

Supporting Information

Polyferrocenylsilane Crystals in Nanoconfinement: Fragmentation, Dissolution, and Regrowth of Cylindrical Block Copolymer Micelles with a Crystalline Core

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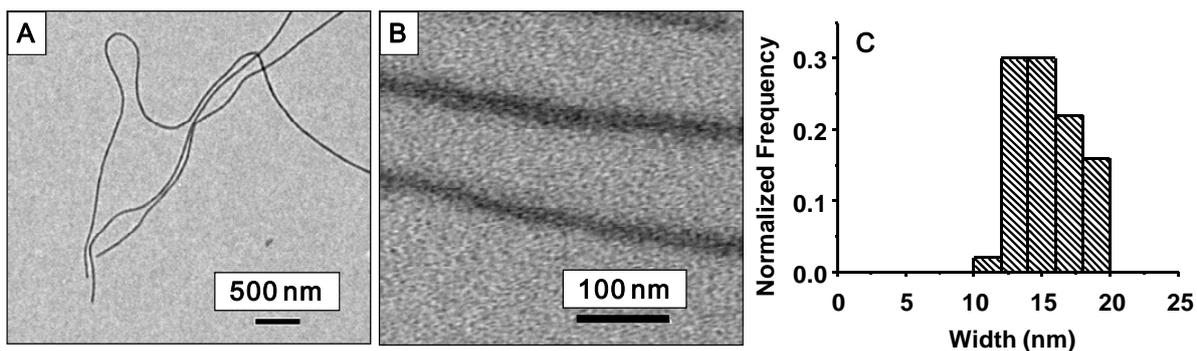


Figure S1. (A) TEM image of one-dimensional micelles formed by the self-assembly of PI₁₀₀₀-PFS₅₀ block copolymer after heating a solution in decane ($c = 0.0200$ mg/mL) at 100 °C for 30 min followed by slow cooling to room temperature. The cooling rate was approximately 1.5 °C/min. (B) A magnified TEM image of the micelles as formed. (C) Distribution histogram of the width of the micelles as formed, $d_n = 15.4$ nm, $d_w = 15.7$ nm.

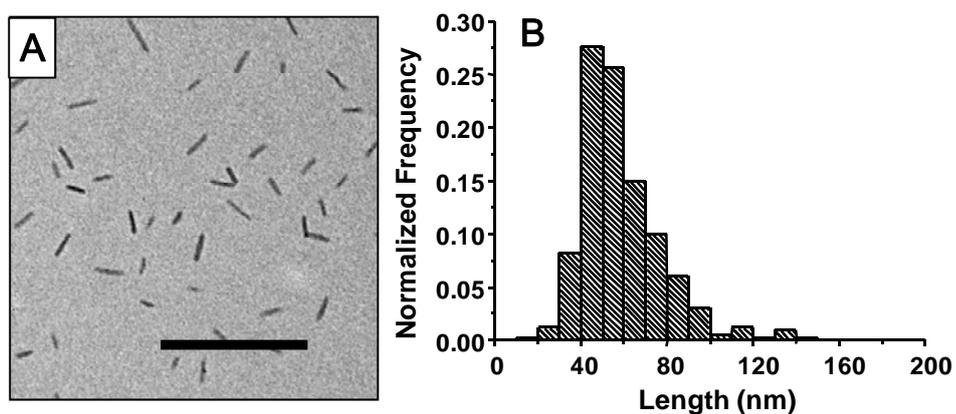


Figure S2. TEM image (A) and size distribution histogram (B) of the micelle seeds formed by sonicating the long micelles in Figure S1 for two 10 min intervals. The micelle seeds are characterized by $L_n = 58$ nm, $L_w = 65$ nm, $L_w/L_n = 1.10$, and $\sigma/L_n = 0.328$. Scale bar is 500 nm.

