

Supporting Information

Low Length Dispersity Fiber-Like Micelles from an A-B-A Triblock Copolymer with Terminal Crystallizable Poly(ferrocenyldimethylsilane) Segments via Living Crystallization-Driven Self-Assembly

Qiwei Zhang^{1,2}, Yunxiang He², Alex M. Oliver², Samuel Pearce², Robert L. Harniman², George R. Whittell², Yanju Liu³, Shanyi Du¹, Jinsong Leng^{*, 1} and Ian Manners^{*, 2, 4}

¹National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin 150080, China

²School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom

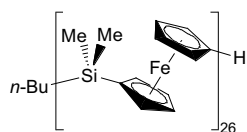
³Department of Astronautical Science and Mechanics, Harbin Institute of Technology, Harbin 150080, China

⁴Department of Chemistry, University of Victoria, Victoria, BC V8W 3V6, Canada

*To whom correspondence should be addressed: lengjs@hit.edu.cn and imanners@uvic.ca

Synthetic Procedures

PFS₂₆ Homopolymer



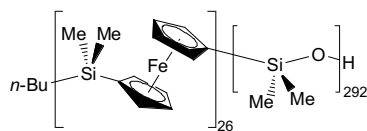
Dimethylsila[1]ferrocenophane (100 mg, 0.413 mmol) was dissolved in dry THF (1 mL) in a glovebox (Mbraun, inert purified nitrogen atmosphere) at room temperature. *n*-butyllithium (1.6 M in hexane, 10.3 μ L, 1.65×10^{-2} mmol) was added to the rapidly stirring solution in one portion. After 30 mins, the colour of the reaction mixture could change from red to amber. The mixture was precipitated in methanol and centrifuged three times before drying in a vacuum oven overnight.

¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) = 0.45 (s, 6H, SiMe₂), 4.00 (m, 4H, Cp), 4.20 (m, 4H, Cp).

²⁹Si NMR (79.5 MHz, CD₂Cl₂): δ (ppm) = -6.4 (Cp₂FeSiMe₂)

M_n (GPC) = 6.5 kg/mol, M_w/M_n = 1.04; yield = 93%.

PFS₂₆-*b*-PDMS₂₉₂



Dimethylsila[1]ferrocenophane (100 mg, 0.413 mmol) was dissolved in dry THF (1 mL) in a glovebox (Mbraun, inert purified nitrogen atmosphere) at room temperature. *n*-butyllithium (1.6 M in hexane, 10.3 μ L, 1.65×10^{-2} mmol) was added to the rapidly stirring solution in one portion. After 30 mins, the colour of the reaction mixture could change from red to amber. An aliquot was then taken from the reaction mixture before the rapid addition of [Me₂SiO]₃ (305 mg, 1.37 mmol). After another 1 h, the mixture was precipitated in methanol and centrifuged three times before drying in a vacuum oven overnight.

¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) = 0.05 (s, 6H, SiMe₂), 0.45 (s, 6H, Me₂SiO), 4.00 (m, 4H, Cp), 4.20 (m, 4H, Cp);

²⁹Si NMR (79.5 MHz, CD₂Cl₂): δ (ppm) = -6.4 (Cp₂FeSiMe₂), -21.3 (Me₂SiO)

M_n (GPC) = 33.4 kg/mol, M_w/M_n = 1.07; yield = 90%.

