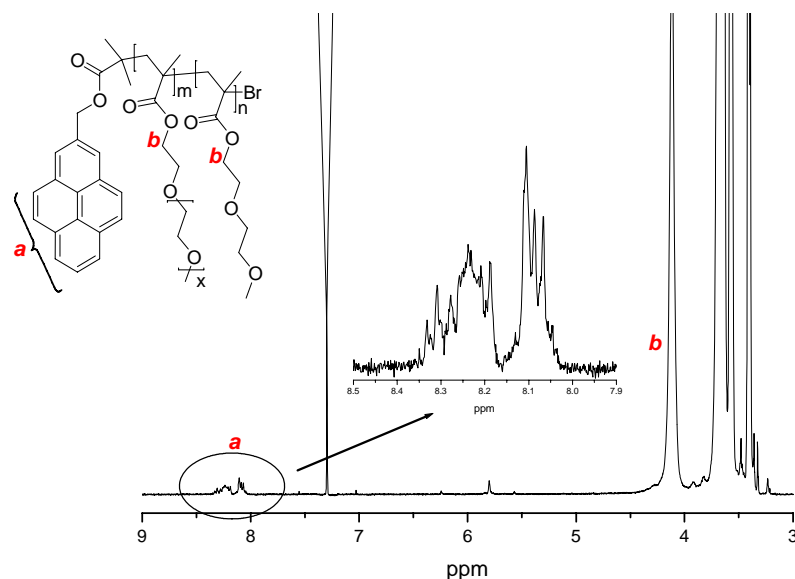
**Figure S4.**  $^1\text{H}$  NMR spectrum of pyrene-containing poly(DEGMA) (Polymer **1**) in  $\text{CDCl}_3$ .



Integration Attempt	Peak A Integral	Peak B Integral	Dp Calculated
1	9	206	103
2	9	216	108
3	9	208	104.5

**Figure S5.**  $^1\text{H}$  NMR spectrum of pyrene-containing poly(PEGMA) (Polymer **2**) in  $\text{CDCl}_3$ .





Integration Attempt	Peak A Integral	Peak B Integral	Dp Calculated
1	9	215	107.5
2	9	212	106
3	9	213	106.8

**Figure S6.**  $^1\text{H}$  NMR spectrum of pyrene-containing PEG copolymer (Polymer **3**) in  $\text{CDCl}_3$ .

### 3.0 Non-covalent modification of carbon nanotubes with pyrene-terminal polymers

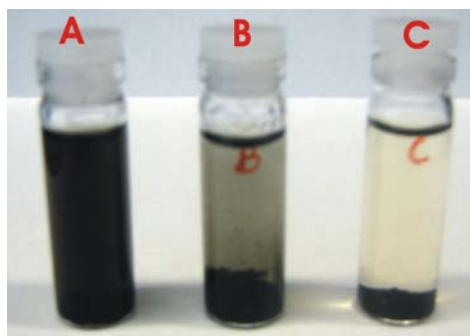
#### 3.1 Procedure of dispersing MWNT in water

In a typical experiment, 5.0 mg of pyrene-terminal polymer was dissolved in 5.0 mL of deionized water in a glass vial. 1.0 mg of MWNT was then added to the polymer solution. After sonication for 5 minutes, the mixture was analysed by TEM. The

modified nanotubes were recovered by centrifugation and washed with water several times in order to eliminate residual non-bound pyrene-terminal polymer. The modified nanotubes were then redispersed in water by sonication for 5 minutes. The thermal-responsive test was carried out in a clear oil bath with temperature control. The MWNT-polymer solution was heated gradually above its cloud point, until the MWNTs started to aggregate and precipitate. The vial was then removed from the oil bath and immersed in a cold water bath. After cooling, the vial was gently shaken and a dispersion of the MWNTs was observed.

### **3.2 Comparative experiments**

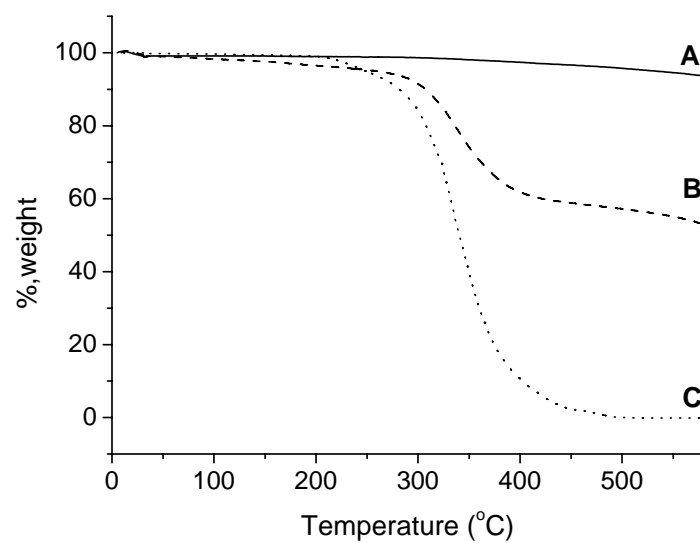
Comparative experiments were carried out using the procedure mentioned above. 5.0 mg of Polymer **2** (Sample A), a non-pyrene-containing PEGMA-DEGMA copolymer, 5.0 mg, (Polymer **4**, made by polymerization mediated by Cu(I)Br using methyl 2-bromopropionate as an initiator,  $M_n = 22,000 \text{ g mol}^{-1}$ ,  $PD_i = 1.37$ ) (Sample B) or a mixture of 1-pyrenebutyric acid, 5 mg, and sodium hydroxide, 1.4 mg, (Sample C) were dissolved in water, and 1.0 mg of MWNT were added to the solution. After 5 minutes of sonication, both Sample A and Sample B gave good dispersions, while Sample C was found to be unable to suspend an appreciable amount of MWNTs. After 12 h a good dispersion was still observed for the Sample A, while MWNTs in B had started to aggregate and precipitate. **Figure S7** shows a picture of such samples after 5 days. As it can be easily seen, the pyrene-terminal Polymer **2** confirmed its good ability to disperse MWNTs. Polymer **4** and 1-pyrenebutyric acid sodium salt showed respectively mediocre and very poor dispersant abilities.



**Figure S7.** Dispersion of MWNTs in water after 5 days in the presence of: A) pyrene-terminated Polymer **2**, B) non-pyrene-terminated Polymer **4**, C) 1-pyrenebutyric acid sodium salt.

### 3.3 TGA analysis

The modified nanotubes were recovered by centrifugation and washed with water several times in order to eliminate residual non-bound pyrene-terminal polymer. The modified nanotubes were collected, dried in a vacuum oven overnight at ambient temperature and analyzed by TGA. Trace A in **Figure S8** refers to unmodified MWNTs, which are stable until 550 °C with negligible weight loss, whereas trace C indicates that native Polymer **2** was completely degraded at below 500 °C. Polymer **2**-modified MWNTs show a ~ 40% weight loss (trace B) at the same temperature at which polymer **2** decomposed. Based on these measurements, the grafting ratio (GR), defined as the mass ratio of grafted polymer to nanotubes, was then estimated to be in the 0.35-0.45 range.



**Figure S8.** TGA traces for (A) MWNT (Solid line); (B) Polymer **2**-modified MWNT (dash line) and (C) pure Polymer **2** (dot line).