Supporting Information for:

Thermoresponsive Dynamers: Thermally Induced, Reversible Chain Elongation of Amphiphilic Polyacylhydrazones

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Experimental Section

General: NMR spectra were recorded on a Bruker Avance 400 spectrometer and are referenced to the solvent. High-Resolution mass spectra were recorded on a Bruker Micro TOF mass spectrometer. MALDI-TOF analyses were performed on a Bruker AutoFlex II mass spectrometer. Turbidimetry profiles were recorded on Varian Carey-3 spectrophotometer. Reagents were used as received from commercial suppliers. All reactions were carried out under an atmosphere of dry N_2 unless otherwise indicated. Anhydrous THF, CH_2Cl_2, and MeOH were obtained by passage through columns of activated molecular sieves. DMF (extra dry, Acroseal) was purchased from Acros Organics. Silica gel chromatography was performed with Geduran silica gel 60 (230-400 mesh, 40-63 ím, Merck). Yields refer to homogenous, analytically pure (^{1}H NMR) material, and have not been optimized. Deionized water was obtained from a Millipore Synergy 185 water purifier. All pH and pD measurements were recorded on a Metler-Toledo Multi-Seven pH meter using a Hamilton Spintrode mini-probe. pD values are uncorrected. Compounds **1** and **2** were synthesized as previously reported.[1]

Size Exclusion Chromatography/Multi-Angle Laser Light Scattering: Size exclusion chromatography was performed using an Agilent 1100 Permeation Chromatograph equipped with Dawn Heleos multi-angle laser light scattering, and Optilab rEX differential refractive index detectors. Shodex OH-pak columns were used

(one precolumn (10 μm, 8 × 50 mm), and three columns (10μm, 8 × 300 mm)). After filtration through a 0.45 μm filter (Millex Millipore), 100-200 μl samples were injected at a flow rate of 0.5 ml/min using a solvent containing 100 mM $NaNO_3$ and 5 mM Na_3PO_4 at pH 7.4.

Transmission Electron Microscopy (TEM): TEM images were recorded on a CM12 Philips microscope operating at 120 kV using a Megaview III camera. Samples were prepared as follows: 450 μl of 5 mM phosphate buffer (pH 7.8) in deionized water was added to glass vials, and small volumes (10-30 μl) of concentrated (0.1-0.2 M) stock solutions of the corresponding dialdehyde and di(acylhydrazide) monomers in D_2O were added *via* microsyringe to give the indicated final concentrations. The solutions were acidified by the addition of μl quantities of a ~ 15% HCl solution. Aliquots were removed from the sample at various intervals and immediately diluted by a factor of 50 in 5.0 mM phosphate buffer (pH 7.8), deposited onto glow-discharged carbon films, stained with 1% $UO_2Ac_2 \cdot 2H_2O$, and air-dried prior to observation.

Synthesis of Model Monomers.

Compound 3. To a solution of 3-hydroxybenzaldehyde (337 mg, 2.76 mmol) and hexaethyleneglycolmonomethylether tosylate[1] (1.176 g, 2.61 mmol) in anhydrous DMF (15 mls) were added K_2CO_3 (1.2 g, 8.68 mmols), and NaI (ca. 100 mg). The reaction was set stirring at 80 °C for 5 h and then allowed to cool to room temperature. The reaction was transferred to a separatory funnel, $CHCl_3$ (250 mls) was added, and washed with water (75 mls). The aqueous phase was extracted with $CHCl_3$ (2 × 75 mls) and the combined organic phase was dried over $MgSO_4$, and concentrated to a yellow oil, which was stored at < 0.1 mmHg for 12 h. The product was isolated by column chromatography

(SiO_2, EtOAc) as a colorless oil (890 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.43-7.37 (m, 3H), 7.19-7.16 (m, 1H), 4.16 (t, *J* = 4.6 Hz, 2H), 3.85 (t, *J* = 4.6 Hz, 2H), 3.71-3.59 (m, 18H), 3.52-3.49 (m, 2H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 159.3, 137.7, 130.0, 123.4, 121.9, 113.0, 71.9, 70.8, 70.6, 70.5, 70.4, 69.5, 67.7, 59.0; HRMS (ESI, *m/z*) calcd for $C_{20}H_{32}NaO_8$: 423.1995, found: 423.2003.

