

## Electronic Supplementary Information

### The role of cooling rate in crystallization-driven block copolymer self-assembly

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## 1. Additional Experimental Details

### 1.1 Materials

Fluorescent dyes BDP 630/650 azide and BDP FL NHS ester were purchased from Lumiprobe Corporation (Product number, 35430 and 41420). All other chemicals were purchased from Sigma Aldrich and were used as received unless otherwise noted. The syntheses and characterization of alkyne-terminated poly(ferrocenyldimethylsilane) polymers (PFS-alkyne,  $DP_n = 35, 45$ ) were described in previous publications.<sup>S1,S2</sup> PFS<sub>35</sub>-*b*-PI<sub>273</sub> ( $D = 1.03$ ) (PI = polyisoprene), PFS<sub>48</sub>-*b*-PI<sub>325</sub> ( $D = 1.03$ ), PFS<sub>134</sub>-*b*-PI<sub>965</sub> ( $D = 1.17$ ) and PFS<sub>48</sub>-*b*-PDMS<sub>340</sub> ( $D = 1.04$ ) (PDMS = poly(dimethylsiloxane)) are the same samples reported in refs S2 and S3. Synthesis of PFS<sub>25</sub>-*b*-P2VP<sub>330</sub> ( $D = 1.16$ ) (P2VP = poly(2-vinylpyridine)) was described in previous publications ref S4 and S5. Synthesis of PFS<sub>25</sub>-*b*-PDMAEMA<sub>184</sub> ( $D = 1.12$ ) (PDMAEMA = poly(2-(*N,N*-dimethylamino)ethyl methacrylate)) and PFS<sub>25</sub>-*b*-PDMAEMA<sub>182</sub> ( $D = 1.75$ ) were described in previous publications ref S6. All the self-assembly experiments were performed in HPLC grade solvents that were acquired from Sigma Aldrich.

### 1.2 Instrumentation

*NMR.* <sup>1</sup>H NMR (500 MHz) spectra were recorded on an Agilent 500 spectrometer with a 45° pulse angle and 10 s delay time. The spectra were obtained at 25 °C in deuterated dichloromethane (CD<sub>2</sub>Cl<sub>2</sub>). Chemical shifts for <sup>1</sup>H NMR were referenced to residual signals from CH<sub>2</sub>Cl<sub>2</sub> ( $\delta = 5.33$  ppm).

*Gel Permeation Chromatography (GPC).* GPC measurements were carried out with a Waters 515 HPLC equipped with a Viscotek VE 3580 RI detector, and a 2500 UV-Vis detector. Calibration of the detectors was performed using PMMA standards. Tetrahydrofuran (THF) containing 2.5 g/L tetra-*n*-butylammonium bromide (TBAB) was used as the eluent (flow rate = 0.6 mL/min). The eluent was warmed to 35 °C.

*Transmission electron microscopy (TEM).* TEM measurements were performed on 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. For samples in decane, which is not easy to vapor, we diluted the 100  $\mu$ L solution into 900  $\mu$ L hexane, and then placed a drop of the hexane solution ( $\sim 10$   $\mu$ L) on the grid and dried. 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 to obtain the length or other information. The number average micelle length ( $L_n$ ) and weight average micelle length ( $L_w$ ) were calculated as shown below ( $L$ , length of object, and also could be referred as long/short axis length;  $N$ , number).

$$L_n = \frac{\sum_{i=1}^n N_i L_i}{\sum_{i=1}^n N_i} \quad L_w = \frac{\sum_{i=1}^n N_i L_i^2}{\sum_{i=1}^n N_i L_i} \quad (S1)$$

Specifically, we measured 200-300 samples using software ImageJ, then we copied and pasted the data into a Microsoft office Excel Worksheet. We used the function *average (all data)* to calculate the mean value  $L_n$ , then we used *stdev.p(all data)* to calculate the standard deviation. In our notation, e.g, 5370  $\pm$  920 in Fig. S3c, “5370” refers to  $L_n$ , and “920” represents the standard deviation.

*Electron diffraction* patterns for 1D fiber-like and branched micelles were collected by a Hitachi HF3300 cold-FEG TEM equipped with Gatan’s DigiScan and Orius-SC200 imaging system at 100 kV. The diffraction data from different locations of the micelles were collected in the scanning mode of the TEM (STEM) using a collimated nanobeam with the size of  $\sim$ 220 nm.

*UV-vis* measurements were performed on either an Agilent Cary 300 UV-vis spectrophotometer or on a microplate reader (TNBSA assay, TECAN, infinite M200 Pro).

*Laser confocal fluorescence microscopy (LCFM)*. Confocal imaging was performed using the Zeiss LSM 880 attached to an inverted epifluorescence microscope with a 63x (numerical aperture 1.4) oil immersion objective. Solutions were aliquoted onto glass coverslips and some samples will be dried before imaging. Fluorophores were excited using a diode-pumped solid state laser at 561 nm, an argon laser operating at 488nm, and an ultraviolet diode laser operating at 405nm. Confocal images were obtained using digital detectors with observation windows of 585 – 733 nm (red), 490 – 607 nm (green) and 410 – 508 nm (blue). The resulting outputs were obtained as digital false-color images, color coded as red, green, and blue.

*Micro-Differential scanning calorimetry ( $\mu$ DSC)*. The crystallization behavior and point ( $T_c$ ) of the PFS homopolymer and block copolymer were determined by a Malvern Panalytical MicroCal PEAQ-DSC on 3.5 mg/mL in decane for homopolymer and 10 mg/mL in decane for block copolymer (to acquire signals we herein fed relatively high sample mass). The sample was dissolved into THF and then injected into the cell and fully dried to remove THF. Then decane was added. Each sample was first heated to 160-180  $^{\circ}$ C and kept for 3 min (above its melting point to remove the thermal

history), then cooled to below 30 °C at different cooling rates, i.e., 20 °C/min, 10 °C/min, 5 °C/min, 2 °C/min, 1 °C/min, 0.5 °C/min. The DSC traces of cooling run were acquired and shown in this work.

## 2. Synthesis of Fluorescence-labeled Polymers

*PFS<sub>45</sub>-R* ('R' refers to red). The homopolymer PFS<sub>45</sub> (DP = 45, Scheme 1) was chosen. The reaction to label the fluorescent has been reported in previous literatures.<sup>S7,S8</sup> After elimination of the silane end group [-Si(CH<sub>3</sub>)<sub>3</sub>] by treatment with sodium methoxide in a mixed solvent of THF/methanol (10:1, v/v), the product PFS<sub>45</sub>-C≡CH was coupled to the azide terminated fluorescent dye BDP 630/650 by the Cu(I) catalyzed azide-alkyne coupling reaction. PFS<sub>45</sub>-alkyne (30 mg, 2.68 μmol), BDP 630/650 (2.14 mg, 4 μmol), and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (16 μL, 75 μmol) were dissolved in THF (6 mL) in a Schlenk tube. After three cycles of freeze-pump-thaw, CuCl (7.6 mg, 75 μmol) was added. Then the reaction was allowed to stir at 50 °C for 48 h before quenching by exposure to air. The solution was then diluted with THF and passed through basic Al<sub>2</sub>O<sub>3</sub> column to remove the residual copper catalyst. The eluent was concentrated and poured into methanol to precipitate the polymer. After centrifugation, the supernatant was removed. To fully remove the unreacted free dye, the solid was washed with acetonitrile for ten times until the supernatant's UV absorption spectrum did not display corresponding peaks. The solid product was dried in vacuum and stored in the dark (26 mg, yield 81 %).

*PFS<sub>48-b</sub>-PI<sub>325</sub>-G* ('G' refers to green). The block copolymer PFS<sub>48-b</sub>-PI<sub>325</sub> (Scheme 1) and fluorescent dye BDP FL NHS ester were chosen. PFS<sub>48-b</sub>-PI<sub>325</sub> (30 mg, 0.89 μmol), azobisisobutyronitrile (AIBN, 1.6 mg, 10 μmol) and cysteamine (0.8 mg, 10 μmol) were dissolved into 12 mL THF. After three cycles of freeze-pump-thaw, the reaction was initiated at 60 °C for 10 h before being quenched. The mixture was poured into methanol to precipitate the polymer. After washing and drying, the solid was re-dissolved into 10 mL THF. BDP 630/650 NHS ester (3.9 mg, 10 μmol) was added and the mixture was stirred for another 72 h. And then the polymer was precipitated in methanol. Ethanol was employed to wash and remove impurities. After drying, 25 mg polymer product was obtained (yield 71 %) and stored in the dark.

UV-vis measurements and <sup>1</sup>H NMR spectra (Fig. S5) were employed to confirm that the fluorescent dyes were covalently attached onto the polymer.

### 3. Self-assembly Experiments

The PFS homopolymers and block copolymers (BCPs) were dissolved into THF to afford polymer solutions. The concentrations were set as 0.5 mg/mL for homopolymer and 10 mg/mL for BCPs respectively unless otherwise noted.

