Electronic Supplementary Information

Single-step self-assembly to uniform fiber-like core-crystalline block copolymer micelles

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TABLE OF CONTENTS

1. ADDITIONAL EXPERIMENTAL DETAILS

1.1 Materials

All chemicals were purchased from Sigma-Aldrich and were used as received unless otherwise noted. The syntheses and characterization of alkyne-terminated polyferrocenylsilane (PFS-alkyne, DP_n = 35, 55) were described in previous publications.[1,2] PFS_{54}-*b*-$PDMS_{800}$ ($Đ$ = 1.04) and PFS_{35}-*b*-PI_{273} ($Đ$ = 1.03) are the same samples reported in ref 2 and 3. The PFS block was characterized by MALDI-TOF with m/z peaks found at 243.0n+260. (The molecular weight of PFS repeat unit is 243.0 Da; the sum of *n*-butyl and the TMS-aryl-alkyne end groups is 260 Da). The block ratio was characterized by ^{1}H NMR by comparing the integrations of the PFS signal at 4.1 ppm, for example, to those of the PDMS (0.25 ppm). All the self-assembly experiments were performed in HPLC grade solvents that were acquired from Sigma-Aldrich.

1.2 Instrumentation

Transmission electron microscopy (TEM). TEM measurements were performed on a Hitachi D-7000 microscope or a Hitachi HT7700 microscope operating at an accelerating voltage of 80 kV in the bright-field TEM mode. Copper grids from Agar Scientific, mesh 200, were coated with a carbon film. Samples were prepared by placing a drop of solution on the grid and removing excess liquid with the edge of a filter paper. Images were analyzed with the software Image J (NIH, USA). For the statistical analyses, more than 100-200 micelles in several images were traced by the software in order to obtain the length or other information. The number average micelle length (L_n) (the same to width W_n and height H_n) and weight average micelle length (L_w) (the same to width W_w and height H_w) were calculated as shown below (L, length of object, and also could be referred as long/short axis length; N, number).

$$L_n = \frac{\sum_{i=1}^{n} N_i L_i}{\sum_{i=1}^{n} N_i} \qquad L_w = \frac{\sum_{i=1}^{n} N_i L_i^2}{\sum_{i=1}^{n} N_i L_i} \tag{S1}$$

Atomic force microscopy (AFM). Samples for AFM were prepared by drop-casting 8 μL of the micelle solution onto a freshly cleaved mica substrate or carbon-coated copper grid. Height imaging was conducted under ambient conditions using a Bruker Dimension Icon atomic force microscope. All images were obtained with Olympus silicon cantilevers at 320 kHz resonance frequency. Images were analyzed using Gwyddion or Nanoscope Analysis software program.

X-ray diffraction (XRD). Power X-ray diffraction measurements were performed on a Rigaku Miniflex 600 diffractometer using Cu Kα (λ = 1.5406 Å) radiation in the 2θ range of 5–80° with a step size of 0.02°. *d*-Spacing is calculated based on Bragg's law $2d \times \sin\theta = n\lambda$. Micelles were prepared on a large scale and then the solution was centrifuged to precipitate the micelles. Collecting the precipitates which was allowed to dry before taking the measurement.

2. SELF-ASSEMBLY EXPERIMENTS

Additional details for some of the self-assembly experiments are provided here.

Direct self-assembly of PFS BCP in decane. Long fiber-like micelles of PFS_{54}-*b*-$PDMS_{800}$ or PFS_{35}-*b*-PI_{273} in decane were prepared by the direct assembly approach. Samples of the block copolymer (BCP) and solvent were mixed at a concentration of 1.0 mg/mL in a 4-mL vial. The sealed vials were placed in a hot oil bath at 90 °C for 1 h, followed by slow cooling in which the block was left to cool to room temperature (RT, 23 °C) (over ca. 2.5 h). Subsequently, the solutions were allowed to age for 24 h. Fig. S1a and S5 reveal the TEM images of the long micelles at different magnifications.

