Supporting Information

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New Perspectives for the Design of Molecular Actuators:
Thermally Induced Collapse of Single Macromolecules from Cylindrical Brushes to Spheres

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Materials.
2-Hydroxyethyl methacrylate (HEMA Aldrich 99 %) was purified according to the literature[1]. N-isopropylacrylamide (NIPAM Aldrich 99 %) was recrystallized twice from a benzene/n-hexane (3:2) mixture. α-bromoisobutyryl bromide (98 %), ethyl 2-bromoisobutyrate (BriB 99 %), Copper bromide (CuBr 99.99 %) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA 97 %) were purchased from Aldrich and used without further purification. 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me₄Cyclam 97 %, Fluka) was also used without further purification. Tetrahydrofuran (THF Merck) was stirred with LiAlH₄ overnight and distilled prior to use.
Synthesis

The macro initiator poly(2-(2-bromoisobutyryloxyethyl methacrylate) (PBIEM) was prepared as follows: First, poly(2-hydroxyethyl methacrylate) (poly(HEMA)) was synthesized according to the literature[2]: 13 g (0.1 mol) freshly purified HEMA, 28.8 mg (0.2 mmol) CuBr and 46.1 mg (0.2 mmol) HMTETA were dissolved in 24.4 ml ethanol. The mixture was stirred 1 hour in an argon atmosphere until the solution was homogeneous. 39.1 mg (0.2 mmol) BrI-B were injected with a syringe. Then the solution was degassed by two freeze-thaw cycles and immersed in a thermostated oil bath at 70 °C to polymerize 24 hours. The poly(HEMA) was purified by passing through an Al₂O₃ column, followed by precipitation in cyclohexane. The yield was 10.1 g (77.6 %). 4 g of poly(HEMA) (0.0311 mol OH groups) were dissolved in 50 ml of anhydrous pyridine. Then 14.3 g α-bromoisobutyryl bromide was added slowly at 0°C under dry argon. The solution was kept stirring at 0°C for 3 hours and for another 24 hours at room temperature. The precipitated pyridinium salt was filtered off, and the solvent was removed by means of a rotating evaporator. The crude product was purified by dissolving in toluene and passing through an Al₂O₃ column, followed by precipitation in methanol. Finally the product was freeze-dried from benzene.

Yield: 6.2 g (81.1 %). ¹H-NMR (CDCl₃) δ(ppm)=4.31, 4.17 (-CH₂-OCO), 1.96 (-C(Br)(CH₃), 1.54 (-CH₂-C), and 1.06-0.89 (-CH₃), .

Typical ATRP Procedure: 11.3 g (0.1 mol) NIPAM, 144 mg (1 mmol) CuBr, 256 mg (1 mmol) Me₄Cyclam in 160 ml of THF and 294.1 mg (1 mmol bromine) PBIEM in 40 ml of THF were placed in two Schlenk flasks under dry argon and stirred for 1 hour at room temperature. The two solutions were degassed by two freeze-thaw cycles, put into an ice bath for two hours, and mixed together to polymerize while stirring. After 40 minutes the polymerization was terminated by precipitation in n-hexane. The crude product was further purified by fractional precipitation into n-hexane/acetone followed by membrane ultrafiltration (cut off molar mass: 10⁴ g/mol) in deion-
ized water. Yield after freeze drying from water: 2.2 g (19 % with respect to the monomer).

