Supplementary Material (ESI) for Soft Matter

Electronic Supplementary Information (ESI)

Self-Assembly of Double Thermoresponsive Block Copolymers End-capped with Complementary Trimethylsilyl Groups

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Synthesis of Monomers

N-Propylacrylamide. Acryloylchloride (9.11 g, 0.10 mol) in dry benzene (20 ml) was cooled in a dried 250 ml Schlenk flask to 0°C. Then, dry triethylamine (11.36 g, 0.11 mol) and propylamine (5.91 g, 0.10 mol) in dry benzene (20 ml) were added dropwise. The solution was allowed to reach room temperature and was stirred for 1 h. The precipitated salt was filtered off, and the solvents were removed in vacuo. The crude product was distilled in vacuo at 105°C to give N-propylacrylamide as a slightly yellow liquid (6.54 g, 58%) which solidifies upon storage at -25°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.4 Hz, 3H, C*H*$_3$), 1.46-1.58 (m, 2H, C*H*$_2$CH$_3$), 3.20-3.27 (m, 2H, NHC*H*$_2$), 5.54-5.58 (m, 1H, C*H*$_2$CH), 6.08-6.25 (m, 2H, C*H*$_2$CH, CH$_2$C*H*), 6.41 (bs, 1H, N*H*). ^{13}C NMR (75MHz, $CDCl_3$): δ = 11.4 (*C*H$_3$), 22.8 (*C*H$_2$CH$_3$), 41.4 (NH*C*H$_2$), 125.8 (*C*H$_2$CH), 131.3 (CH$_2$*C*H), 165.9 (*C*=O).

N-Ethylacrylamide. Ethylamine (9.20 g, 0.20 mol) was cooled to -25°C, transferred into a dried Schlenk flask and cooled to -40°C. Then, dry CH_2Cl_2 (80 ml) and dry triethylamine (21.10 g, 0.21 mol) were added. Acryloylchloride (18.35 g, 0.20 mol) in dry CH_2Cl_2 (40 ml) was added dropwise. The reaction was stirred at -40°C over night, then allowed to warm up to room temperature and stirred for additional 2 h. The precipitated salt was filtered off and the solvents were removed in vacuo. The crude product was distilled in vacuo at 100°C to yield N-ethylacrylamide as a slightly brown liquid (10.40 g, 53%), which solidified upon storage at -25°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (t, J = 7.2 Hz, 3H, C*H*$_3$), 3.23-3.27 (m, 2H, NHC*H*$_2$), 5.50 (dd, J = 7.2 Hz, 1H, C*H*$_2$CH), 6.13-6.15 (m, 2H, C*H*$_2$CH, CH$_2$C*H*), 6.98 (bs, 1H, N*H*). ^{13}C NMR (75MHz, $CDCl_3$): δ = 14.5 (*C*H$_3$), 34.3 (*C*H$_2$CH$_3$), 125.5 (*C*H$_2$CH), 131.2 (CH$_2$*C*H), 165.8 (*C*=O).

Synthesis of Polymers.

Synthesis of poly(N-propylacrylamide)$_{137}$ (P0.1). In a 10 ml Schlenk tube N-propylacrylamide (3.0 g, 26.5 mmol), 4-(trimethylsilyl)benzyl 4'-(trimethylsilyl)butane-dithioate (45 mg, 0.13 mmol) and AIBN (2.0 mg, 0.012 mmol) were dissolved in dry THF (15 ml) and degassed by three freeze-pump-thaw cycles. The polymerization was carried out at 65°C for 5 h. The reaction mixture was precipitated two times into diethylether to yield poly(N-propylacrylamide)$_{137}$ as slightly yellow solid (1.9 g, 63%).

Synthesis of poly(N-ethylacrylamide)$_{133}$ (P0.2). In a 10 ml Schlenk tube N-ethylacrylamide (1.6 g, 16.1 mmol), 4-(trimethylsilyl)benzyl 4'-(trimethylsilyl)butane-dithioate (32 mg, 0.09 mmol) and AIBN (2.0 mg, 0.012 mmol) were dissolved in dry THF (3.6 ml) and degassed by three freeze-pump-thaw cycles. The polymerization was carried out at 65°C for 6 h. The reaction mixture was precipitated two times into hexane to yield poly(N-ethylacrylamide)$_{133}$ as slightly yellow solid (1.22 g, 76%).