*Structures formed by PFS homopolymer in decane.* Samples of a PFS sample and decane were mixed at a concentration of 0.05 mg/mL in a 4-mL vial. Typically, 100  $\mu$ L of the homopolymer solution in THF was injected into a 4-mL vial, and THF was fully removed by a flow of dry air, and then 1 mL decane was added. The sealed vial was placed in a hot oil bath at  $\geq 140$  °C for 30 min, followed by slow/quick cooling to RT. Subsequently, the solutions were aged for 24 h. Most of the samples precipitated, but we examined the supernatant for residual crystals. Fig. S1 shows TEM images of these structures.

*Self-assembly of PFS BCPs in decane.* The PFS BCPs were purified twice to ensure there are no homopolymer residuals and other impurities. Long polydisperse fiber-like micelles of PFS BCPs in decane were prepared by the direct assembly approach. Typically, 100  $\mu$ L of a BCP solution in THF was injected into a 4-mL vial, and then THF was fully removed by a flow of dry air. After that, 1 mL (or 2 mL) decane was added. Samples of the BCP and solvent were mixed at a concentration of 1 mg/mL (or 0.5 mg/mL). The sealed vial was placed in a hot oil bath at 90 °C for 30 min, followed by slow cooling in which the block was left to cool to room temperature (RT, 23 °C). Specifically, after heating for 30 min, we turned off the heater and let the hot oil bath and vial cool to room temperature naturally in the air or just took out the vial. Subsequently, the solutions were allowed to age for 24 h. TEM images in Fig. S2 and S18 revealed that long polydisperse fiber-like micelles had formed.

*Co-self-assembly of PFS homopolymer/BCP in decane.* Samples of PFS<sub>45</sub> (0.5 mg/mL in THF) and PFS<sub>48-b</sub>-PI<sub>325</sub> (10 mg/mL in THF) were individually injected into 4-mL vials by pipet according to their initially-set mass ratios. The THF was fully removed by a flow of dry air. Decane was added to afford a solution with 1 mg/mL. The sealed vials were placed in a hot oil bath, typically 80 or 90 °C, for 30 min, followed by cooling to RT. Subsequently, the solutions were left in the dark to age for 24 h at RT prior to taking aliquots for TEM measurements.

*Self-assembly of PFS-b-PDMAEMA BCPs in alcohols.* Micelles of PFS BCPs in alcohols were prepared by the direct assembly approach. Typically, 1 mg BCP was weighed out with a microbalance

and then mixed with 1 mL solvent in a 7 mL vial. A stir was placed inside to help dissolve the sample while it was heated. The sealed vials were placed in a hot oil bath at 80 °C for 30 min, followed by cooling without stirring, in which the bath was left to cool to room temperature (RT, 23 °C). Subsequently, the solutions were allowed to age for 24 h at RT. TEM samples were prepared by placing 10  $\mu$ L droplets on the carbon-coated copper grids and fully drying.

#### 4. Additional Results and Discussion

##### *Self-assembly of PFS<sub>45</sub> in decane*

It should be noted that most of the PFS homopolymer that had dissolved at high temperature precipitated out upon cooling to RT even at a very low concentration (0.05 mg/mL). This result indicates that decane at 23 °C is a poor solvent for PFS homopolymer. Nevertheless, there were always some PFS homopolymer crystals remaining suspended in decane, TEM images taken from these samples are presented in Fig. S1. From the supernatant, we found isolated lamellae and stacked lamellae on the grid. These platelet-like micelles were somewhat irregular in shape.

##### *Karstedt's catalyst for vinyl group staining and for in-situ loading of metal nanoparticles*

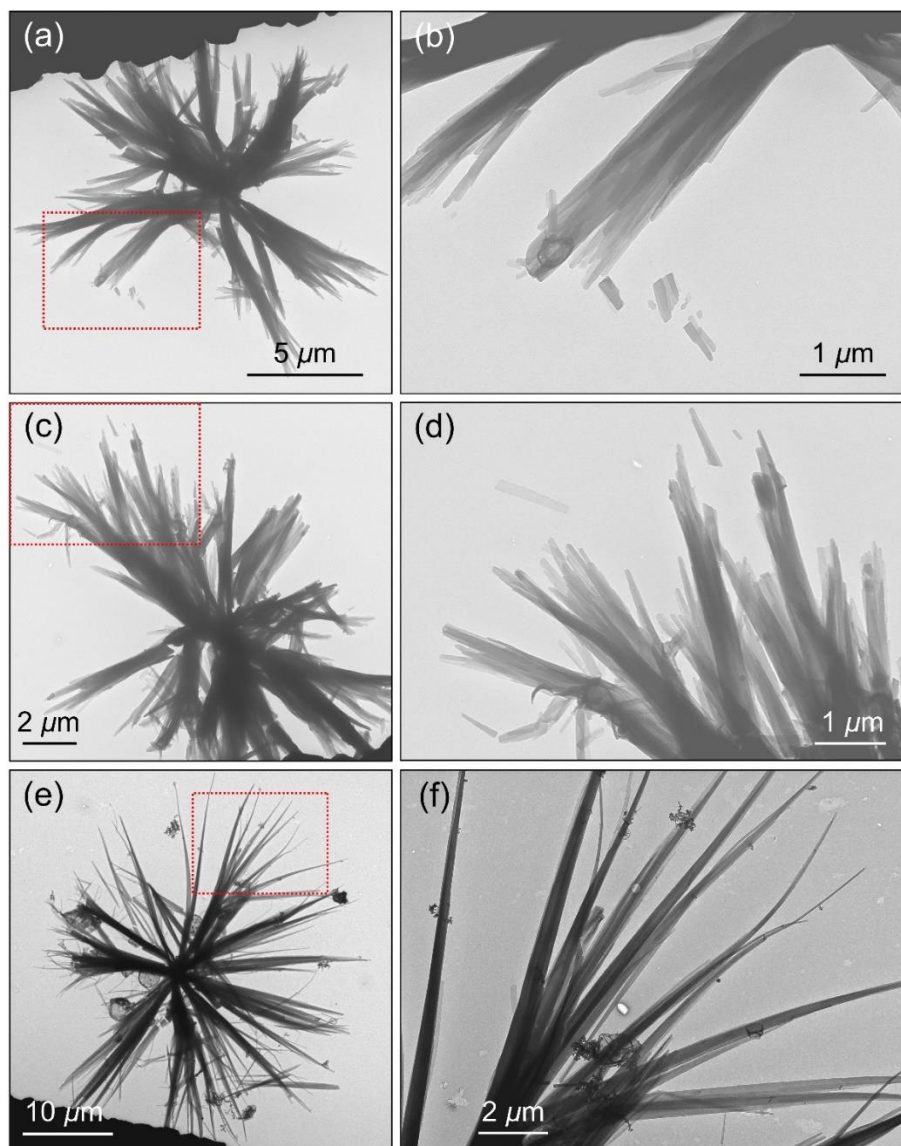
In previous studies,<sup>S9-S13</sup> we have learnt that PFS BCP micelles with polyisoprene (PI) corona chains or other olefin polymers, i.e., with pendant vinyl groups in the corona, can undergo Pt-catalyzed (Pt = Platinum) hydrosilylation cross-linking with Karstedt's catalyst. This reaction can effectively load Pt nanoparticles (PtNPs) into the coronae. In addition, these PtNPs also serve as an effective stain of the PI domains in comicelles to distinguish them from PDMS segments, as revealed in this work. In this way, one can characterize block or patchy comicelles. Typically, the micelle solution was diluted in decane. Karstedt's catalyst was added and mixed. The solution was swirled for 30 seconds and then allowed to age for 48 h. Then PtNPs were formed and were selectively introduced into the PI domains. By TEM, these stained domains can be easily discerned and clearly displayed the block or patchy structural details.

##### *Melting transition of the PFS homopolymer*

As a point of comparison for some of our experiments involving blends of PFS homopolymer and block copolymer, we present a DSC trace of the melting transition of homopolymer PFS<sub>45</sub> (3.5 mg/mL in decane) in Fig. S23. It shows a sharp melting point at ca. 100 °C. Note that melting temperatures of

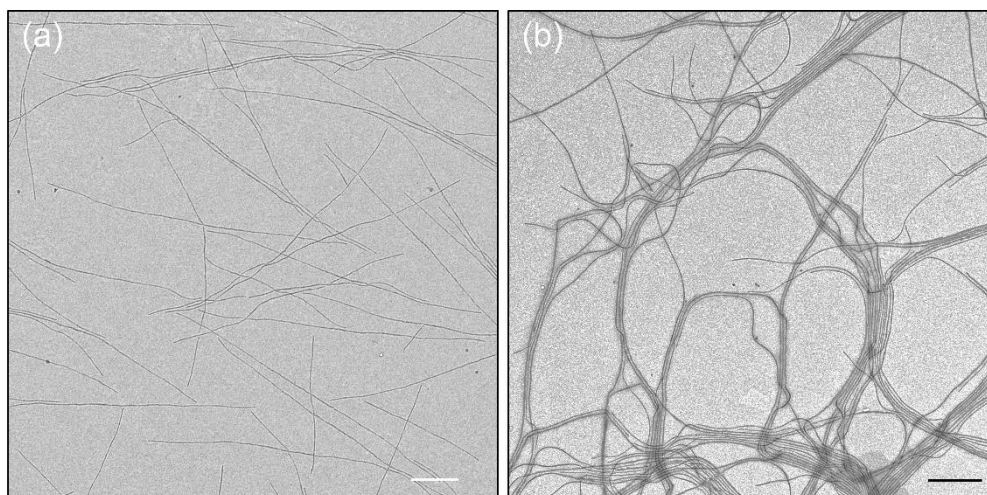
PFS homopolymer vary with the degree of polymerization (DP) of PFS. <sup>S14</sup>Note that this sample was first heated to 180 °C to remove its thermal history, cooled to 0 °C, and then reheated to generate this trace.