Supplementary Figures

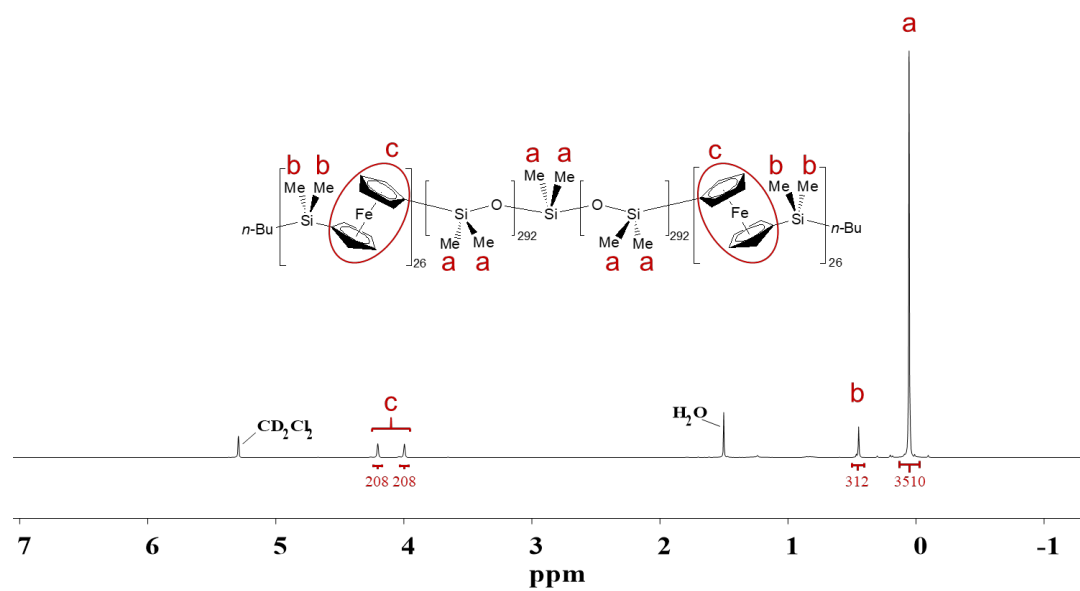


Figure S1. ¹H NMR spectrum (CD₂Cl₂) of PFS₂₆-*b*-PDMS₅₈₄-*b*-PFS₂₆.

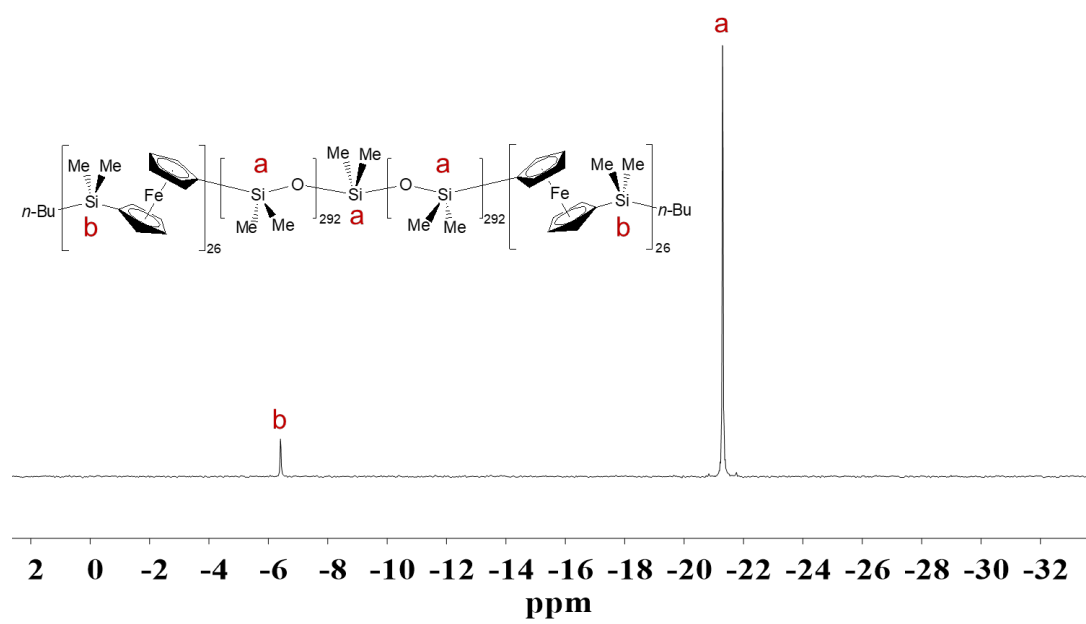


Figure S2. ^{29}Si NMR spectrum (CD_2Cl_2) of $\text{PFS}_{26}\text{-}b\text{-PDMS}_{584}\text{-}b\text{-PFS}_{26}$.

