

Supporting Information

Experimental

Reagents and equipment. All reagents were purchased from Aldrich and used without further purification. THF was distilled over Na/benzophenone and redistilled over *n*-BuLi under vacuum. DMF was vacuum distilled over CaH₂ and freeze-thawed three times. Ethyl acetate was distilled over CaH₂. 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane was vacuum distilled over sodium at 40 °C and redistilled over dibutylmagnesium. Distilled reagents were used immediately. Dimethyl-[1]-silaferrocenophane and *v*-benzyl-L-glutamate α -NCA were prepared by literature methods.¹ Column chromatography was performed with Silia-P flash silica gel (40-63 μ m) (Silicycles). All reactions were carried out in M-Braun drybox under purified N₂ atmosphere. ¹H NMR spectra were obtained on a Varian Mercury 300 or Mercury 400 spectrometer. FT-IR was performed on a Perkin-Elmer Spectrum One spectrometer. Thermal characterization was performed on a TA instruments DSC 2920 modulated DSC equipped with a refrigeration cooling unit. The ramp rate for scans was 10 °C/min. A Nikon Optiphot2-Pol microscope equipped with a Mettler FP82HT hot stage and Nikon digital camera were used for optical microscopy experiments. Molecular weights of

polymers were measured on a Viscotek GPC max system (VE 2001 GPC solvent/sample module and TriSEC Model 302 triple detector array) with THF or THF (0.003 M tetrabutylammonium bromide) as an eluent. TEM was performed on a Hitachi H-600 microscope with 75 kV acceleration voltage. TEM specimens were prepared on a carbon-coated copper grid (200 mesh).

Synthesis of PFS-NH₂ (2). All reactions were carried out in a drybox under purified N₂ atmosphere. To a 12 mL THF solution of ferrocenophane monomer **1** (1.2 g) was added 110 μ L of *sec*-BuLi (1.3M in cyclohexane, Acros) at room temperature. Upon stirring, the colour of the solution gradually changed from deep red to dark amber. After 45 min, the solution was immersed in a cold bath (-76 ^\circ C) and stirred for a further 10 min. 120 μ L of 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane was added to the cooled solution and the solution was stirred for 30 min at -76 ^\circ C . After an additional 1 h stirring at room temperature, the solution was taken out of the drybox and precipitated into methanol. The amber precipitate was collected, washed with methanol, and redissolved in THF (5 mL). After a second precipitation of the THF solution into methanol an amber powder was obtained. The collected powder was vacuum dried for 8 h. The dried polymer was charged on a silica gel column and separated with CH₂Cl₂ as an

eluent. After removal of the first amber-color band ($R_f = 1$, TLC(silica), CH_2Cl_2), the eluent was changed to THF/ CH_2Cl_2 (9:1 v/v). Purified **2** was dried under vacuum for 24 h. Yield: 45 % (540 mg). ^1H NMR (C_6D_6 , ppm): 4.24 (br, s, Cp), 4.07 (br, s, Cp), 2.47 (t, J = 6.7 Hz, $-\text{CH}_2\text{NH}_2$), 1.49-1.57 (br, $-\text{CH}_2-$), 0.87-0.84 (m, CH_3-), 0.51-0.53 (br, s, CH_3-Si), 0.24 (s, $-\text{CH}_2-\text{Si}$). GPC (THF): $M_n = 9330$ g/mol, PDI (M_w/M_n) = 1.10. $\text{DP}_n = 38$ (^1H NMR).

Synthesis of Block Copolymers (3-5). Procedures for the synthesis of block copolymers were identical except the amount of α -NCA used for the polymerizations. ν -benzyl-L-glutamate α -NCA (0.5 g) was dissolved in dry DMF (10mL). To this solution was added 10mL THF solution of polymer **2** (0.2 g) at once. The solution was stirred for 48 h at ambient temperature. The amber viscous solution was then precipitated into methanol and the amber precipitate was filtered, thoroughly washed with methanol, and vacuum dried overnight. Yield: 85 % (480 mg) for **3**, 83 % (540 mg) for **4**, 83 % (680 mg) for **5**. ^1H NMR (CDCl_3 , ppm): 8.15-8.50 (br, $-\text{NHCO}-$), 7.19-7.31 (br, $\text{Ph}-$), 5.03 (br, s, $\text{Ph}-\text{CH}_2-$), 4.20 (s, Cp), 4.00 (s, Cp), 3.82-3.99 (br, α -CH-), 1.98-2.72 (β , γ - CH_2-), 0.45 (s, CH_3-Si). GPC (THF/ $n\text{Bu}_4\text{NBr}$ 0.003 M): For **3**: 94,200 g/mol, PDI (M_w/M_n) = 1.14. For **4**: 104,400 g/mol, PDI (M_w/M_n) = 1.13. For **5**: 121,800 g/mol, PDI (M_w/M_n) = 1.16. FT-IR