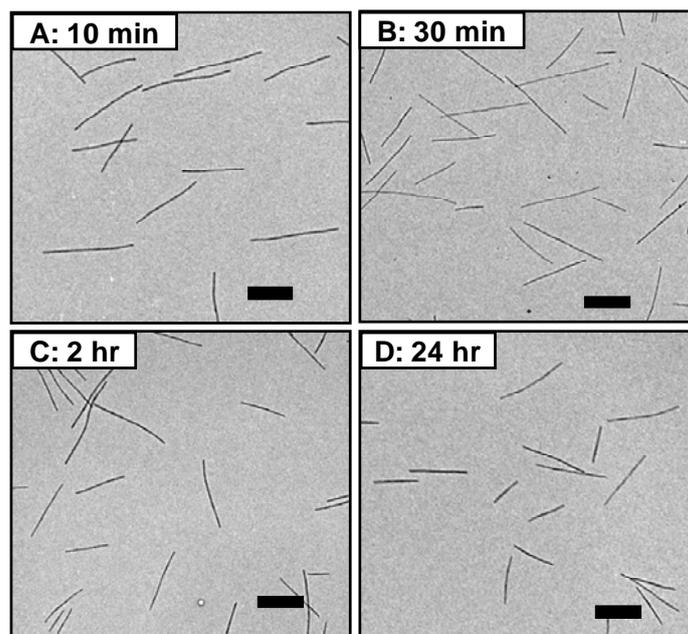


Figure S3. (A) to (D) Representative TEM images of sample L-1250 after being annealed at 55 °C for different lengths of time: (A) 10 min ($L_n = 1153$ nm, $L_w/L_n = 1.02$, $\sigma/L_n = 0.158$), (B) 30 min ($L_n = 1014$ nm, $L_w/L_n = 1.09$, $\sigma/L_n = 0.307$), (C) 2 hr ($L_n = 923$ nm, $L_w/L_n = 1.13$, $\sigma/L_n = 0.368$), (D) 24 hr ($L_n = 752$ nm, $L_w/L_n = 1.16$, $\sigma/L_n = 0.400$). All scale bars are 500 nm.

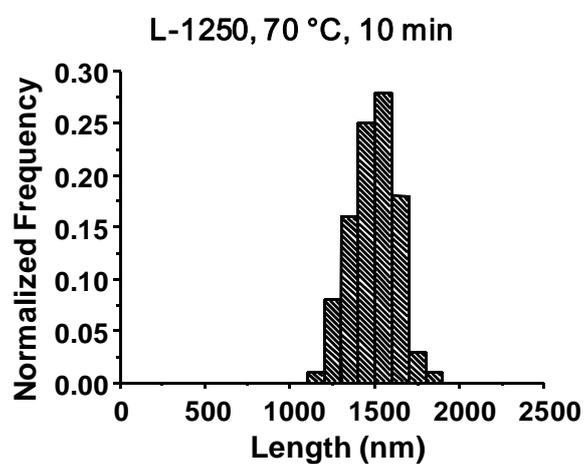


Figure S4. Length distribution histograms of L-1250 after being annealed at 70 °C for 10 min ($L_n = 1491$ nm, $L_w/L_n = 1.01$, $\sigma/L_n = 0.089$).

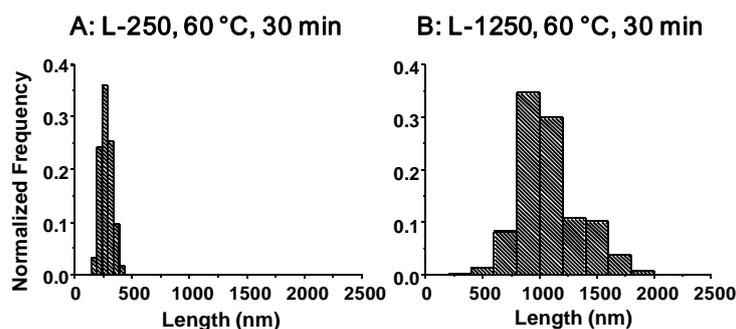


Figure S5. Histograms of PI₁₀₀₀-PFS₅₀ micelle sample (A) L-250 and (B) L-1250 after being annealed at 60.0 °C for 30 min. (A) $L_n = 275$ nm, $L_w/L_n = 1.04$, (B) $L_n = 1082$ nm, $L_w/L_n = 1.06$.