Synthesis of poly(N-ethylacrylamide)$_{94}$ (P0.3). In a 10 ml Schlenk tube N-ethylacrylamide (3.2 g, 28.5 mmol), 4-(trimethylsilyl)benzyl 4'-(trimethylsilyl)butane-dithioate (52 mg, 0.15 mmol) and AIBN (2.2 mg, 0.013 mmol) were dissolved in dry THF (25 ml) and degassed by three freeze-pump-thaw cycles. The polymerization was carried out at 65°C for 5 h 30 min. The reaction mixture was precipitated two times into diethylether to yield poly(N-ethylacrylamide)$_{94}$ as slightly yellow solid (1.77 g, 55%).

Synthesis of poly(N-propylacrylamide)$_{137}$-*b*-poly(N-ethylacrylamide)$_{67}$ (P1). In a 10 ml Schlenk tube poly(N-propylacrylamide)$_{137}$ (1.0 g, 0.07 mmol), N-ethylacrylamide (588 mg, 5.9 mmol) and AIBN (0.8 mg, 0.005 mmol) were dissolved in dry THF (5.5 ml) and degassed

by three freeze-pump-thaw cycles. The polymerization was carried out at 65°C for 4 h. The reaction mixture was precipitated two times into diethylether to yield poly(N-propylacrylamide)$_{137}$-*b*-poly(N-ethylacrylamide)$_{67}$ as slightly yellow solid (1.1 g).

Synthesis of poly(N-propylacrylamide)$_{133}$-*b*-poly(N-ethylacrylamide)$_{133}$ (P2). In a 10 ml Schlenk tube poly(N-ethylacrylamide)$_{133}$ (250 mg, 0.02 mmol), N-propylacrylamide (360 mg, 3.2 mmol) and AIBN (0.01 mg, 0.00006 mmol) were dissolved in dry THF (1.5 ml) and degassed by three freeze-pump-thaw cycles. The polymerization was carried out at 65°C for 4 h 30 min. The reaction mixture was precipitated two times into diethylether to yield poly(N-propylacrylamide)$_{133}$-*b*-poly(N-ethylacrylamide)$_{133}$ as slightly yellow solid (310 mg).

Synthesis of poly(N-ethylacrylamide)$_{94}$-*b*-poly(N-propylacrylamide)$_{34}$ (P3). In a 10 ml Schlenk tube poly(N-ethylacrylamide)$_{94}$ (1.0 g, 0.11 mmol), N-propylacrylamide (900 mg, 8.0 mmol) and AIBN (1.5 mg, 0.009 mmol) were dissolved in dry THF (5.5 ml) and degassed by three freeze-pump-thaw cycles. The polymerization was carried out at 65°C for 4 h. The reaction mixture was precipitated two times into diethylether to yield poly(N-ethylacrylamide)$_{94}$-*b*-poly(N-propylacrylamide)$_{34}$ as slightly yellow solid (1.15 g).