**Characterization**

Gel permeation chromatography (GPC) of the macro initiators were performed in THF (35 °C, flow rate 1 ml/min) employing an apparatus consisting of a Waters 515 HPLC-pump, a Waters 2487 UV/VIS detector (λ = 254 nm) and a Waters 2410 refractive index detector equipped with styragel columns (MZ-Analysentechnik, Mainz, 5 µm, pore size: 10^6 Å, 10^5 Å, 10^4 Å, 10^3 Å). The GPC measurements of the NIPAM containing polymer samples were conducted in N,N-dimethylformamide (1 g/l LiBr, 60 °C, flow rate 1 ml/min) utilizing a Waters 510 HPLC-pump, a Waters 486 UV/VIS-detector (λ = 275 nm), a Waters 410 refractive index detector and a styragel column set (MZ-Analysentechnik, Mainz, 5 µm, pore size: 10^6 Å, 10^4 Å, 10^3 Å). Narrowly distributed polystyrene samples (PSS, Mainz), which cover a broad range of molar mass (10^4 ≤ M ≤ 2·10^6 g/mol) were used for calibration of both systems. Static light scattering measurements were performed with an JDS Uniphase 1145p-3083 He-Ne laser source (632.8 nm wave length, 25 mW output power), an ALV-SP86 goniometer and an ALV/High QEAPD Avalanche photodiode fiber optic detection system. The dilute polymer solutions in methyl ethylketone, THF or water (typically 4-5 concentrations 0.05 ≤ c ≤ 1 g/l) were measured from 30° to 150° in steps of 5°. Prior to the measurements the solutions were filtered through 0.2 µm pore size Dime filters (Millipore LG) for organic solvents or through 0.22 µm Millex GS filters (Millipore) for aqueous solutions.

Temperature dependent static light scattering was performed by a multi angle fiber optical instrument (ALV-1500) with a Krypton ion laser (300 mW, 647.1 nm) as described elsewhere [3]. Data were recorded from four different concentrations and evaluated according to Zimm.
Temperature dependent dynamic light scattering measurements were performed by means of an apparatus consisting of a Spectra Physics Argon laser 2060 ($\lambda = 496.5$ nm, 300 mW), an ALV SP125 goniometer (thermostated from 20 °C to 40 °C with a Haake F3 thermostat) and an ALV-5000 multitau correlator. The dilute polymer solutions were measured from 30° to 150° in steps of 20° at four different concentrations at 20 and 34 °C. At all other temperatures only one concentration ($c = 0.031$ g/l) was measured because the concentration dependence of the diffusion coefficient was found to be negligible. The initial slope of the correlation functions were determined by a Simplex algorithm utilizing a fit of 2 exponential functions.

The refractive index increment ($dn/dc$) was measured by a home built Michelson interferometer using a Uniphase 1104P He/Ne laser ($\lambda = 632.8$ nm) as described elsewhere [4]. The results were $dn/dc = 0.1659$ cm$^3$/g for the PNIPAM brushes in water at 20 °C. The small temperature dependence of $dn/dc$ was neglected; for the macro initiator PBIEM the refractive index increment was determined to $dn/dc = 0.095$ cm$^3$/g in THF.

Atomic force microscopy (AFM) images of the adsorbed polymer brushes on mica substrates in air were obtained using a Nanoscope IIIa (Multimode) scanning force microscope (Veeco Instruments, Santa Barbara, CA, USA) operating in intermittent contact mode (Tapping-Mode™). Microfabricated silicon tips with an approximate resonant frequency of 300 kHz and a force constant of 48 N/m (Nanosensors, Wetzlar-Blankenfeld, Germany) were used. Imaging of the polymer brushes in aqueous solution employing intermittent contact mode was achieved with a Molecular Force Probe instrument (MFP-3D) from Asylum Research, Santa Barbara, CA, USA) using oxide sharpened silicon nitride tips (Veeco Instruments, Santa Barbara, CA, USA) with a tip radius of 5-10 nm, a nominal spring constant of 0.01 - 0.05 N/m, and a resonance frequency in water of about 5 - 10 kHz.
Figure 1: GPC-traces of the unfractionated (a) and fractionated (b) PNIPAM brushes in DMF.

Figure 2: Scattering envelopes of the PNIPAM brushes in water at three different temperatures: (a) 20 °C, (b) 31.7 °C, (c) 33.2 °C (for clarity, only one concentration (c = 0.031 g/l) is shown).
Figure 3: The apparent diffusion coefficient $D_z$ as function of $q^2$ for the PNIPAM brushes at $T = 20 \, ^\circ C$ (a) and at $T = 34 \, ^\circ C$ (b). The smaller slope for the collapsed brushes is explained by a more narrow particle size distribution of the collapsed brushes as compared to the extended cylindrical brushes. This difference also clearly emerges from the decay of the autocorrelation functions $g_1(t)$ which are close to single exponential for the collapsed brushes.

Figure 4: Concentration dependence of the diffusion coefficient $D_z$ for the PNIPAM brushes at $T = 20 \, ^\circ C$ (a) and at $T = 34.2 \, ^\circ C$ (b).