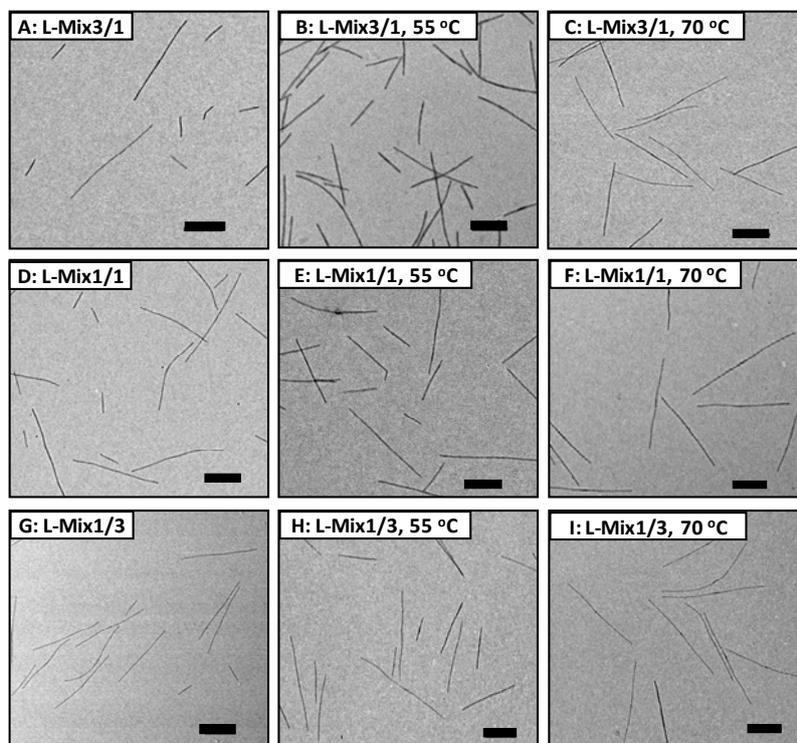


Figure S6. (A-C) TEM images of PI₁₀₀₀-PFS₅₀ micelle sample (A) L-Mix3/1 as prepared, and L-Mix3/1 after being annealing at (B) 55.0 °C and (C) 70.0 °C for 30 min. (D-F) TEM images of PI₁₀₀₀-PFS₅₀ micelle sample (D) L-Mix1/1 as prepared, and L-Mix1/1 after being annealing at (E) 55.0 °C and (F) 70.0 °C for 30 min. (G-I) TEM images of PI₁₀₀₀-PFS₅₀ micelle sample (G) L-Mix1/3 as prepared, and L-Mix1/3 after being annealing at (H) 55.0 °C and (I) 70.0 °C for 30 min. All scale bars are 500 nm.