Direct self-assembly of PFS homopolymer in decane. Samples of the PFS and solvent were mixed at a concentration of 0.1 mg/mL in a 4-mL vial. The sealed vials were placed in a hot oil bath at 90 °C for 1 h, followed by slow cooling in which the block was left to cool to room temperature (RT, 23 °C) (over ca. 2.5 h). Subsequently, the solutions were allowed to age for 24 h. Most sample hadn’t been dissolved into the solution. Fig. S1b shows TEM images of the micelles obtained at different magnifications.

Co-self-assembly of PFS homopolymer/BCP in decane. Uniform fiber-like micelles of PFS/PFS_{54}-*b*-$PDMS_{800}$ in decane were prepared by the direct assembly approach. Samples of the PFS (1mg/mL in tetrahydrofuran (THF)) and PFS_{54}-*b*-$PDMS_{800}$ (10 mg/mL in THF) were injected into the 4-mL vials individually according to their onset mass ratio. Then the mixture was fully dried to remove the THF. Decane was added to afford a solution with 1.0 mg/mL. The sealed vials were placed in a hot oil bath at 90 °C for 1 h, followed by slow cooling in which the block was left to cool to room temperature (RT, 23 °C). Subsequently, the solutions were allowed to age for 24 h and then for TEM samples. Fig.S2 presents TEM images of the fiber-like micelles at different homopolymer weight percent.

3. ADDITIONAL RESULTS AND DISCUSSION

Self-assembly of PFS_{55} in decane

Even at a very low concentration (0.1 mg/mL) at room temperature, PFS homopolymer samples did not dissolved into the decane, indicating that decane is a poor solvent for PFS homopolymer. At elevated temperatures, the samples appeared to partially dissolve. TEM image taken from a sample that was heated and then cooled is presented in Fig. S1b. From the supernatant, we found isolated lamellae and stacked lamellae on the grid. These platelet-like micelles were irregular in shape.

Self-assembly of PFS_{55}/PFS_{54}-b-$PDMS_{800}$ in decane at higher content of PFS_{55}

When we increased the PFS_{55}/PFS_{54}-*b*-$PDMS_{800}$ mass ratio to 10 wt %, the mixture in decane appeared to dissolve when heated. We obtained a yellow precipitate suspended in a pale-yellow supernatant after cooling the sample to room temperature. We believe that the precipitate is PFS homopolymer. It should result from the homopolymer's limited solubility in decane.[4]

