

Experimental:

The MWCNTs were kindly donated by Bayer Material Science (Baytubes C 150 P) and used as received. All solvents were dried and distilled before use. Methyl methacrylate (from Acros) was distilled before usage, α' -azoisobutyronitrile (AIBN, from Fluka) was recrystallized from diethyl ether, dioxane and tetrahydrofuran (THF) were dried and distilled before usage, all other solvents were used without further purification. Gel permeation chromatography (GPC) was carried out in THF as solvent and the detector system contained refractive index (Jasco RI 1570), UV-Vis (Jasco UV 1575) and light scattering (Wyatt minDAWN) detectors. Differential scanning calorimetry (DSC) was carried out using a Pyris DSC 7 and analysed by the Pyris Software.

Synthesis

Synthesis of 4-cyano-4-methyl-4-thiobenzoylsulfanyl-butyric acid 4-pyren-1-yl-butyl ester (RAFT reagent, modified procedure from ref. 22): 204 mg (0.73 mol) (4-cyanopentanoic acid)-4-dithiobenzoate (synthesized according to ref. 22), 200 mg (0.73 mol) 4(1-pyrenyl)butanol and 9 mg (0.073 mol) 4-(dimethylamino)-pyridine were dissolved in 5 ml THF and a solution of 151 mg (0.73 mol) N,N'-dicyclohexylcarbodiimide in 3 ml CH₂Cl₂ was added at 0 °C. The mixture was stirred and allowed to warm up to room temperature over night. The suspension with white precipitate was filtered over Celite, washed with chloroform and purified by column chromatography (pure chloroform). The product, 4-cyano-4-methyl-4-thiobenzoylsulfanyl-butyric acid 4-pyren-1-yl-butyl ester was freeze dried from benzene (366 mg, 95%). δ_{H} (100 MHz; CDCl₃; Me₄Si) 8,23 (1H, d, pyrene-H), 8,13 (4H, q, pyrene-H), 8,01 (3H, s, pyrene-H), 7,84 (3H, m, phenyl-H + pyrene-H), 7,53 (1H, t, phenyl-H), 7,35 (2H, t, phenyl-H), 4,16 (2H, t, C₄H₈), 3,37 (2H, t, C₄H₈), 2,72 - 2,58 (2H, m, C₄H₈), 2,01 - 1,66 (9H, m, C₄H₈ + CH₃ + C₂H₄).

Synthesis of **pyrene-PMMA X**: 1g (10mmol) of methyl methacrylate, **X = 90**: 29.4 mg ($5.5 \cdot 10^{-5}$ mol); **X = 180**: 53.9 mg ($1.0 \cdot 10^{-4}$ mol); **X = 270**: 107.2 mg ($2.0 \cdot 10^{-4}$ mol) (4-cyano-4-methyl-4-thiobenzoylsulfanyl-butyric acid 4-pyren-1-yl-butyl ester and **X = 90**: 2.2 mg ($1.34 \cdot 10^{-5}$ mol); **X = 180**: 4.1 mg ($2.5 \cdot 10^{-5}$ mol); **X = 270**: 8.0 mg ($4.87 \cdot 10^{-5}$ mol) AIBN were dissolved in 2 ml dioxane in a schlenk-tube and oxygen was exchanged by nitrogen by five freeze-pump-thaw cycles. Polymerisation was carried out at 70°C for 20 h. The polymers

were purified by dissolving in THF and precipitating in methanol for three times to yield **pyrene-PMMA X = 90**: 996.5 mg, 97%; **X = 180**: 992.0 mg, 99%; **X = 270**: 788.5 mg, 79%. δ_{H} (100 MHz; CDCl₃; Me₄Si) 3.54 (3H, s, O-CH₃), 1.84 (2H, m, CH₂), 0.96 (1H, s, CH), 0.80 (3H, m, CH₃). Molecular weights and PDIs are given in table 1.

Miscibility of PEG and PMMA

- 1.) The miscibility of PEG and PMMA has been extendedly investigated by H. Ito, T. P. Russell and G. D. Wignall (*Macromolecules* 1987, **20**, 2213-2220). They found out that PMMA chains were unperturbed in a PEG matrix and that the Flory-Huggins interaction parameter is almost zero (χ_{AB} varies from $-5 \cdot 10^{-3}$ to $-1 \cdot 10^{-3}$ as the fraction of PMMA increases from 0.3 to 0.7). Therefore they demonstrated that high molecular PEG ($M_{\text{w}} = 145000$ g/mol) and PMMA ($M_{\text{w}} = 125000$ g/mol) are completely miscible.
- 2.) In our former work on PMMA coated TiO₂ nanorods (see ref. 11) we demonstrated that also oligomeric PEG ($M_{\text{n}} = 400$ g/mol) disperses the PMMA coated nanorods. We found very stable dispersions that did not demix over time or upon heating.
- 3.) In the case of **pyrene-PMMA 90** we tested the miscibility with PEG 400 by a DSC experiments (scanning rate = 40 °C/min from -80 °C to 150 °C):
 - a. The glass transition temperature (T_{g}) of **pyrene-PMMA 90** is 70 °C
 - b. PEG 400 has a T_{g} of -63 °C and a melting temperature (T_{m}) of 5.5 °C
 - c. A mixture of 2:1 PEG 400 : **pyrene-PMMA 90** has a single T_{g} of -56 °C and a T_{m} of -0.5 °C.

The T_{g} of **pyrene-PMMA 90** is missing, the T_{m} (PEG 400) is lowered by 6 °C and the T_{g} (PEG 400) is raised by 7 °C in the mixture. Thus we believe that both polymers are also miscible in the low molecular weight regime.