## 5. Supporting Figures and Tables

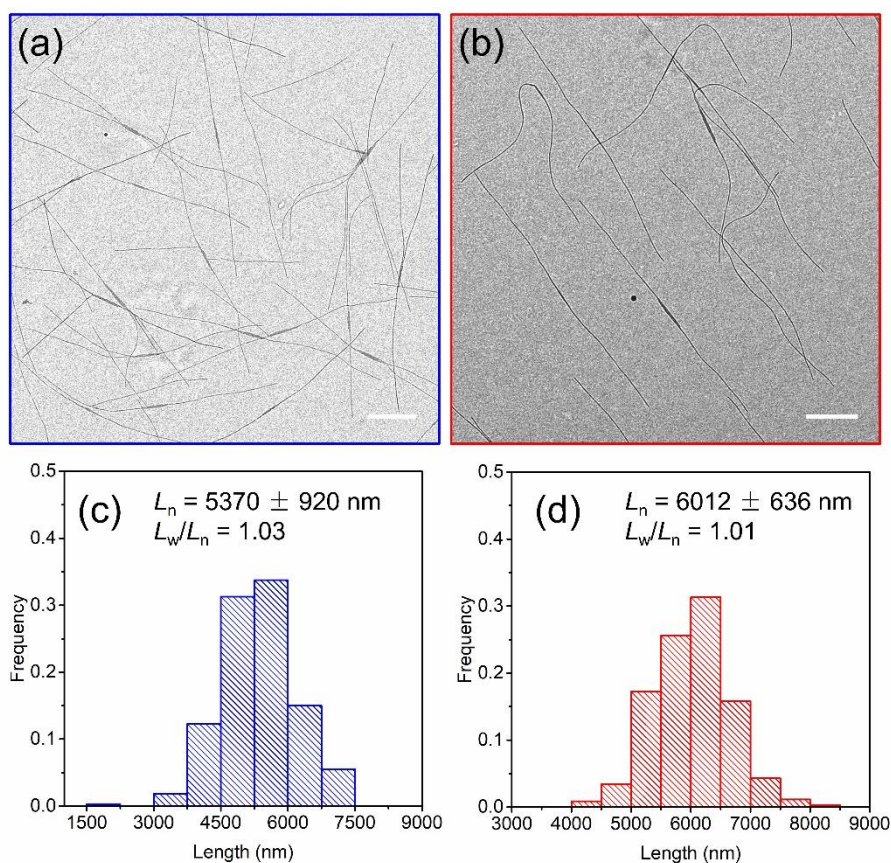


**Fig. S1** TEM images of micelles formed by PFS<sub>45</sub> through (a) (b) (c) (d) quick cooling process and (e) (f) slow cooling after heating in decane (0.05 mg/mL) at 140 °C for 30 min and then cooling to RT. (b) (d) (f) are the zoom-in images of (a) (c) (e), respectively.

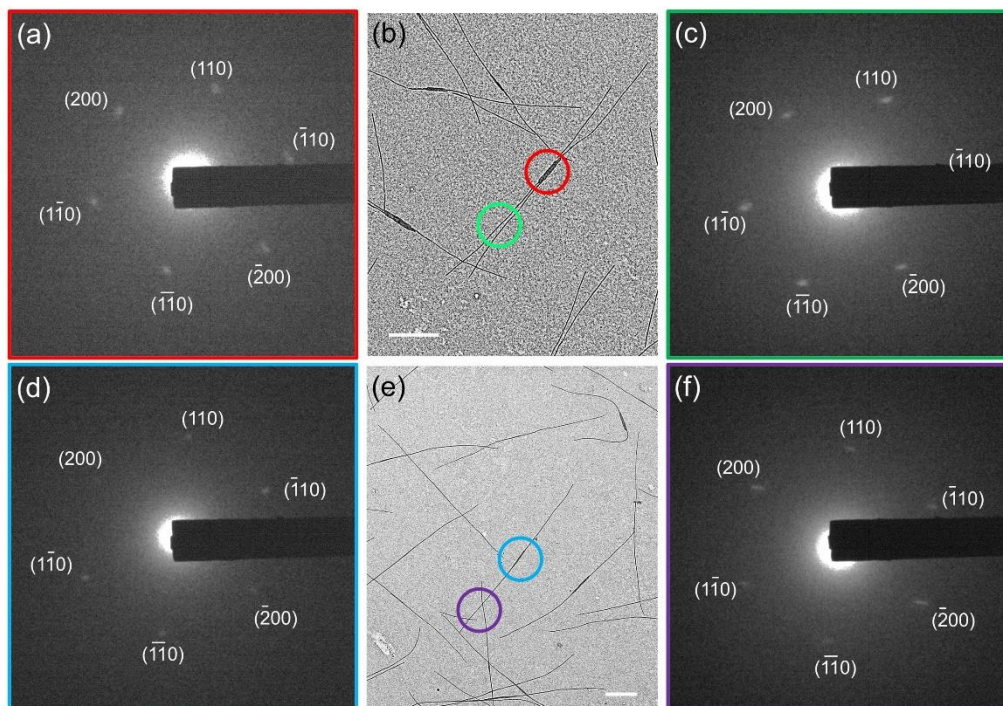




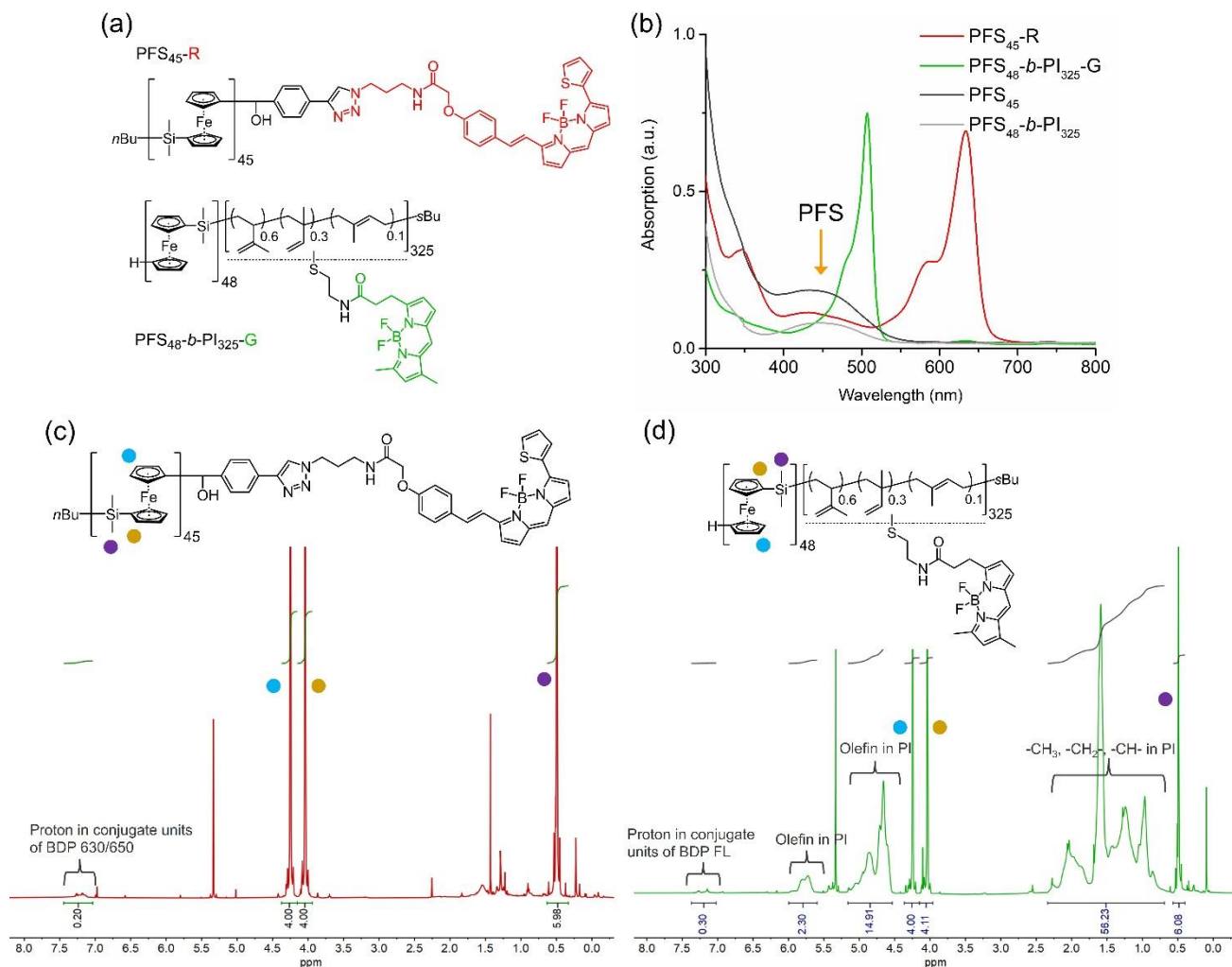
**Fig. S2** TEM images of micelles formed by PFS<sub>48</sub>-*b*-PI<sub>325</sub> through (a) quick cooling and (b) slow cooling after heating in decane (0.5 mg/mL) at 90 °C for 30 min and then cooling to RT. Scale bars: 1 μm.