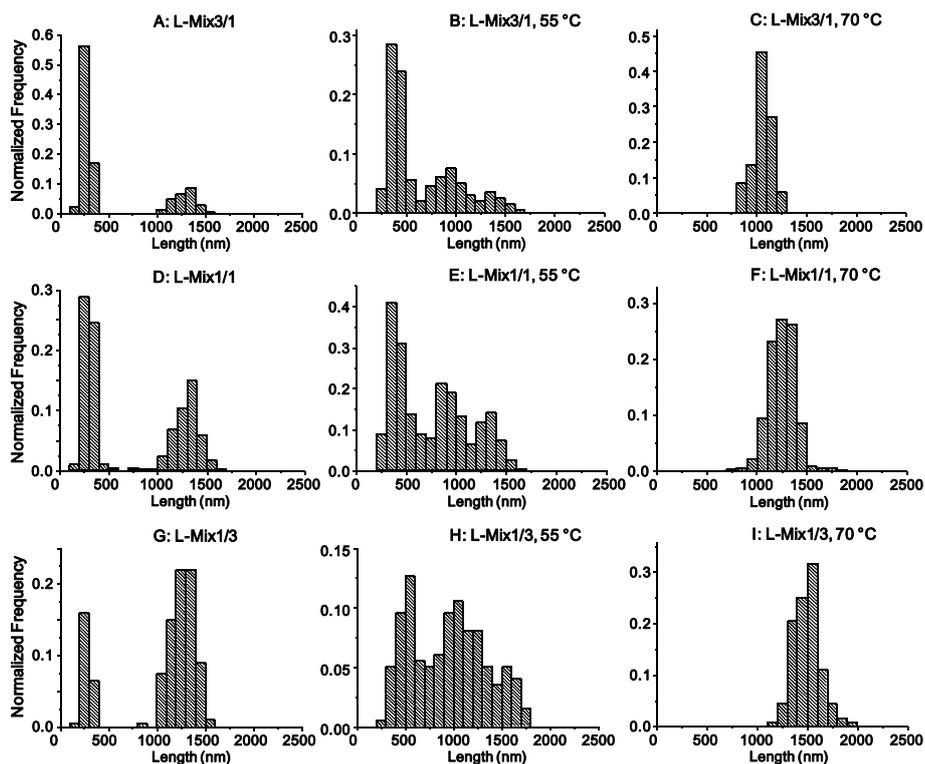


Figure S7. (A-I) Histograms of the length distribution of the corresponding micelles as shown in Figure S6(A-I). (A) $L_n = 518$ nm, $L_w/L_n = 1.72$, $\sigma/L_n = 0.851$, (B) $L_n = 644$ nm, $L_w/L_n = 1.31$, $\sigma/L_n = 0.557$, (C) $L_n = 1056$ nm, $L_w/L_n = 1.01$, $\sigma/L_n = 0.091$, (D) $L_n = 735$ nm, $L_w/L_n = 1.47$, $\sigma/L_n = 0.683$, (E) $L_n = 756$ nm, $L_w/L_n = 1.24$, $\sigma/L_n = 0.492$, (F) $L_n = 1248$ nm, $L_w/L_n = 1.01$, $\sigma/L_n = 0.111$, (G) $L_n = 1041$ nm, $L_w/L_n = 1.17$, $\sigma/L_n = 0.410$, (H) $L_n = 944$ nm, $L_w/L_n = 1.17$, $\sigma/L_n = 0.409$, (I) $L_n = 1493$ nm, $L_w/L_n = 1.01$, $\sigma/L_n = 0.089$.

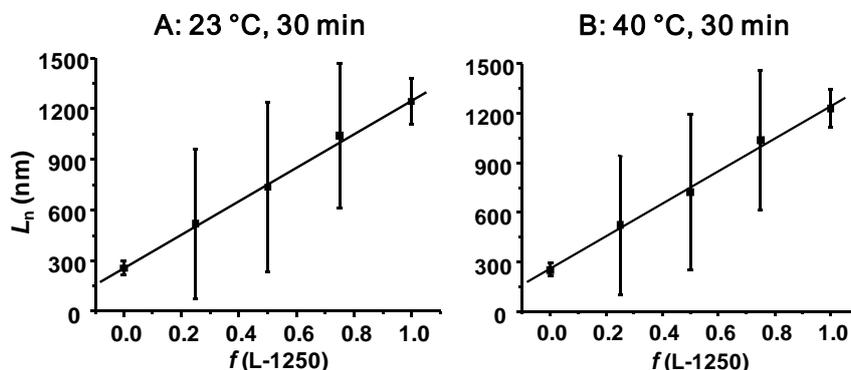


Figure S8. Plots of the measured value of L_n vs the number fraction of L-1250 micelles ($f(L-1250)$) in the L-1250/L-250 micelle mixture following annealing at (A) 23 and (B) 40 °C.

Table S1. Values of L_n , L_w , L_w/L_n , and σ/L_n of PI₁₀₀₀-PFS₅₀ micelle sample L-1250 with $L_n \approx 1250$ nm and micelles formed after the micelle solution in decane was annealed at 55.0 °C for different lengths of time followed by cooling to room temperature.

Time	L_n (nm)	L_w (nm)	L_w/L_n	σ/L_n
10 min	1153	1181	1.02	0.158
30 min	1014	1109	1.09	0.307
2 hr	923	1048	1.13	0.368
24 hr	752	971	1.16	0.400

Table S2. Values of L_n , L_w , L_w/L_n , and σ/L_n of PI₁₀₀₀-PFS₅₀ micelle sample L-1250 with $L_n \approx 1250$ nm and micelles formed after the micelle solution in decane was annealed at 70.0 °C for different lengths of time followed by cooling to room temperature.