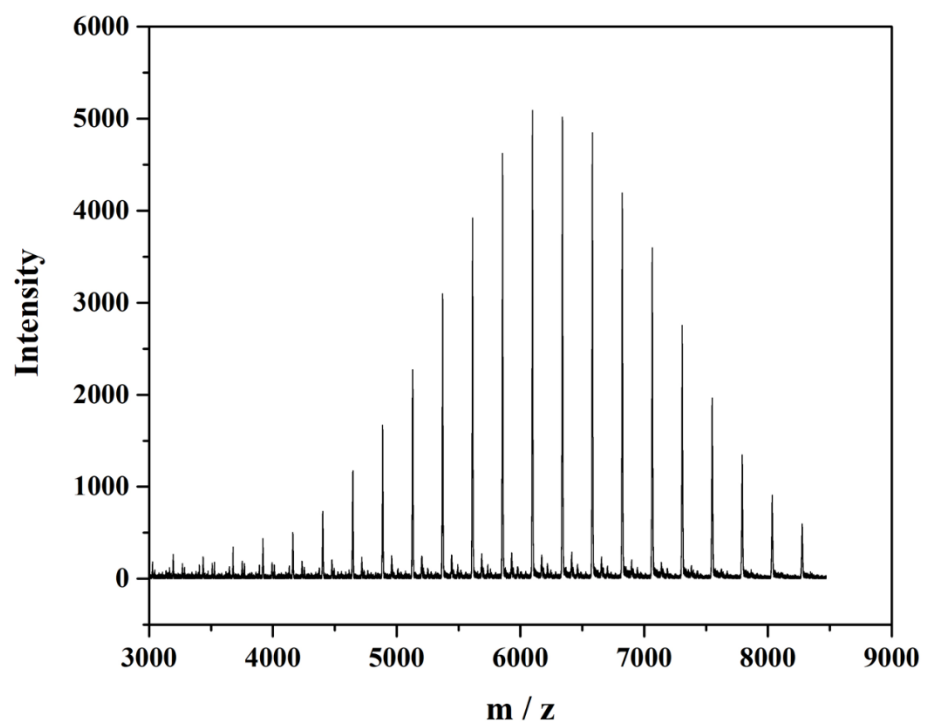


Figure S3. MALDI-TOF mass spectrum of PFS₂₆

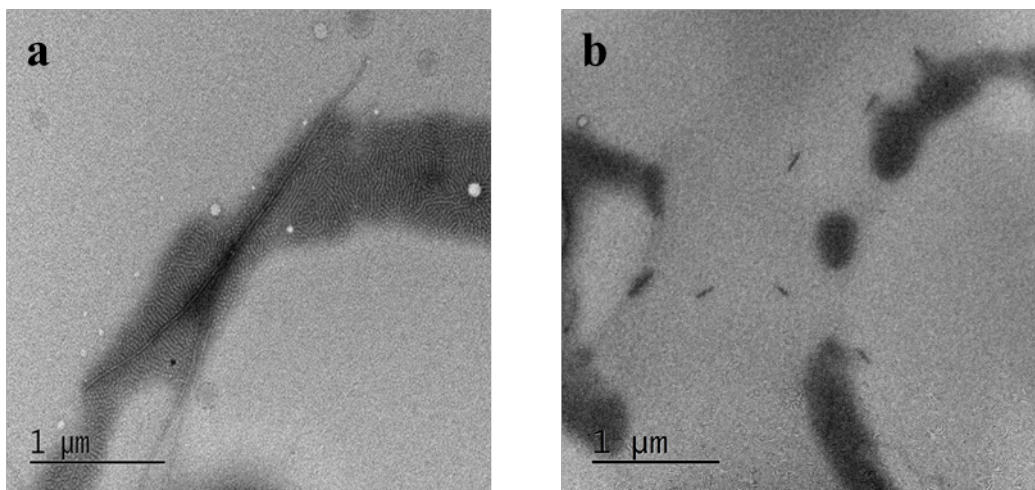


Figure S4. TEM of a micellar solution of PFS₂₆-*b*-PDMS₅₈₄-*b*-PFS₂₆ in (a) decane and (b) *n*-hexane after solvent evaporation.