**Fig. S3** TEM images of (a) branched micelles formed by rapid cooling and (b) linear fiber-like micelles formed by slow cooling in the co-self-assembly of PFS<sub>45</sub>/PFS<sub>48</sub>-*b*-PI<sub>325</sub> (1 w/w%) in decane (1 mg/mL). Both samples were heated at 90 °C for 30 min and then cooled to 23 °C. Corresponding histograms (c) for (a) and (d) for (b). Scale bars: 1 μm.

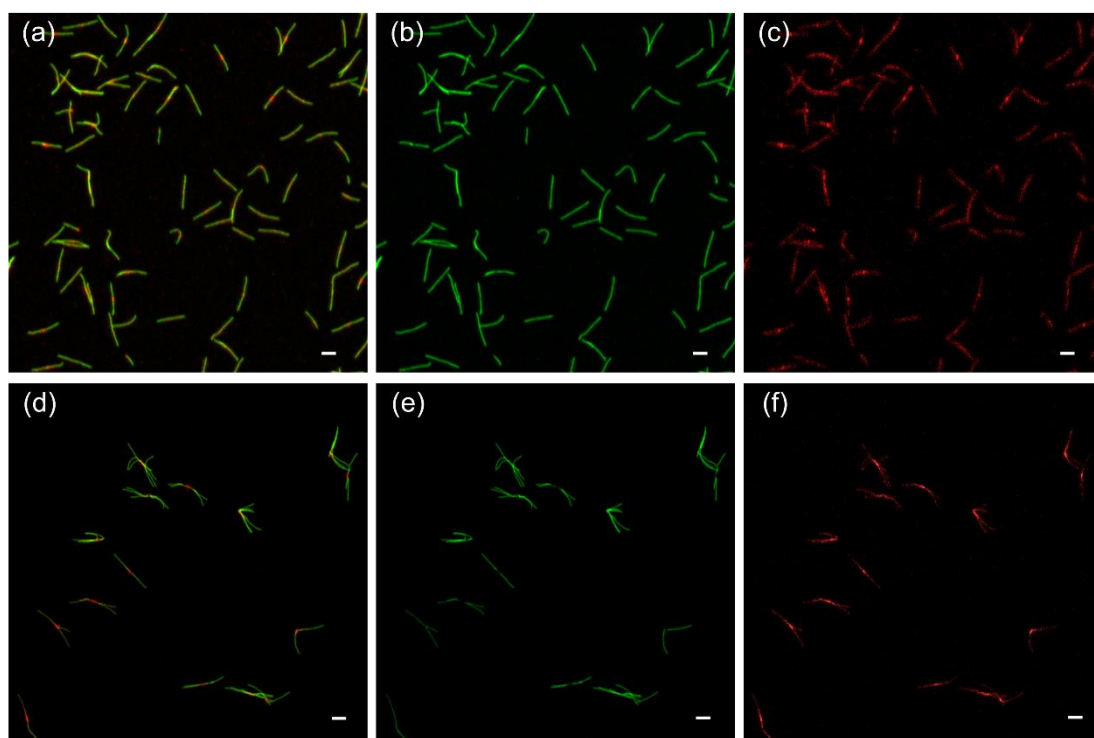


**Fig. S4** Electron diffraction patterns of the micelle samples depicted in Fig. 3. The micelles were formed by PFS<sub>45</sub>/PFS<sub>48</sub>-*b*-PI<sub>325</sub> (1 w/w%) in decane (1 mg/mL) after heating at 90 °C for 30 min and then cooling to 23 °C. (b) Rapid cooling. (e) Slow cooling. (a) (c) Diffraction patterns of the micelles in regions as marked by the circles in (b). (d) (f) Diffraction patterns of the micelles in regions as marked by the circles in (e). Scale bars in TEM images (b) (e): 1  $\mu\text{m}$ . The diffraction patterns shown here were detected from both center region and the region near the edge of the structures as marked by the circles in (b) (e). These images have identical electron diffraction patterns with three pairs of diffraction spots separated by  $\sim 60^\circ$ , indicating that the PFS core of the structures exhibit a single crystal order with monoclinic symmetry. <sup>S15</sup>

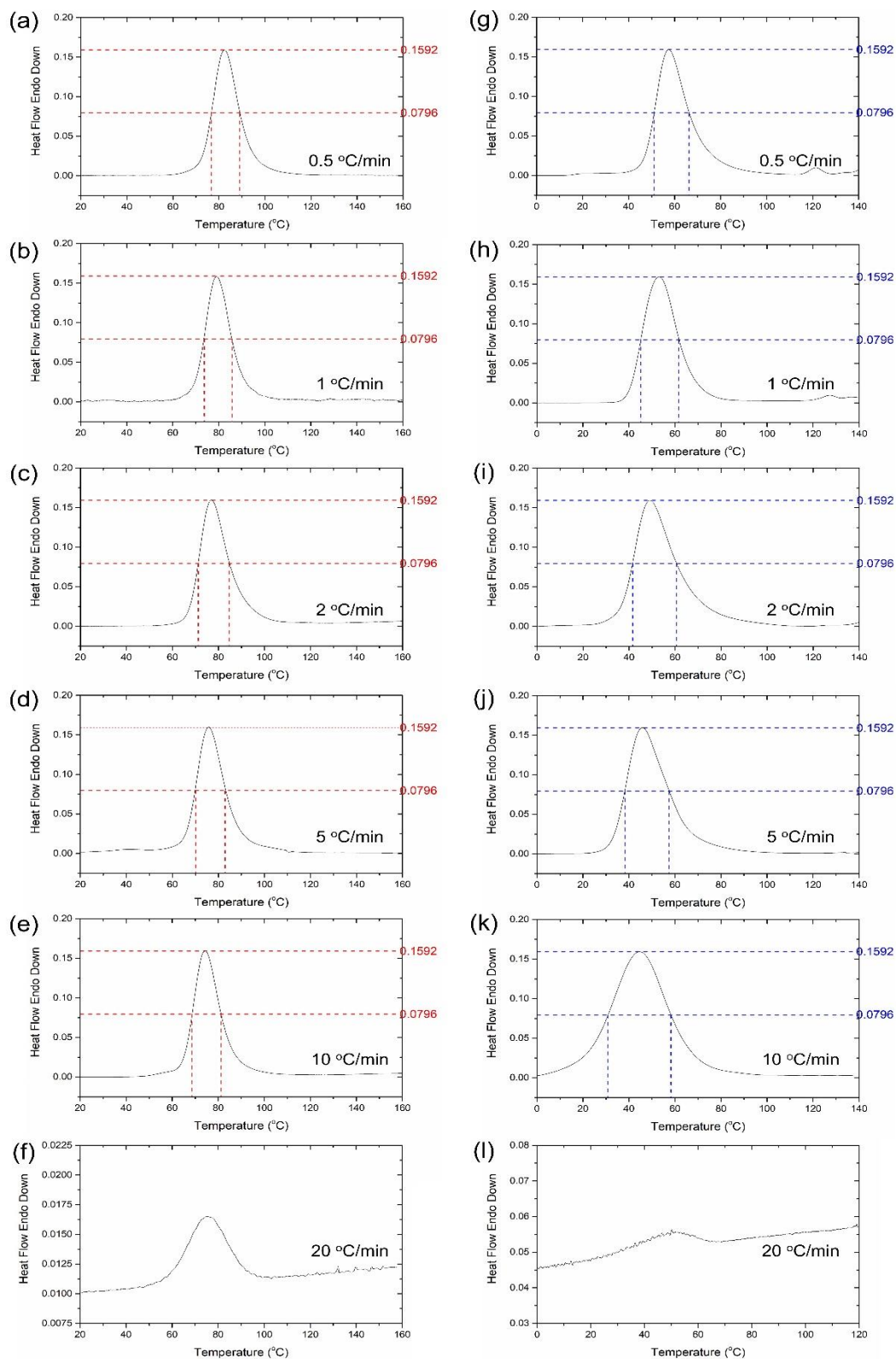


**Fig. S5** (a) Structures of PFS<sub>45</sub>-R and PFS<sub>48</sub>-b-PI<sub>325</sub>-G. (b) Absorption spectra for fluorescent-labeled PFS homopolymer PFS<sub>45</sub>-R, block copolymer PFS<sub>48</sub>-b-PI<sub>325</sub>-G, and unlabeled PFS homopolymer PFS<sub>45</sub> and block copolymer PFS<sub>48</sub>-b-PI<sub>325</sub>. These polymers were dissolved in THF (0.1 mg/mL). R refers to red; G is green. An absorption band due to the PFS block can be observed at 450 nm. (c) (d) <sup>1</sup>H NMR spectra of PFS<sub>45</sub>-R and PFS<sub>48</sub>-b-PI<sub>325</sub>-G. These spectra were obtained at 25 °C in deuterated dichloromethane (CD<sub>2</sub>Cl<sub>2</sub>, 5.33 ppm). After comparing the integration values of cyclopentadiene C-H signals with those of the aromatic protons of the fluorescent dyes, we calculated that 82 mol% PFS homopolymer was labeled with the red dye BDP 630/650, and ~3.6 BDP FL green dyes were attached to each PFS<sub>48</sub>-b-PI<sub>325</sub>-G polymer.

