Electronic Supplementary Information

Thermo- and light responsive micellation of azobenzene containing

block copolymers

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Experimental Section

Materials. All chemicals and solvents were commercially available and used as received unless otherwise stated. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from diethyl ether and stored at -7°C. Tetrahydrofuran (THF) and 1,4-dioxane were distilled over sodium previously. Pentafluorophenylacrylate (PFPA), *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide (3) and PEO macro-CTA with an molecular weight of $M_n = 5000$ g mol⁻¹ (1) were synthesized as described earlier.^{4,10} A concentrated coumarin 102 aqueous solution was prepared as followed: 200 mg of coumarin 102 were stirred vigorously in 500 mL of millipore water overnight. The insoluble excess amount of dye was filtered and the concentrated solution of coumarin 102 was used without further treatment. As dialysis membranes Spectra/Por 3 (MWCO 3500) were used.

Instrumentation. ¹H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer in deutorated solvents. ¹⁹F-NMR spectra were recorded on a Bruker 400 MHz FT-NMR spectrometer. Chemical shifts (δ) were given in ppm relative to TMS. Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions, M_w/M_n , of polymer samples with respect to polystyrene standards. GPC measurements were performed in THF as solvent. The flow rate was 1 mL/min at a temperature of 25°C. UV/Vis spectra were recorded on a Jasco V-630 photospectrometer. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer using an ATR unit. Cloud points were determined in Millipore water at a concentration of 10 mg/mL and were observed by optical transmittance of a light beam ($\lambda = 632$ nm) through a 1 cm sample quartz cell. The measurements were performed in a Jasco V-630 photospectrometer with a Jasco ETC-717 peltier element. The intensities of the transmitted light were recorded versus the temperature of the sample cell. The heating rate was 1°C per minute. Irradiation experiments of the polymer solutions were performed in the sample cell of the photospectrometer using an Oriel Instruments 500 W mercury lamp with a 365 nm filter and an optical fiber.³ Dynamic light scattering (DLS) measurements were performed at a concentration of 1 mg/mL in millipore water in a 40 µL low volume quartz cuvette on a Malvern Zetasizer Nano S. The solution was filtered through a 0.2 μ m PTFE filter prior. The angle of the light scattering detector was 90°. For the determination of the hydrodynamic radius R_H, the measured scattering intensities (volume) were used (Zetasizer software: "Malvern version 6.12"). In a typical DLS diagram, the intensities of the volume of scattering particles were plotted versus the radius R_{H} of the corresponding particles (volume intensity/size). Temperature dependant fluorescence measurements were performed on a Jasco spectrofluorometer FP-6500 with a Jasco ETC-273 peltier element. For the temperature dependent fluorescence measurement, 5 mg of the PEOb-PNIPAM (4) was dissolved in 10 mL of a concentrated solution of coumarin 102 in water. An excitation at 390 nm was chosen, because no absorption of azobenzene occurs at this wavelength.

Synthesis of poly(ethyleneoxide)-block-poly(pentafluorophenylacrylate) (PEO-b-PPFPA, 2) 2.0 g (0.381 mmol) PEO macro-CTA (1) and 16.3 g (0.0685 mol) PFPA were dissolved in a schlenk tube in 30 mL of dry 1,4-dioaxane. Next, 10.4 mg (0.0634 mmol) AIBN were added and the schlenk tube was sealed. After four freeze-pump-thaw cycles, the polymerization was performed in a preheated oil bath at 80°C under argon atmosphere. After a reaction time of 12 h, the solution was cooled to room temperature and then precipitated into hexane three times. After each precipitation step, the pink colored block copolymer was redissolved in dry THF. The product was dried in a vacuum oven at 40°C overnight. Usually, 9.0 g (55 %) of pink colored block polymer was obtained. Next, the dithioester was removed by treatment with an excess amount of AIBN. Therefore, 7.0 g of the previous obtained pink colored block copolymer was dissolved in a schlenk tube in 30 mL dry 1,4-dioxane with 2.0 g (30 equiv.) of AIBN. The tube was sealed and placed under vigorous stirring in a preheated oil bath at 80°C. After 3 h, the solution color turned from pink into colorless. The product was isolated by several precipitation steps into hexane. After centrifugation and drying in a vacuum oven, 5.3 g (76 %) of the final white colored PEO-b-PPFPA (2) was obtained. UV/Vis measurements in chloroform proved successful removal of the dithioester end group, as the characteristic absorption band at 302 nm completely vanished. ¹H NMR (CDCl₃): δ/ppm: 3.85 (t), 3.69 (s), 3.62 (s), 3.56 (s); 3.38 (t), 3.52 (s), 3.05 (br s), 2.83 (br s), 2.46 (br s), 2.09 (br s); FT-IR (ATR-mode): 2880 cm⁻¹ (-CH₂- valence), 1784 cm⁻¹ (C=O reactive ester band), 1519 cm⁻¹ (PFP C=C aromatic band), 1090 cm⁻¹ (C-O ether valence), 990 cm⁻¹ (C-O ester valence); Mol. Weight: M_n (GPC) = 22000 g mol⁻¹, M_w/M_n (GPC) = 1.22.