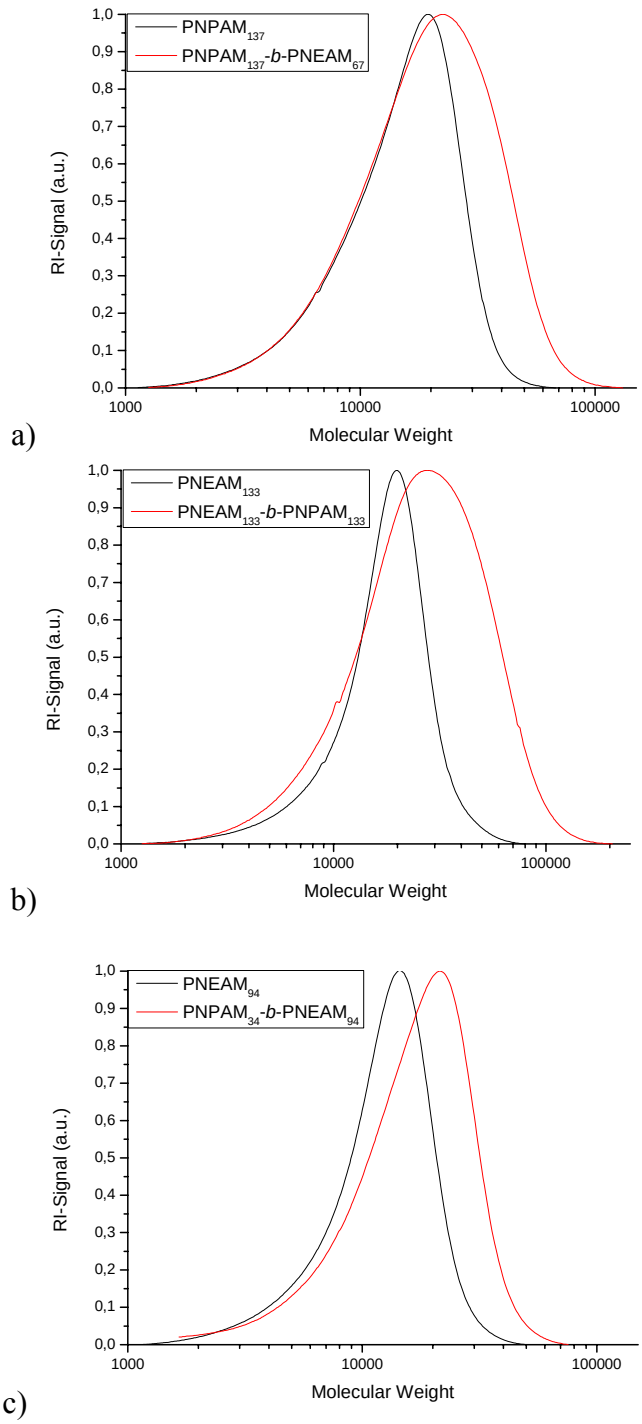

Fig. S1 SEC traces of polymers in N,N-Dimethylacetamide/0.1 wt% LiBr: a) poly(N-propylacrylamide)$_{137}$ (**P0.1**) and poly(N-propylacrylamide)$_{137}$-*b*-poly(N-ethylacrylamide)$_{67}$ (**P1**); b) poly(N-ethylacrylamide)$_{133}$ (**P0.2**) and poly(N-propylacrylamide)$_{133}$-*b*-poly(N-ethylacrylamide)$_{133}$ (**P2**).; c) Poly(N-ethylacrylamide)$_{94}$ (**P0.3**) and poly(N-ethylacrylamide)$_{94}$-*b*-poly(N-propylacrylamide)$_{34}$ (**P3**).

Transmission Electron Microscopy

Sample Preparation:

The samples for TEM were prepared at ambient temperature of 45°C and saturated humidity in a custom-made CEVS apparatus ("controlled environment vitrification system") according to Talmon and coworkers [1]. For staining experiments, the corresponding staining solution was also kept in the CEVS. Under these temperature and humidity controlled conditions a droplet (6 μL) of the solution was placed on hydrophilized (60 s plasma treatment at 8 W using a BALTEC MED 020 device) carbon filmed copper grids. The excess fluid was blotted off with a filter paper and a droplet of the staining solution (phosphotungstic acid at pH7.0) was added for 30s. After removal of the staining excess the grids were left to air-dry.

A second batch of grids were prepared without adding staining material. The air-dried grids were transferred into a BALTEC MED020 device for platinum/carbon shadowing at 45° using the system's electron beam evaporator. A Pt/carbon layer of approximately 10 nm was applied.

[1] J. R. Bellare, H. T. Davis, L. E. Scriven, Y. Talmon (1988)
Controlled environment vitrification system (CEVS): An improved sample preparation technique. J. Electron Microsc. Tech. **10**, 87-111.

Microscopy:

The air-dried grids were transferred into a Philips Tecnai F20 transmission electron microscope (FEI company, Oregon, USA). Microscopy was carried out at calibrated primary magnifications between 6000× and 25000x. Images were recorded using the 2k-Eagle CCD camera at full resolution (2048×2048 pixel). The accelerating voltage was 160 kV and the defocus was chosen to be about 1 μm.