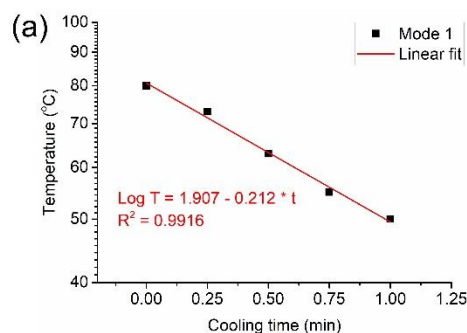




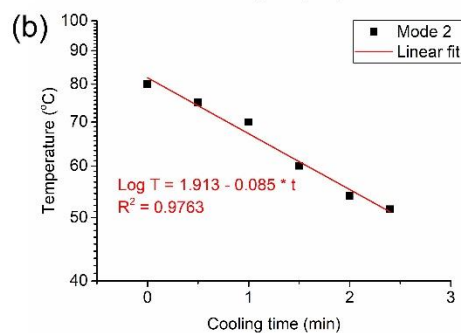
**Fig. S6** (a) (b) (c) Laser confocal fluorescence microscopy (LCFM) images of the 1D fiber-like micelles formed by co-self-assembly of PFS<sub>45</sub>-R/PFS<sub>48</sub>-*b*-PI<sub>325</sub>-G (1.5 w/w%) in decane (1 mg/mL, 90 °C, 30 min, slow cooling). The samples were imaged in the dry state. (a) The merged image and (b) green and (c) red channels illuminated individually. Scale bars: 2  $\mu$ m. (d) (e) (f) LCFM images of the branched micelles formed by co-self-assembly of PFS<sub>45</sub>-R/PFS<sub>48</sub>-*b*-PI<sub>325</sub>-G (1.5 w/w%) in decane (1 mg/mL, 90 °C, 30 min, quick cooling). The samples were dispersed in a small amount of decane. (d) The merged image and (e) green and (f) red channels illuminated individually. Scale bars: 2  $\mu$ m.



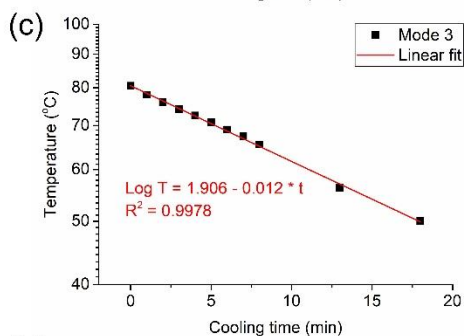
**Fig. S7** DSC traces (cooling runs) of (a) - (f) homopolymer PFS<sub>45</sub> (3.5 mg/mL in decane) and (g) - (l) block copolymer PFS<sub>48</sub>-*b*-PI<sub>325</sub> (10 mg/mL in decane), respectively. The x-axis scale, (a) – (f) 20 °C -160 °C, (g) – (k) 0 °C - 140 °C, and (l) 0 °C - 120 °C. The y-axis values were re-scaled for comparison. We label the full width at half of the maximum (FWHM) in each figure. For curves obtained at a cooling rate of 20 °C/min, because the signals were weak and the baselines were not flat, we did not measure the FWHM panels (f), (l).



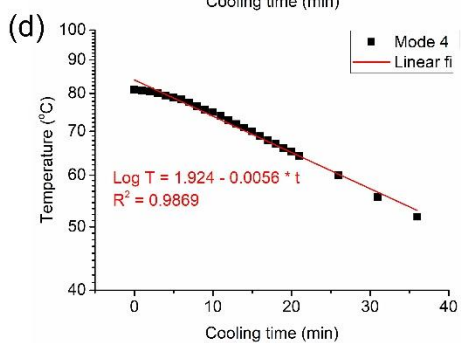
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.78902E-4		
Pearson's r	-0.99684		
Adj. R-Square	0.9916		
		Value	Standard Error
L	Intercept	1.90726	0.00598
	Slope	-0.21248	0.00977



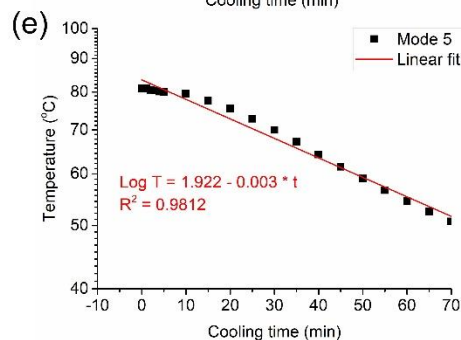
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Residual Sum of Squares	5.82909E-4		
Pearson's r	-0.99048		
Adj. R-Square	0.97632		
		Value	Standard Error
N	Intercept	1.91301	0.00883
	Slope	-0.08547	0.00594



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	7.63345E-5		
Pearson's r	-0.99901		
Adj. R-Square	0.99781		
		Value	Standard Error
P	Intercept	1.90603	0.00136
	Slope	-0.01156	1.7134E-4

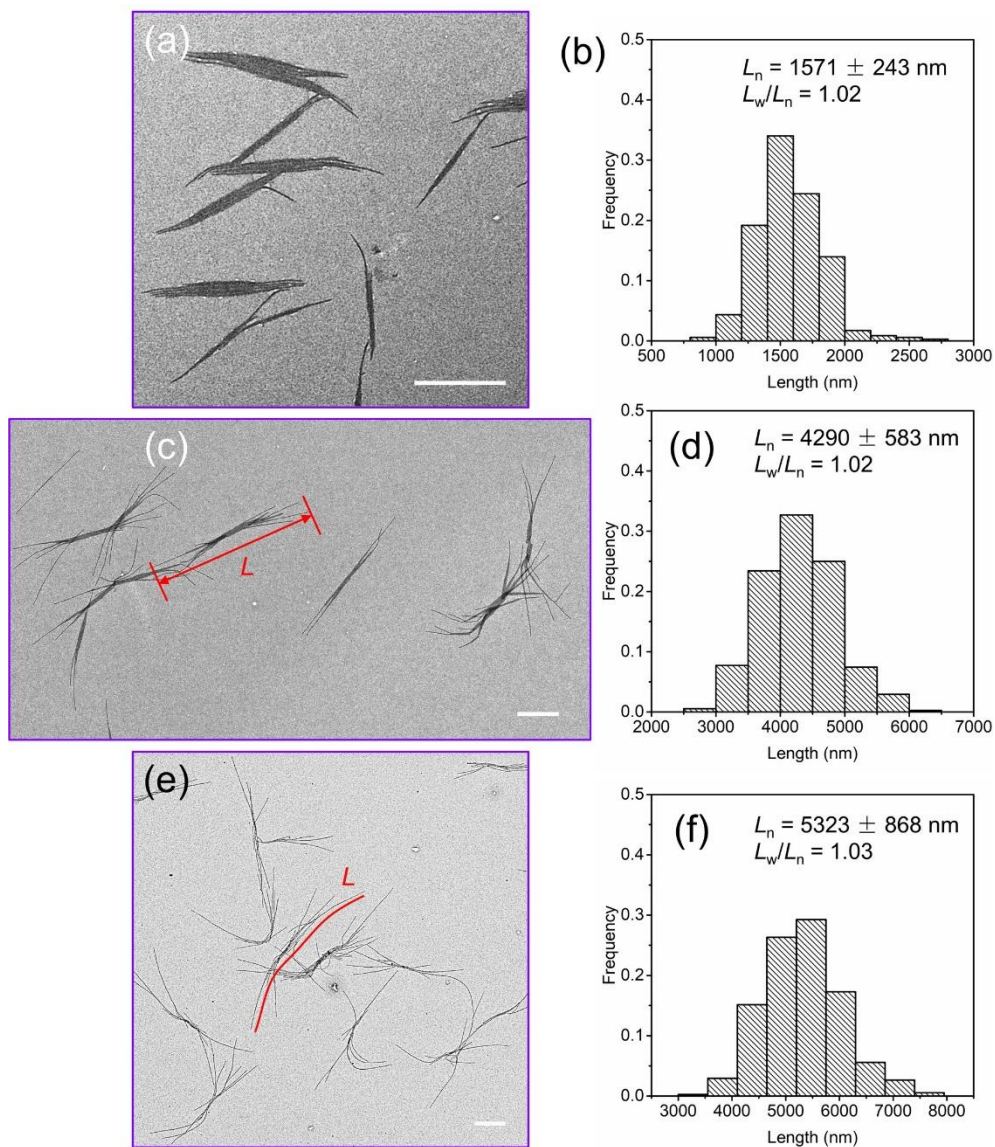


Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	8.0057E-4		
Pearson's r	-0.99369		
Adj. R-Square	0.98688		
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R	Intercept	1.92375	0.00206
	Slope	-0.00555	1.30465E-4