4. SUPPORTING FIGURES

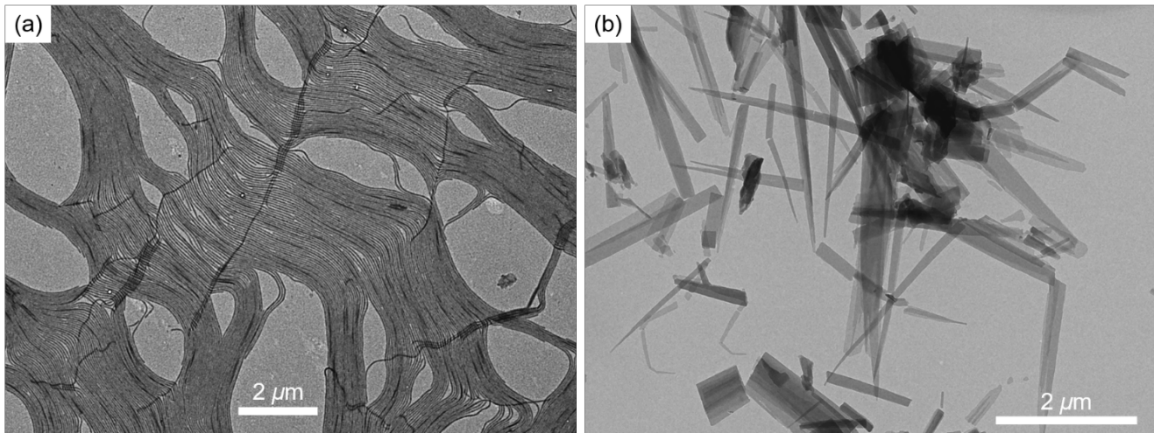

Fig. S1 TEM images of (a) long micelles of PFS_{54}-*b*-$PDMS_{800}$ formed by direct crystallization-driven self-assembly at 1 mg/mL in decane after heating at 90 °C for 1 h followed by slow cooling to room temperature and aging for 1 day. These micelles had lengths greater than 10 *μ*m. (b) Lamellar homopolymer crystals of PFS_{55} at 0.1 mg/mL formed under similar conditions. Here the homopolymer formed irregular platelet-like structures. Scale bar 2 *μ*m.