Compound 4. To a solution of methyl-3-hydroxybenzoate (418 mg, 2.75 mmol) and hexaethyleneglycolmonomethylether tosylate[1] (1.176 g, 2.61 mmol) in anhydrous DMF (15 mls) were added K_2CO_3 (1.2 g, 8.68 mmols), and NaI (ca. 100 mg). The reaction was set stirring at 80 °C for 8 h and then allowed to cool to room temperature. The reaction was transferred to a separatory funnel, $CHCl_3$ (250 mls) was added, and washed with water (75 mls). The aqueous phase was extracted with $CHCl_3$ (2 × 75 mls) and the combined organic phase was dried over $MgSO_4$, and concentrated to a colorless oil, which was stored at < 0.1 mmHg for 12 h. This was dissolved in MeOH (15 mls), hydrazine hydrate (500 μl, ~ 25% in H_2O) was added, and the solution was stirred at room temperature for 24 h. After this period, the reaction was concentrated under reduced pressure at room temperature and stored at < 0.1 mmHg for 72 h. The product was then purified by column chromatography (SiO_2, EtOAc:MeOH 2:1), dissolved in CH_2Cl_2, filtered to remove residual SiO_2, and concentrated under reduced pressure to give the product as a pale yellow oil (255 mg, 22%). ^{1}H NMR (400 MHz, MeOD) δ 7.39-7.38 (m, 3H), 7.14-7.11 (m, 1H), 4.19 (t, *J* = 4.5 Hz, 2H), 3.87 (t, *J* = 4.6 Hz, 2H), 3.73-3.61 (m, 18H), 3.55-3.53 (m, 2H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, MeOD) δ 169.3, 158.5, 133.8, 130.6, 120.2, 118.9, 113.3, 71.3, 70.1, 69.9, 69.8, 69.3, 67.6, 58.4.

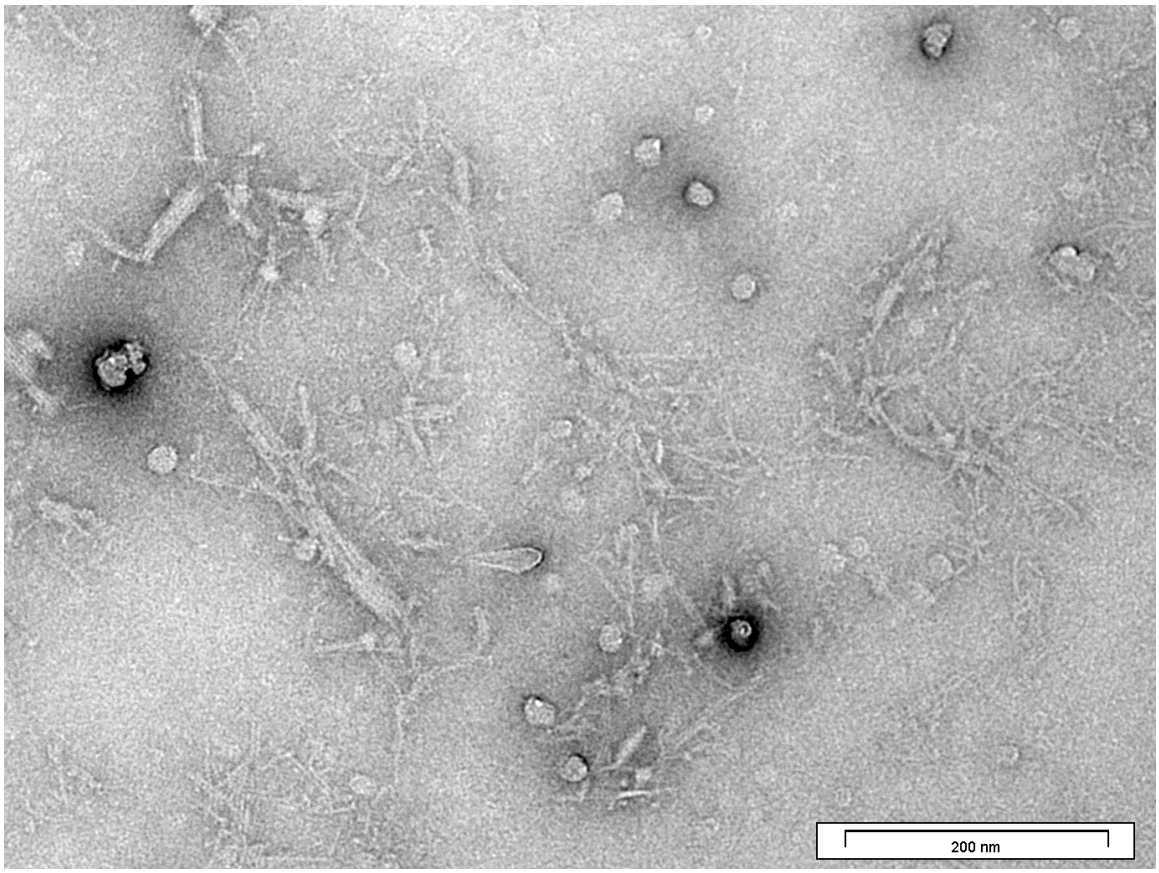

Figure S-1. Larger image of transmission electron micrograph presented in Figure 7a. Sample of **poly(1-2)** ($[\mathbf{1}]_0 = [\mathbf{2}]_0 = 1.1$ mM, pH = 1.9) after equilibration for 3 d at 20 ºC.