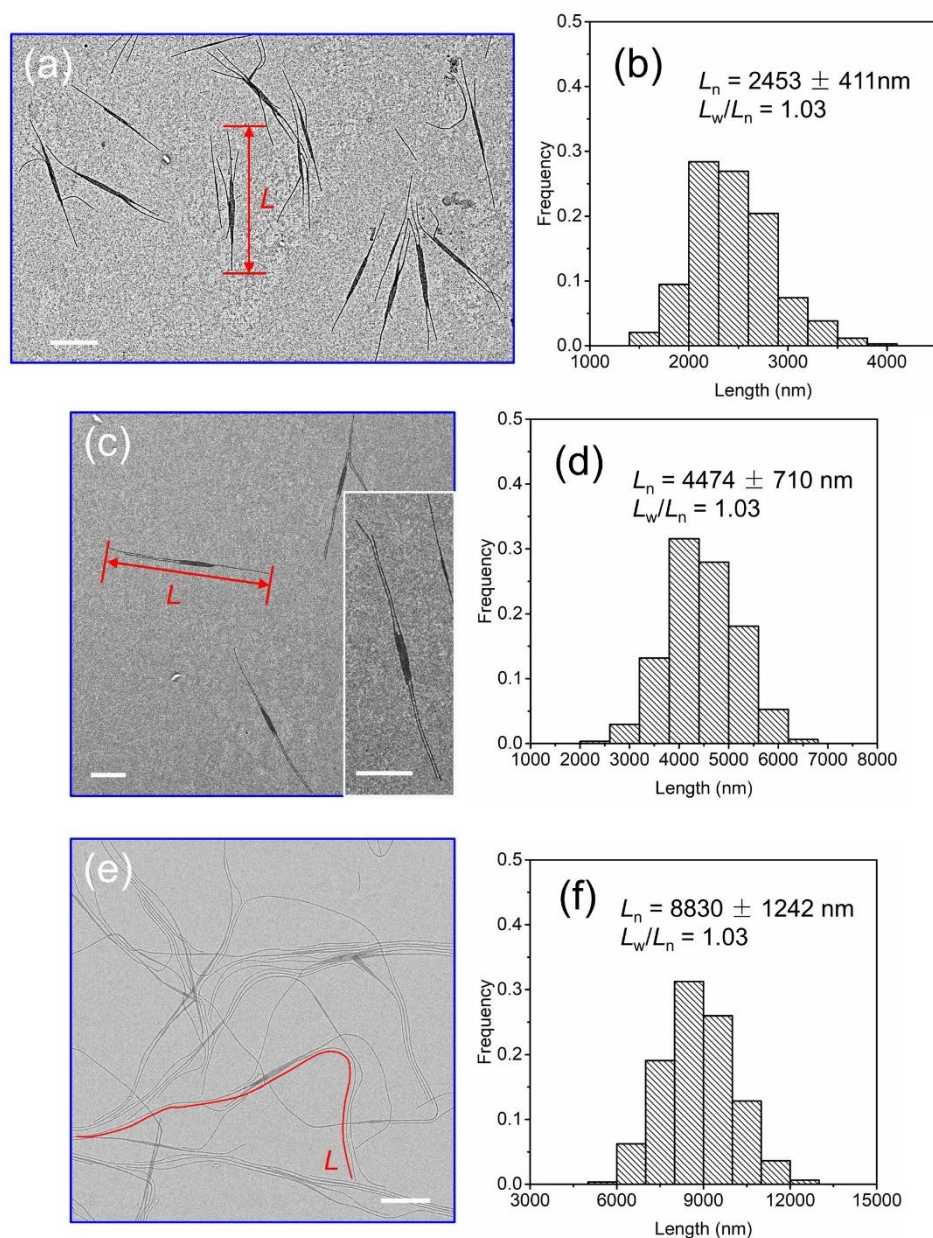
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.00166		
Pearson's r	-0.99108		
Adj. R-Square	0.9812		
		Value	Standard Error
T	Intercept	1.92181	0.00356
	Slope	-0.00298	9.72337E-5

**Fig. S8** Linear semi-logarithmic fit of the curves the temperature changes vs time under different cooling procedures employed in this work. In most cases, Log T showed nearly linear dependence of the cooling time t (in the range from 0 to  $\sim t_{1/2}$ ).



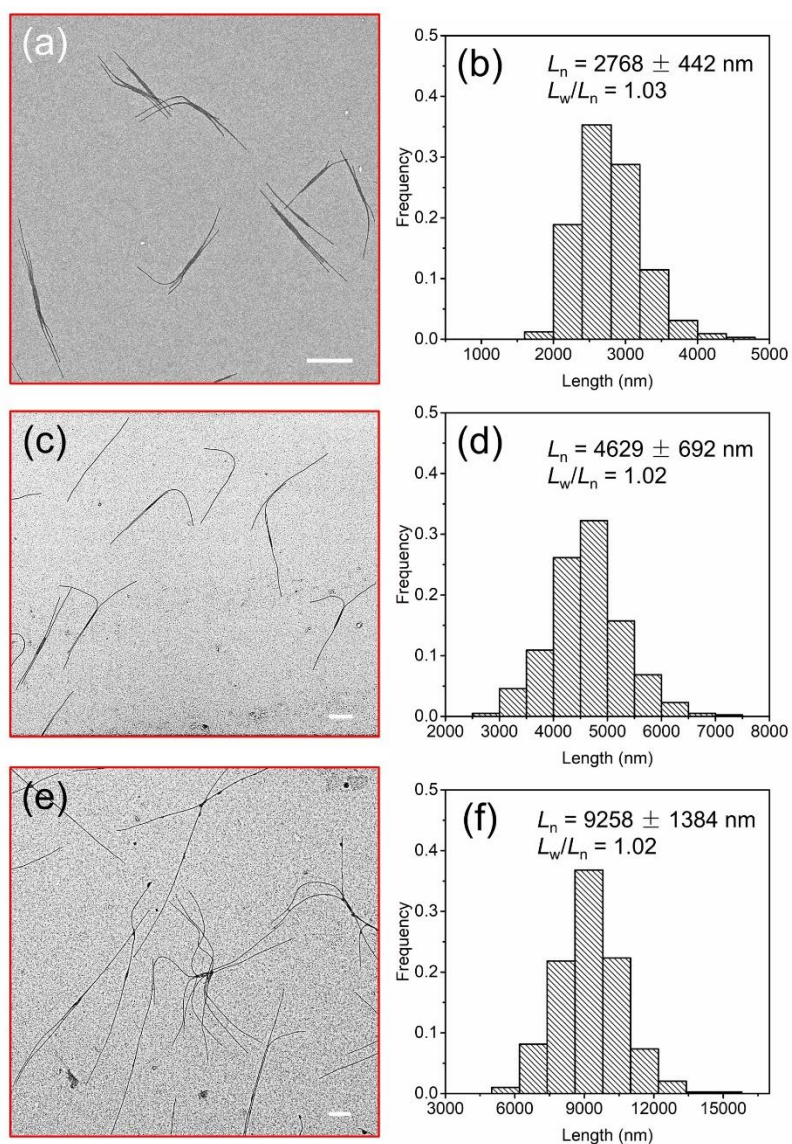
**Fig. S9** TEM images and length histograms of branched micelles formed by PFS<sub>45</sub>/PFS<sub>48</sub>-*b*-PI<sub>325</sub> (0.25 w/w%) in decane (0.5 mg/mL) through preheating at 80 °C for 30 min and then cooling via Mode 1 (Fig. 5) to 23 °C (RT), (a) (b) upon cooling to RT, (c) (d) 6 h after cooling to RT, and (e) (f) 24 h after cooling to RT. Scale bars: 1  $\mu$ m. The length was measured using the longest distance from the ends of the fibers at both ends. With the software ImageJ, one can measure the length of curved objects.