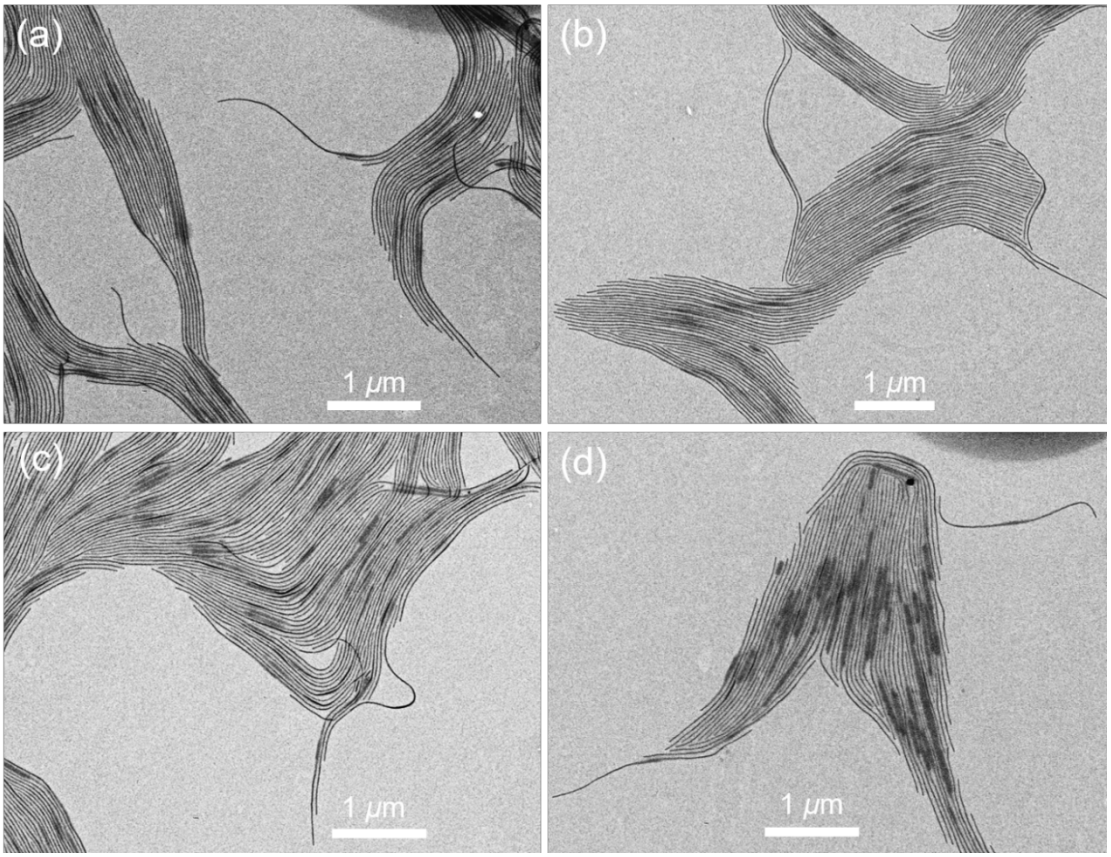

Fig. S2 TEM images of 1D fiber-like micelles formed from blends of PFS_{55}/PFS_{54}-*b*-$PDMS_{800}$ containing different amounts of homopolymer (a) 1 wt % (b) 1.5 wt % (c) 2 wt % (d) 10 wt %. Self-assembly in decane (1 mg/mL), The samples were heated at 90 °C and then cooled and aged as described in Fig. S1. Scale bar 1 *μ*m.

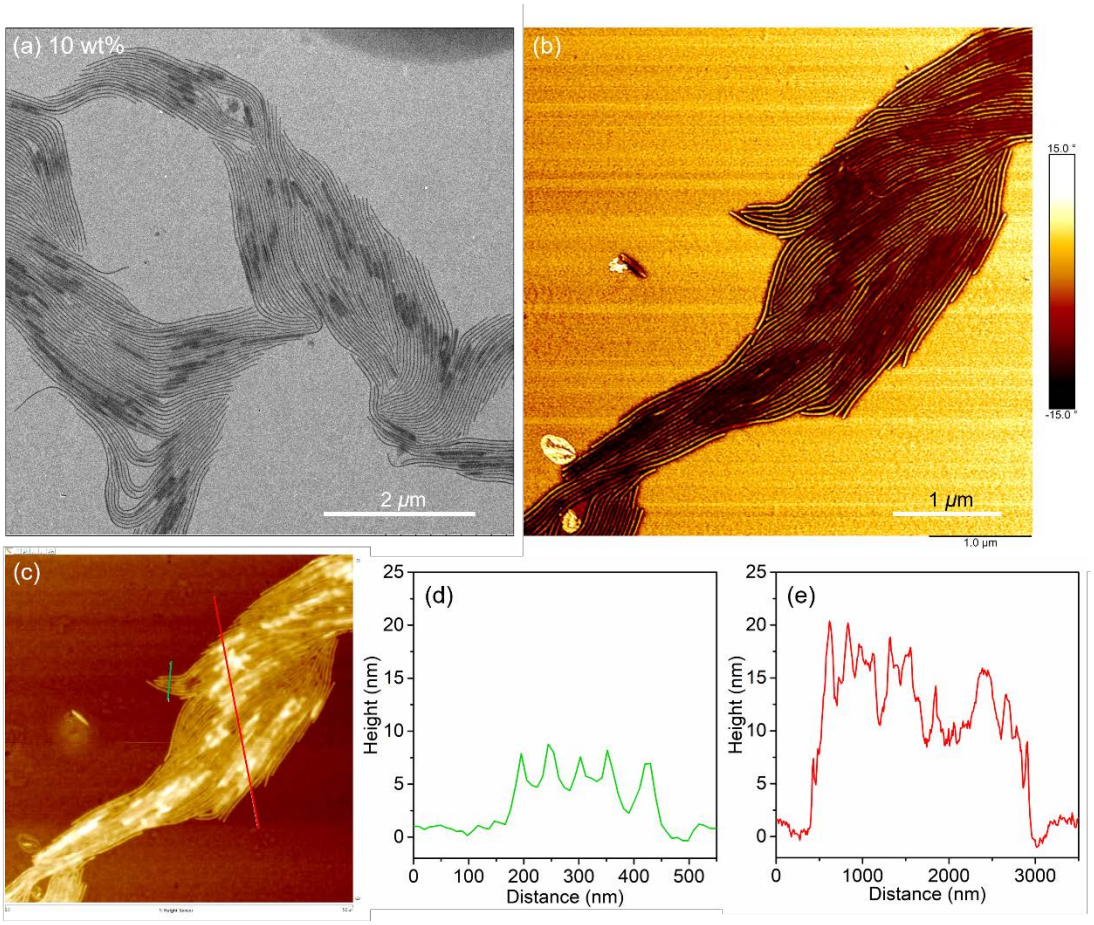

Fig. S3 Images of 1D fiber-like micelles formed from a blend of PFS_{54}-*b*-$PDMS_{800}$ and 10 wt% PFS_{55} homopolymer by self-assembly in decane (1 mg/mL, 90 °C). (a) TEM image, (b) AFM phase image and (c) AFM height images and (d) (e) height profile. Note that the dark platelets in the centers of the each micelle are irregular in length.