Time	L_n (nm)	L_w (nm)	L_w/L_n	σ/L_n
10 min	1491	1502	1.01	0.086
30 min	1686	1702	1.01	0.098
24 hr	1661	1674	1.01	0.087

Table S3. Values of L_n , L_w , L_w/L_n , and σ/L_n of PI₁₀₀₀-PFS₅₀ micelle sample L-1250 with $L_n \approx 1250$ nm and micelles formed after the micelle solution in decane was annealed at different temperatures for 30 min followed by cooling to room temperature.

Temperature	L_n (nm)	L_w (nm)	L_w/L_n	σ/L_n
23.0 °C	1243	1258	1.01	0.109
40.0 °C	1231	1242	1.01	0.093
55.0 °C	1014	1109	1.09	0.307
60.0 °C	1082	1147	1.06	0.246
65.0 °C	1143	1163	1.02	0.133
70.0 °C	1686	1702	1.01	0.098
75.0 °C	2289	2309	1.01	0.093

Table S4. Values of L_n , L_w , L_w/L_n , and σ/L_n of PI₁₀₀₀-PFS₅₀ micelle sample L-250 with $L_n \approx 250$ nm and micelles formed after the micelle solution in decane was annealed at different temperatures for 30 min followed by cooling to room temperature.

Temperature	L_n (nm)	L_w (nm)	L_w/L_n	σ/L_n
23.0 °C	256	263	1.03	0.160
40.0 °C	252	259	1.03	0.167
55.0 °C	245	260	1.06	0.249
60.0 °C	275	284	1.04	0.189
65.0 °C	302	310	1.03	0.162
70.0 °C	542	555	1.02	0.149
75.0 °C	880	890	1.01	0.109

Table S5. Values of L_n , L_w , L_w/L_n , and σ/L_n of PI₁₀₀₀-PFS₅₀ mixture sample L-Mix3/1, containing L-250 and L-1250 with number ratio of 3:1 and micelles formed after the micelle solution in decane was annealed at different temperatures for 30 min followed by cooling to room temperature.

Temperature	L_n (nm)	L_w (nm)	L_w/L_n	σ/L_n
23.0 °C	518	892	1.72	0.851
40.0 °C	524	856	1.63	0.800
55.0 °C	644	844	1.31	0.557
60.0 °C	837	899	1.07	0.274
65.0 °C	615	622	1.01	0.112
70.0 °C	1056	1065	1.01	0.091
75.0 °C	1649	1657	1.005	0.070

Table S6. Values of L_n , L_w , L_w/L_n , and σ/L_n of PI₁₀₀₀-PFS₅₀ mixture sample L-Mix1/1, containing L-250 and L-1250 with number ratio of 1:1 and micelles formed after the micelle solution in decane was annealed at different temperatures for 30 min followed by cooling to room temperature.

Temperature	L_n (nm)	L_w (nm)	L_w/L_n	σ/L_n
23.0 °C	735	1077	1.47	0.683
40.0 °C	722	1023	1.42	0.648
55.0 °C	756	938	1.24	0.492
60.0 °C	740	801	1.08	0.286
65.0 °C	791	804	1.02	0.130
70.0 °C	1248	1263	1.01	0.111
75.0 °C	1950	1966	1.01	0.091

Table S7. Values of L_n , L_w , L_w/L_n , and σ/L_n of PI₁₀₀₀-PFS₅₀ mixture sample L-Mix1/3, containing L-250 and L-1250 with number ratio of 1:3 and micelles formed after the micelle solution in decane was annealed at different temperatures for 30 min followed by cooling to room temperature.

Temperature	L_n (nm)	L_w (nm)	L_w/L_n	σ/L_n
23.0 °C	1041	1215	1.17	0.410
40.0 °C	1039	1209	1.16	0.405
55.0 °C	944	1101	1.17	0.409
60.0 °C	1101	1146	1.04	0.203
65.0 °C	1052	1068	1.01	0.123
70.0 °C	1493	1504	1.01	0.089
75.0 °C	2271	2281	1.004	0.068