Synthesis of poly(ethyleneoxide)-*block*-poly(*N*-isopropylacrylamide) (PEO-*b*-PNIPAM, 4) with azobenzene side groups. 1 g of PEO-*b*-PPFPA (2) and 1 mL (7.214 mmol) of trietylamine were dissolved in 25 mL dry THF. Next, 50 mg (0.187 mmol) of *N*-(2-

aminoethyl)-4-(2-phenyldiazenyl)benzamide (3) was added subsequently and the solution was allowed to stir for 3 h at 50°C under nitrogen atmosphere. Afterwards, 2 mL (23.35 mmol) of isopropylamine were added and the solution was stirred further for 14 h. The crude product was isolated by precipitation into hexane. After drying in vacuum, the yellow colored solid was suspended under vigorous stirring in 10 mL of cold water. After filtration of the insoluble impurities, the filtrate was transferred into a dialysis membrane and dialyzed against water for 2 days. The solution was then evaporated and the residue was redissolved in 5 mL of THF. The final product was isolated by precipitation into hexane. After centrifugation and drying in vacuum at 40°C, 400 mg (64 %) of yellow colored PEO-*b*-PNIPAM (4) was obtained. ¹H NMR (CDCl₃): δ /ppm: 8.09 (br s), 7.93 (br s), 7.52 (br s), 6.43 (br s), 3.96 (br s), 3.83 (t), 3.67 (s), 3.60 (s), 3.53 (s), 3.36 (t), 3.33 (s), 2.12 (br s), 1.62 (br s), 1.33 (br s), 1.12 (br s); FT-IR (ATR-mode): 3300 cm⁻¹ (N-H amide valence), 2900 cm⁻¹ (-CH₂- valence), 1645 cm⁻¹ (C=O amide band II), 1540 cm⁻¹ (C=O amide band II), 1117 cm⁻¹ (C-O ether valence); UV/Vis (H₂O): $\lambda_{max} = 326$ nm, 431 nm; Mol. Weight: M_n (GPC) = 12500 g mol⁻¹, M_w/M_n (GPC) = 1.20.

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Figure S1. FT-IR spectra of PEO-*b*-PPFPA (2, black line) and PEO-*b*-PNIPAM (4, gray line) showing a complete conversion.



Figure S2. GPC curves of PEO-*b*-PPFPA (2, black line) and PEO-*b*-PNIPAM (4, gray line).



Figure S3. ¹H NMR spectra of PEO-*b*-PPFPA (2, black line, CDCl₃) and PEO-*b*-PNIPAM (4, gray line, CD₂Cl₂) indicating a successful reaction.



Figure S4: Temperature dependent (20°C, 40°C and 60°C) ¹H NMR measurement of PEO-*b*-PNIPAM (4) in deuteroxide (7 mg/mL) showing the formation of micelles.



Figure S5: DLS measurements (volume intensity/size) of PEO-*b*-PNIPAM (4) at different temperatures showing the reversible formation of micellar structures.