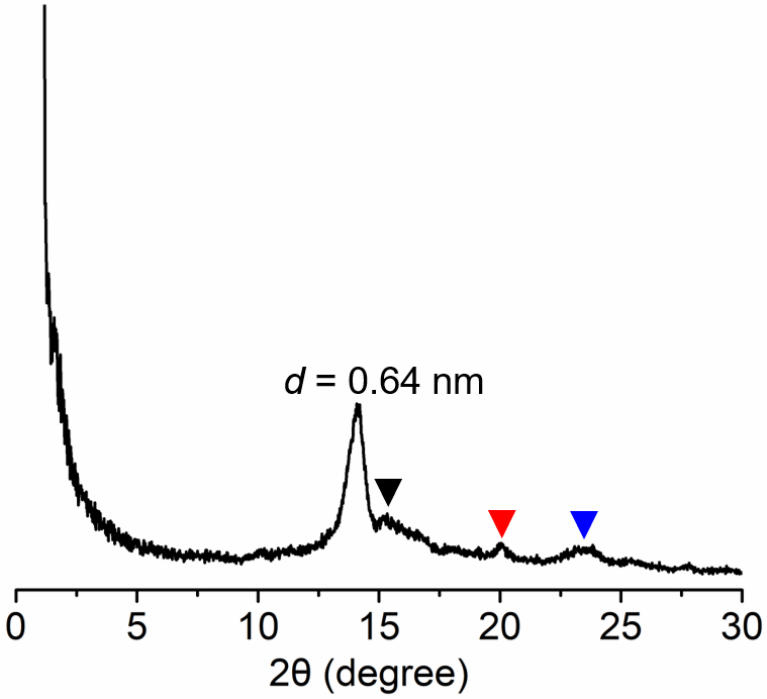

Fig. S4 X-ray diffraction (XRD) patterns obtained for a dried sample of 1D fiber-like micelles of PFS_{55}/PFS_{54}-*b*-$PDMS_{800}$ (1 w/w %) formed by self-assembly in decane (1 mg/mL, 90 °C). The *d* spacing of the main peak is 0.64 nm, which is consistent with that of other examples of PFS BCP micelles.[5-8] Three weak peaks marked by inverted triangles at 2θ = 15.3 °, 20.1 °, 23.5 ° respectively, correspond to *d* spacings of 0.58 nm, 0.44 nm, 0.38 nm, respectively.

