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

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Synthetic Procedures

PFS$_{26}$ 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 µL, 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. 

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 0.45 (s, 6H, SiMe$_2$), 4.00 (m, 4H, Cp), 4.20 (m, 4H, Cp).

$^{29}$Si NMR (79.5 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = -6.4 (Cp$_2$FeSiMe$_2$)

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

PFS$_{26}$-b-PDMS$_{292}$

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 µL, 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 [Me$_2$SiO]$_3$ (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.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 0.05 (s, 6H, SiMe$_2$), 0.45 (s, 6H, SiMe$_2$O), 4.00 (m, 4H, Cp), 4.20 (m, 4H, Cp);

$^{29}$Si NMR (79.5 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = -6.4 (Cp$_2$FeSiMe$_2$), -21.3 (Me$_2$SiO)

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

Figure S1. $^1$H NMR spectrum (CD$_2$Cl$_2$) of PFS$_{26}$-b-PDMS$_{584}$-b-PFS$_{26}$.
Figure S2. $^{29}\text{Si}$ NMR spectrum (CD$_2$Cl$_2$) of PFS$_{26}$-b-PDMS$_{584}$-b-PFS$_{26}$.
Figure S3. MALDI-TOF mass spectrum of PFS$_{26}$
Figure S4. TEM of a micellar solution of PFS$_{26}$-b-PDMS$_{584}$-b-PFS$_{26}$ in (a) decane and (b) $n$-hexane after solvent evaporation.
Figure S5. TEM micrographs of micelle aggregates of a PFS$_{26}$-b-PDMS$_{384}$-b-PFS$_{26}$/PFS$_{26}$ 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 PFS$_{26}$-b-PDMS$_{584}$-b-PFS$_{26}$ using seeds of PFS$_{26}$-b-PDMS$_{292}$ as initiators ($L_\text{n} = 102$ 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 PFS$_{26}$-b-PDMS$_{292}$ using PFS$_{26}$-b-PDMS$_{584}$-b-PFS$_{26}$ seeds as initiators ($L_\text{n} = 94$ 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.