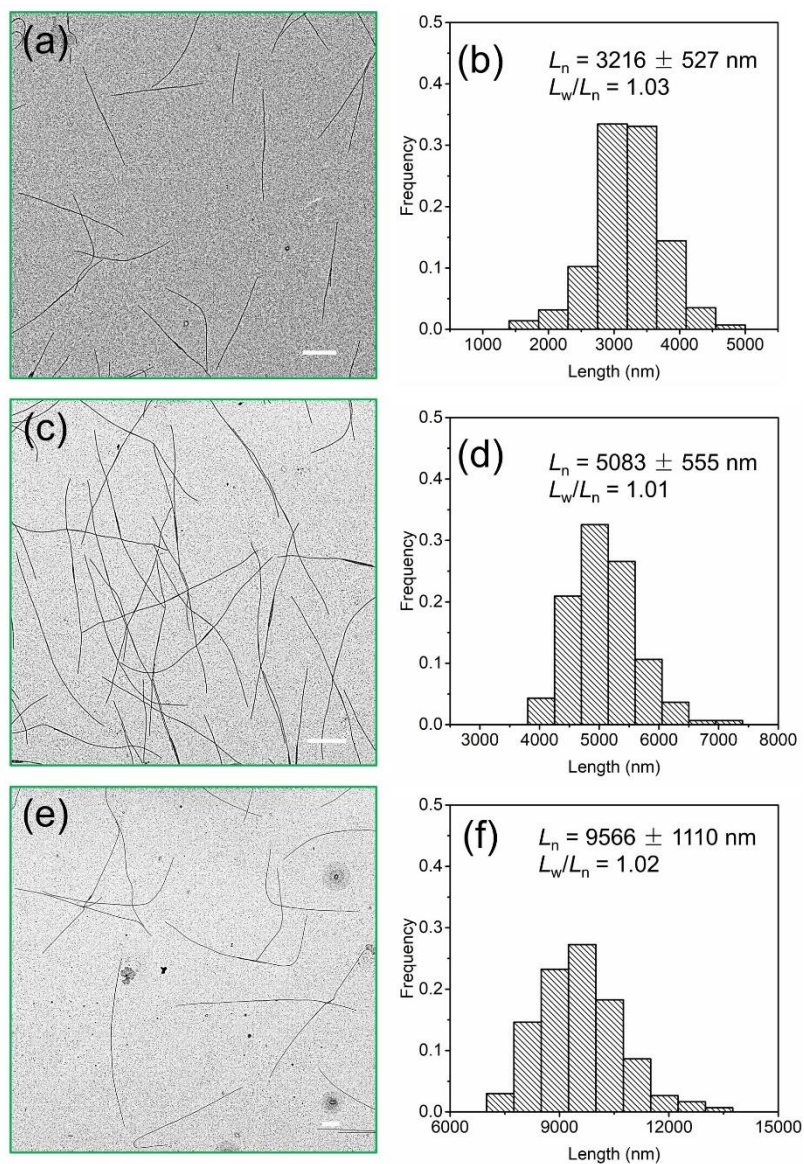


**Fig. S10** TEM images and histograms of branched micelles formed by PFS<sub>45</sub>/PFS<sub>48-*b*</sub>-PI<sub>325</sub> (0.25 w/w%) in decane (0.5 mg/mL) through preheating at 80 °C for 30 min and then cooling via Mode 2 (Fig. 5) to 23 °C, (a) (b) upon cooling to RT, (c) (d) 6 h after cooling to RT, and (e) (f) 24 h after cooling to RT. Scale bars: 1 μm. The length was measured using the longest distance from the ends of the fibers at both ends. With the software ImageJ, one can measure curved objects.

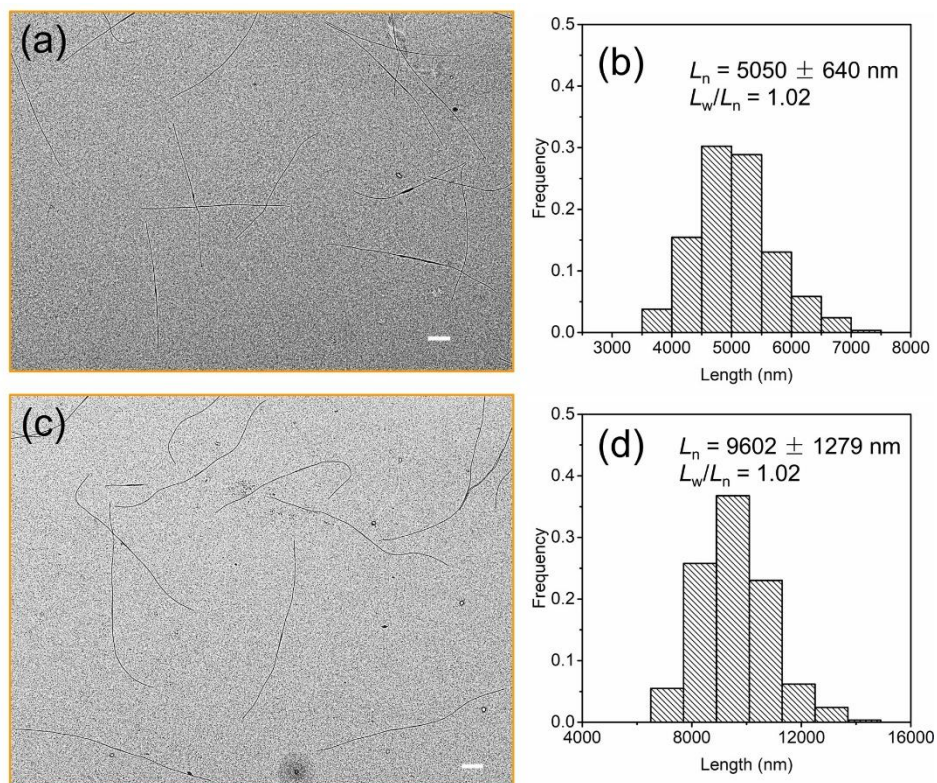




**Fig. S11** TEM images and histograms of branched micelles formed by PFS<sub>45</sub>/PFS<sub>48</sub>-*b*-PI<sub>325</sub> (0.25 w/w%) in decane (0.5 mg/mL) through preheating at 80 °C for 30 min and then cooling via Mode 3 (Fig. 5) to 23 °C (RT), (a) (b) upon cooling to RT, (c) (d) 6 h after cooling to RT, and (e) (f) 24 h after cooling to RT. Scale bars: 1  $\mu$ m.



**Fig. S12** TEM images and histograms of fiber-like micelles formed by PFS<sub>45</sub>/PFS<sub>48</sub>-*b*-PI<sub>325</sub> (0.25 w/w%) in decane (0.5 mg/mL) through preheating at 80 °C for 30 min and then cooling via Mode 4 (Fig. 5) to 23 °C, (a) (b) upon cooling to RT, (c) (d) 6 h after cooling to RT, and (e) (f) 24 h after cooling to RT. Scale bars: 1  $\mu$ m.



**Fig. S13** TEM images and histograms of fiber-like micelles formed by PFS<sub>45</sub>/PFS<sub>48</sub>-*b*-PI<sub>325</sub> (0.25 w/w%) in decane (0.5 mg/mL) through preheating at 80 °C for 30 min and then cooling via Mode 5 (Fig. 5) to 23 °C, (a) (b) upon cooling to RT or 6 h after cooling to RT, and (c) (d) 24 h after cooling to RT. Scale bars: 1 μm.

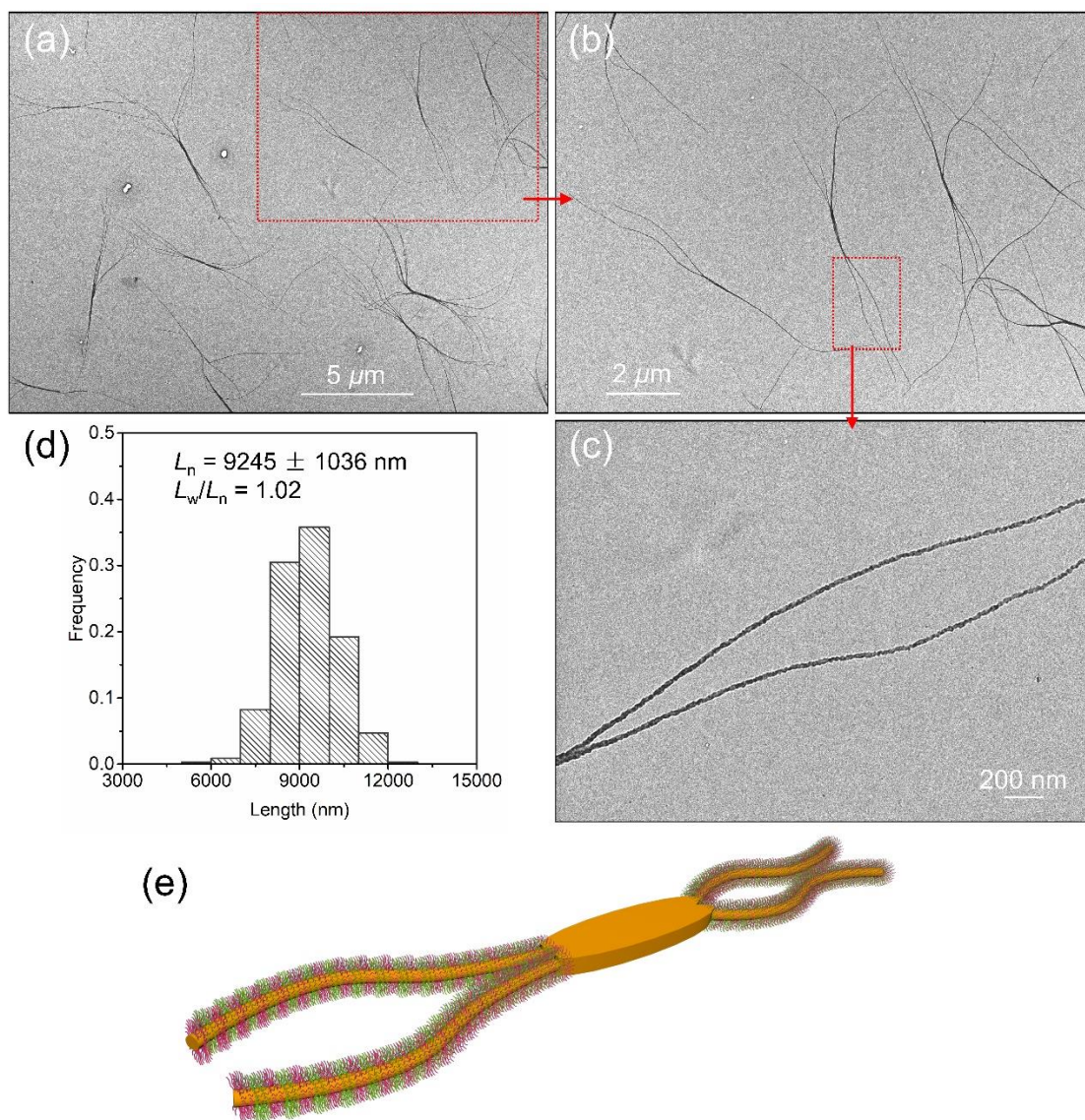
**Table S1.** Summary of the lengths ( $L_n$ , nm) and distributions ( $L_w/L_n$ ) of the micelles after cooling for a certain time.