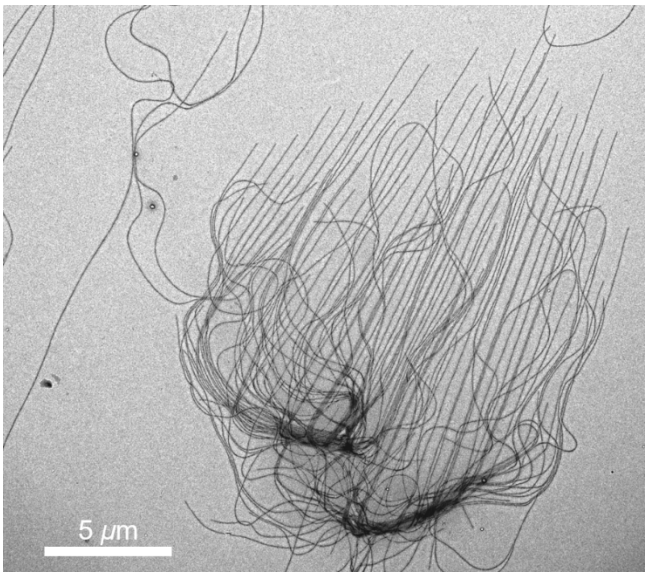

Fig. S5 TEM image of long micelles of PFS_{35}-*b*-PI_{273} formed by direct crystallization-driven self-assembly at 1 mg/mL in decane after heating at 90 °C for 1 h followed by slow cooling to room temperature and aging for 1 day. These micelles had lengths greater than 10 μm.

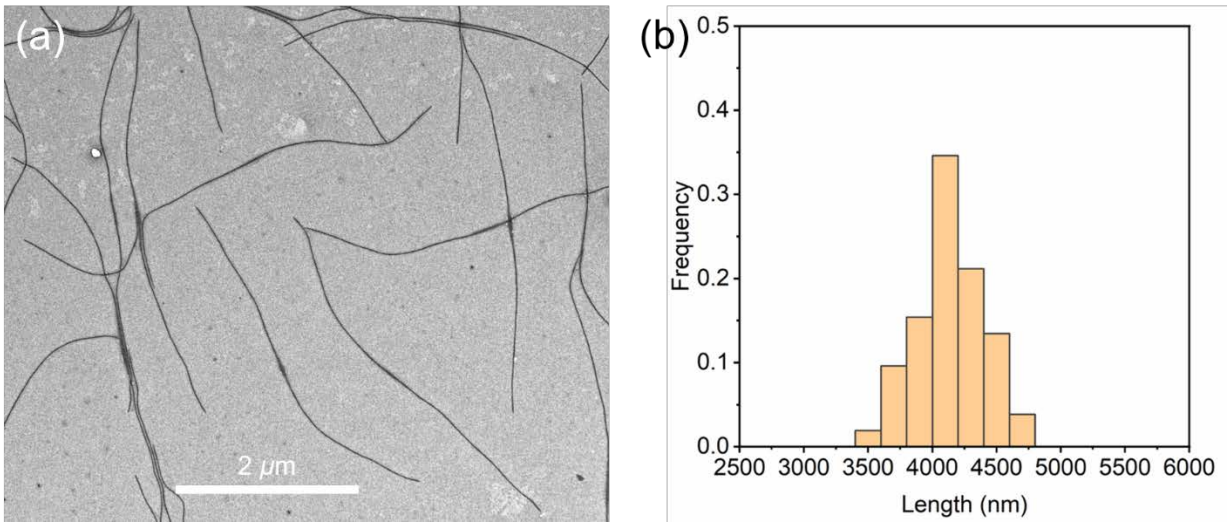

Fig. S6 (a) TEM images of uniform 1D fiber-like micelles of PFS_{35}/PFS_{54}-*b*-$PDMS_{800}$ (1 w/w %) by self-assembly in decane (1 mg/mL, 90 °C). (b) The length histogram for the micelles of PFS_{35}/PFS_{54}-*b*-$PDMS_{800}$ (1 w/w %) (L_n = 4033 nm, L_w/L_n = 1.01).

5. SUPPORTING TABLES

Table S1. Size of 1D fiber-like micelles formed by direct self-assembly of PFS_{55}/PFS_{54}-*b*-$PDMS_{800}$ at various mass ratio in decane (90 °C, 1 mg/mL). [a]

Mass ratio (w/w %)	L_n (nm)	L_w (nm)	L_w/L_n
0.5	3307	3321	1.01
1	2816	2837	1.01
1.5	2450	2499	1.02
2	2265	2300	1.02
3	2222	2245	1.01
5	2246	2284	1.02

[a] Analysis of multiple micelles with ImageJ determined by measuring more than 100 samples in several images.

6. REFERENCES

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