(cm^{-1} , NaCl/Nujol): 1750 (C=O benzyl ester), 1650 (amide I), 1550 (amide II). DSC (scan rate = 10 $^{\circ}\text{C}/\text{min}$): For **3**: 27.1 $^{\circ}\text{C}$ (T_g), 104.6 $^{\circ}\text{C}$ (helix-to-helix), 78.4 $^{\circ}\text{C}$ (T_c), 91.9 $^{\circ}\text{C}$ (T_m). For **4**: 29.3 $^{\circ}\text{C}$ (T_g), 110.7 $^{\circ}\text{C}$ (helix-to-helix), 76.9 $^{\circ}\text{C}$ (T_c), 91.2 (T_m). For **5**: 37.1 $^{\circ}\text{C}$ (T_g and associated relaxation), 110.0 $^{\circ}\text{C}$ (helix-to-helix), 79.2 $^{\circ}\text{C}$ (T_c), 92.8 $^{\circ}\text{C}$ (T_m). The helix-to-helix transitions were only detected on the first heating scan.

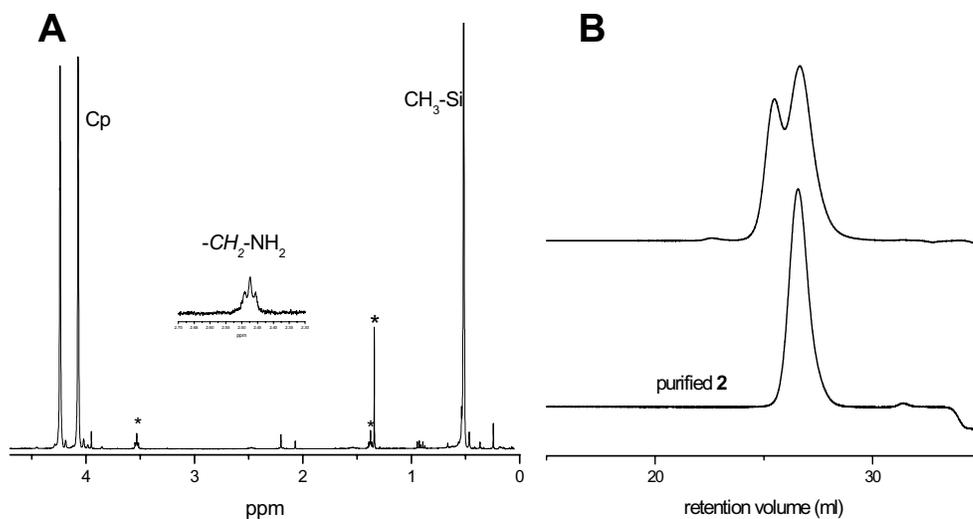
Hydrogenation of 5, PFS-*b*-PGA. (8). 100 mg of **5** was dissolved in CH_2Cl_2 (5 mL) and 10 mL of DMF was added to the solution. After adding a fraction of 10 % Pd/C (Aldrich), the solution was bubbled with H_2 for 24 h with stirring. Subsequently, the black solution was filtered through a pad of Celite to remove the catalyst. The amber solution was precipitated into diethyl ether and the precipitate was collected and vacuum dried. The dried polymer was dissolved in basic water (0.1 M NaOH) and the resulting aqueous solution was dialyzed over distilled water for 36 h. After dialysis, water was removed under vacuum and the aqueous solution was lyophilized with methanol. A yellow powder was collected and vacuum dried. Yield was quantitative. Completion of the reaction was confirmed by the disappearance of benzyl protons (5 ppm) in ^1H NMR (D_2O). Only chemical shifts of the poly(L-glutamate) block were observed in ^1H NMR (D_2O) due to

the micelle formation of the block copolymer. ^1H NMR (D_2O , ppm): 7.18-7.26 (br, -
 NHCO-), 4.04-4.12 (br, $\alpha\text{-CH}$), 1.62-2.10 (br, β , $\gamma\text{-CH}_2$).