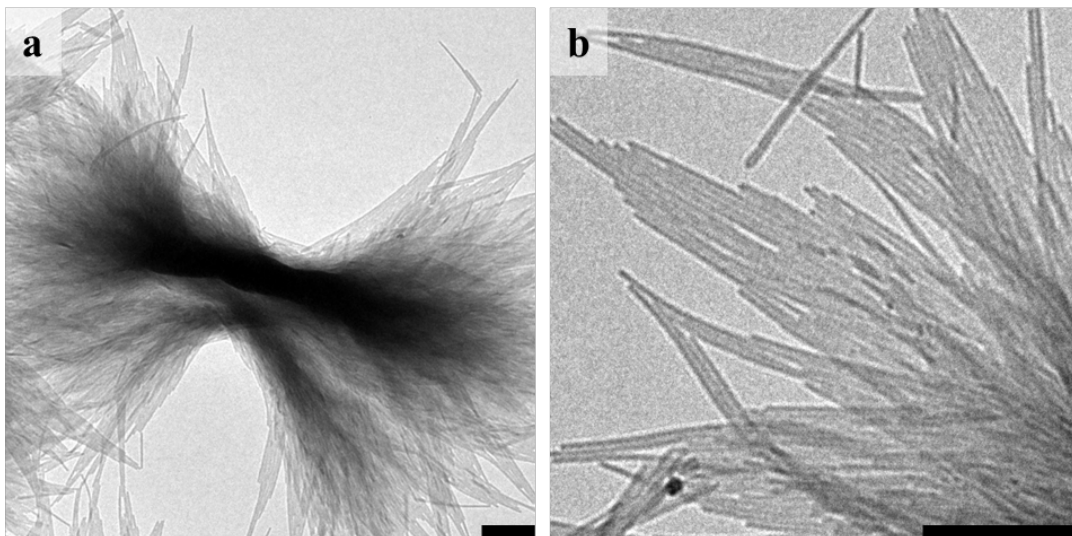


Figure S5. TEM micrographs of micelle aggregates of a PFS₂₆-b-PDMS₅₈₄-b-PFS₂₆ / PFS₂₆ blend prepared in hexane/decane ($v : v = 1 : 1$) at 60 °C after solvent evaporation. Scale bars are 1 μm .

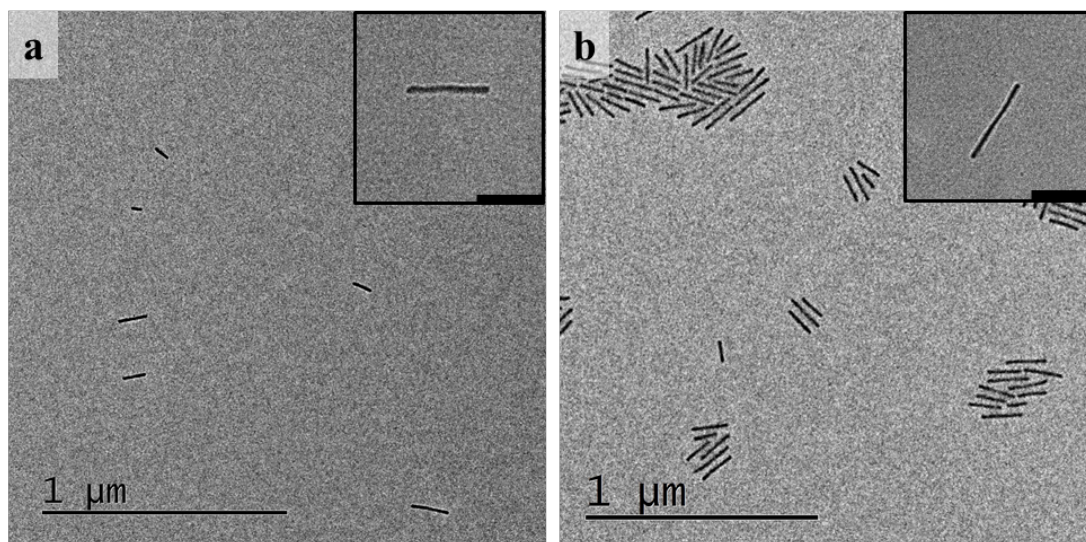


Figure S6. TEM micrographs (after solvent evaporation) after experiments involving (a) the attempted growth of PFS₂₆-*b*-PDMS₅₈₄-*b*-PFS₂₆ using seeds of PFS₂₆-*b*-PDMS₂₉₂ as initiators ($L_n = 102$ nm) in 1:1 (v/v) *n*-hexane/*n*-decane with a unimer to seed ratio of 5:1 and (b) the attempted growth of PFS₂₆-*b*-PDMS₂₉₂ using PFS₂₆-*b*-PDMS₅₈₄-*b*-PFS₂₆ seeds as initiators ($L_n = 94$ nm) in *n*-hexane with unimer to seed ratio of 5:1. In each case the solutions were analyzed after 12 h. Scale bars for the insets are 100 nm.