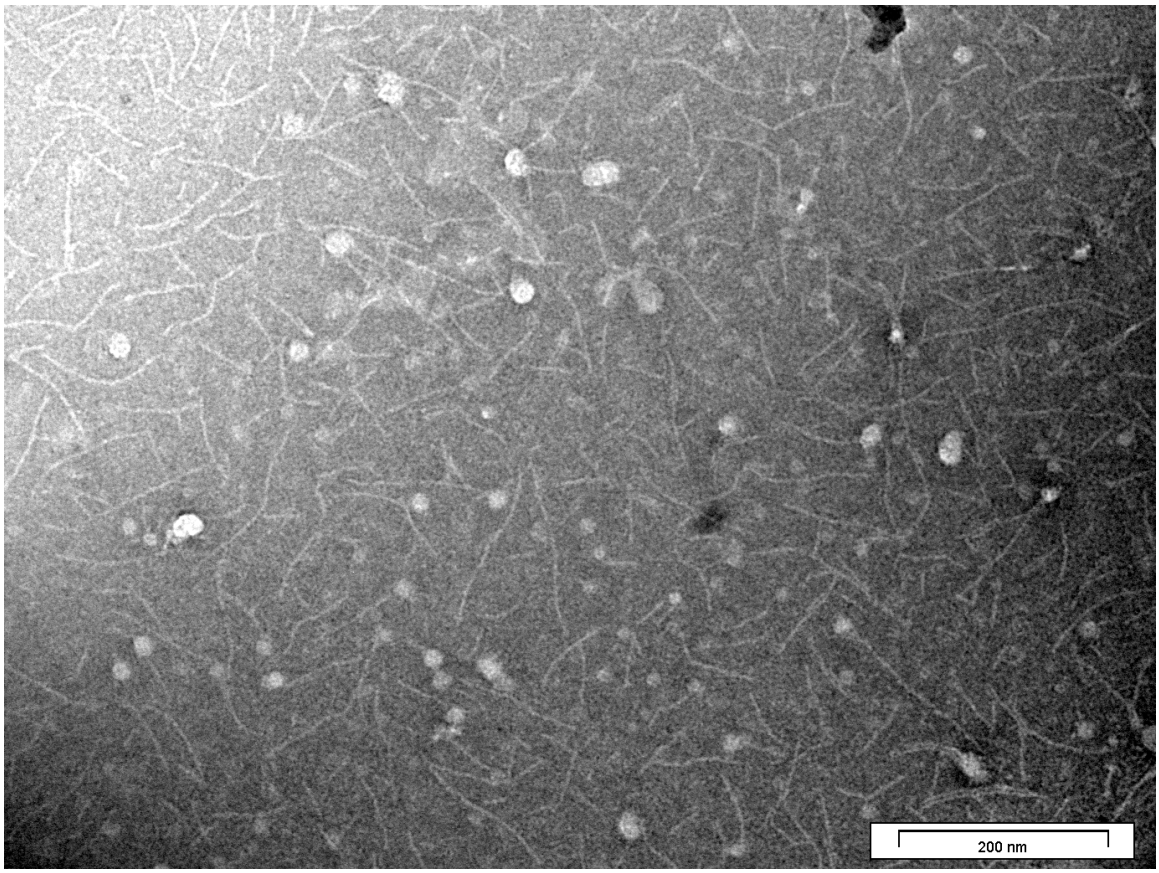

Figure S-2. Larger image of transmission electron micrograph presented in Figure 7d. Sample of **poly(1-2)** ($[\mathbf{1}]_0 = [\mathbf{2}]_0 = 1.1$ mM, pH = 1.9) after equilibration for 3 d at 20 ºC, heating to 60 ºC for 4 h, and standing at 20 ºC for 1 week.

References:

1. Folmer-Andersen, J. F.; Buhler, E.; Candau, S.-J.; Joulie, S.; Schmutz, M.; Lehn, J.-M.

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