References:

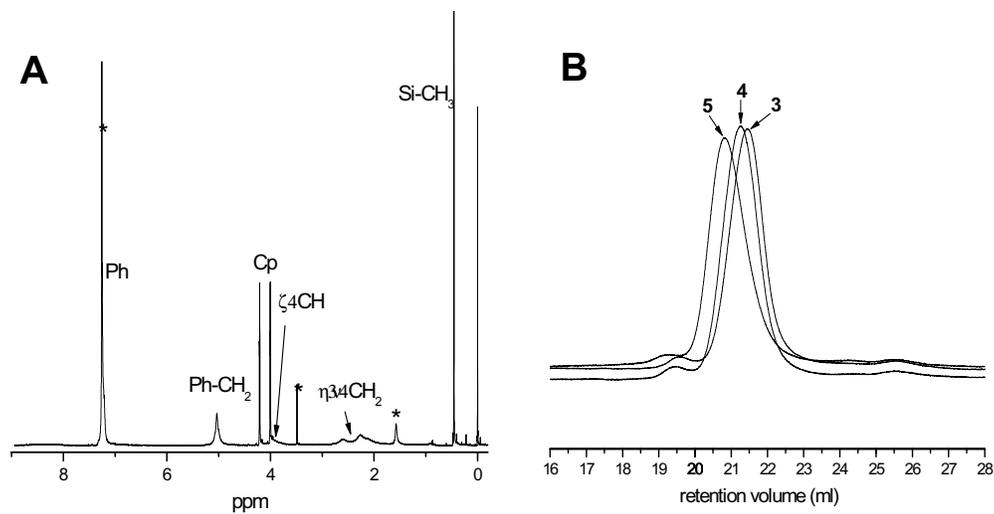
1. (a) Massey, J.; Power, K. N.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 9533. (b) Poché, D. S.; Moore, M. J.; Bowles, J. L. *Synth. Commun.* **1999**, *29*, 843.

Figure S1.



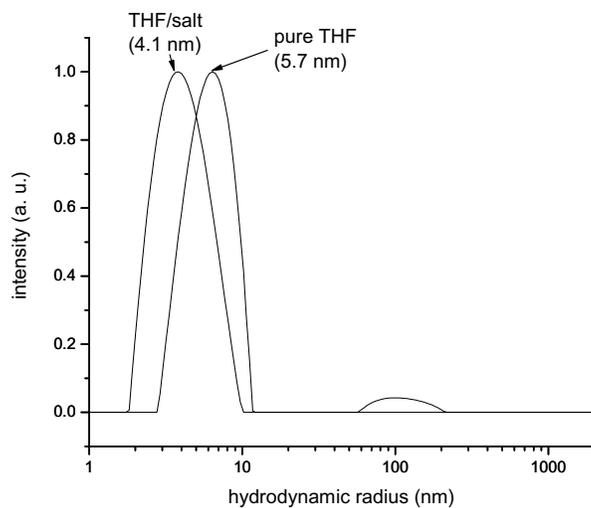
A) ^1H NMR spectrum of PFS-NH₂ (**2**). Inset in A indicates magnified spectrum from 2.7 ppm to 2.3 ppm. Residual solvents marked with asterisks. B) GPC traces of **2**. Upper trace shows isolated PFS quenched by metal-halogen exchange reactions and residual protic impurities in the quenching agent. Lower trace shows the purified PFS-NH₂.

Figure S2.



A) Representative $^1\text{H-NMR}$ spectrum of PFS-*b*-PBLG (**5**) (in CDCl_3). B) GPC traces of block copolymers **3**, **4**, and **5** in 0.03 M $[\text{Bu}_4\text{N}]\text{Br}$ in THF (Asterisks in A indicate residual solvents).

Figure S3.



DLS results at 90° (CONTIN profiles) of solutions of **5** in pure THF and 0.03 M $[\text{nBu}_4\text{N}]\text{Br}$ in THF. A concentrations of 2 mg/ml was used in both solvents. It has to be noted that no corrections were made to account for the difference in viscosity of the two eluents. The viscosity of pure THF was used for both THF and THF/salt solutions.