Cooling time	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5
Upon to RT	1571 (1.02)	2453 (1.03)	2768 (1.03)	3216 (1.03)	
6 hours	4290 (1.02)	4474 (1.03)	4629 (1.02)	5083 (1.01)	5050 (1.02)
24 hours	5323 (1.03)	8830 (1.03)	9258 (1.02)	9566 (1.02)	9602 (1.02)

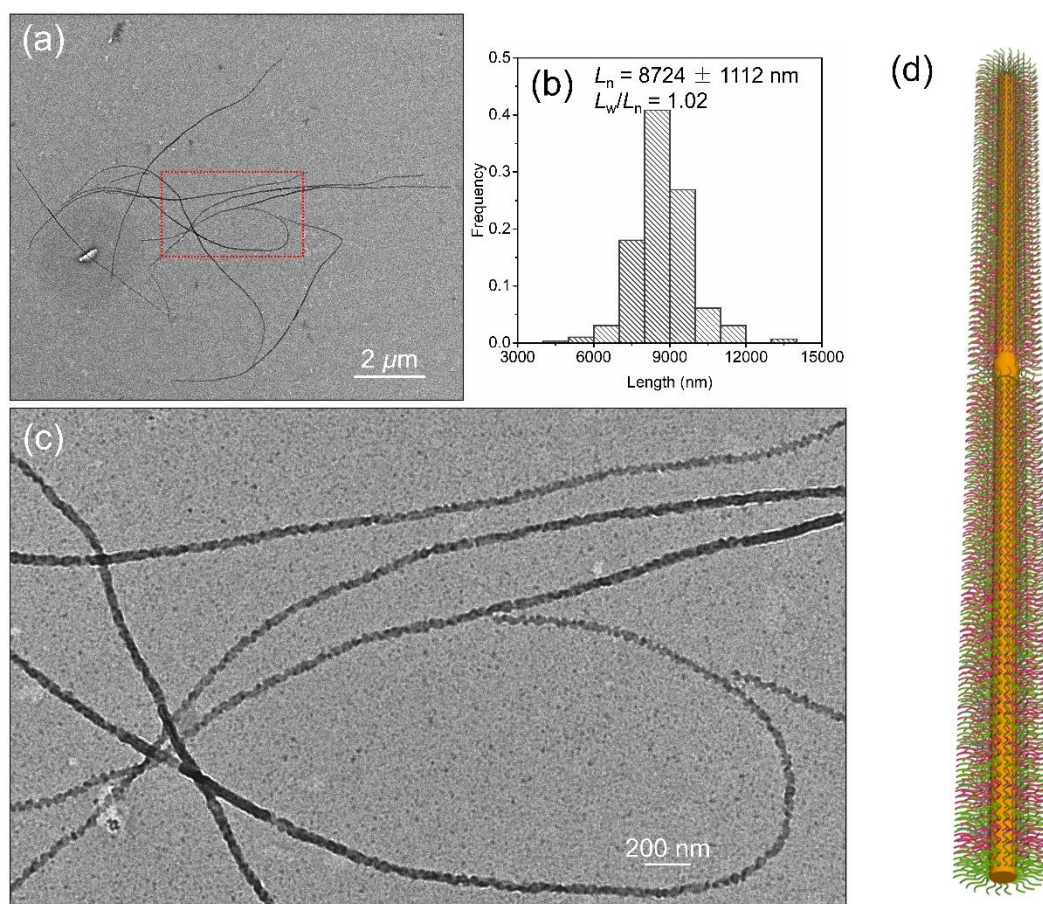
**Table S2.** Summary of the lengths of as-obtained micelles after cooling/aging for 24 hours.

Cooling Modes	$L_n$ (nm)	$L_w$ (nm)	$L_w/L_n$
Mode 1	5323	5483	1.03
Mode 2	8830	9095	1.03
Mode 3	9258	9443	1.02
Mode 4	9566	9757	1.02
Mode 5	9602	9794	1.02



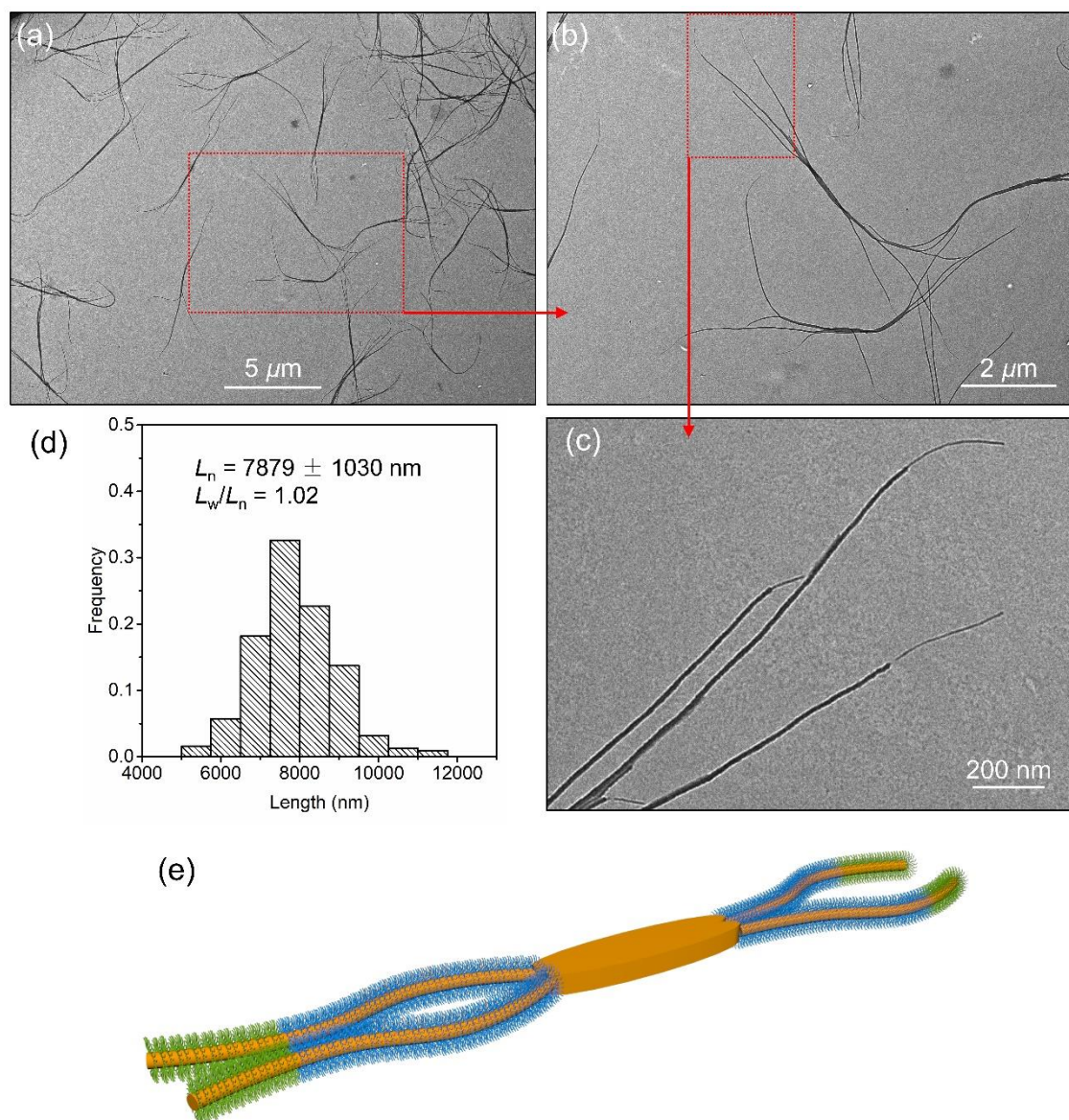


**Fig. S14** (a) (b) (c) TEM images, (d) histogram and (e) scheme of the branched micelles with patchy details along the branches formed by PFS<sub>45</sub>/(PFS<sub>48</sub>-*b*-PI<sub>325</sub> + PFS<sub>48</sub>-*b*-PDMS<sub>340</sub>) (0.2 w/w%, 90 °C, 30 min) (BCP mass ratio 2:3) through the quick cooling process.

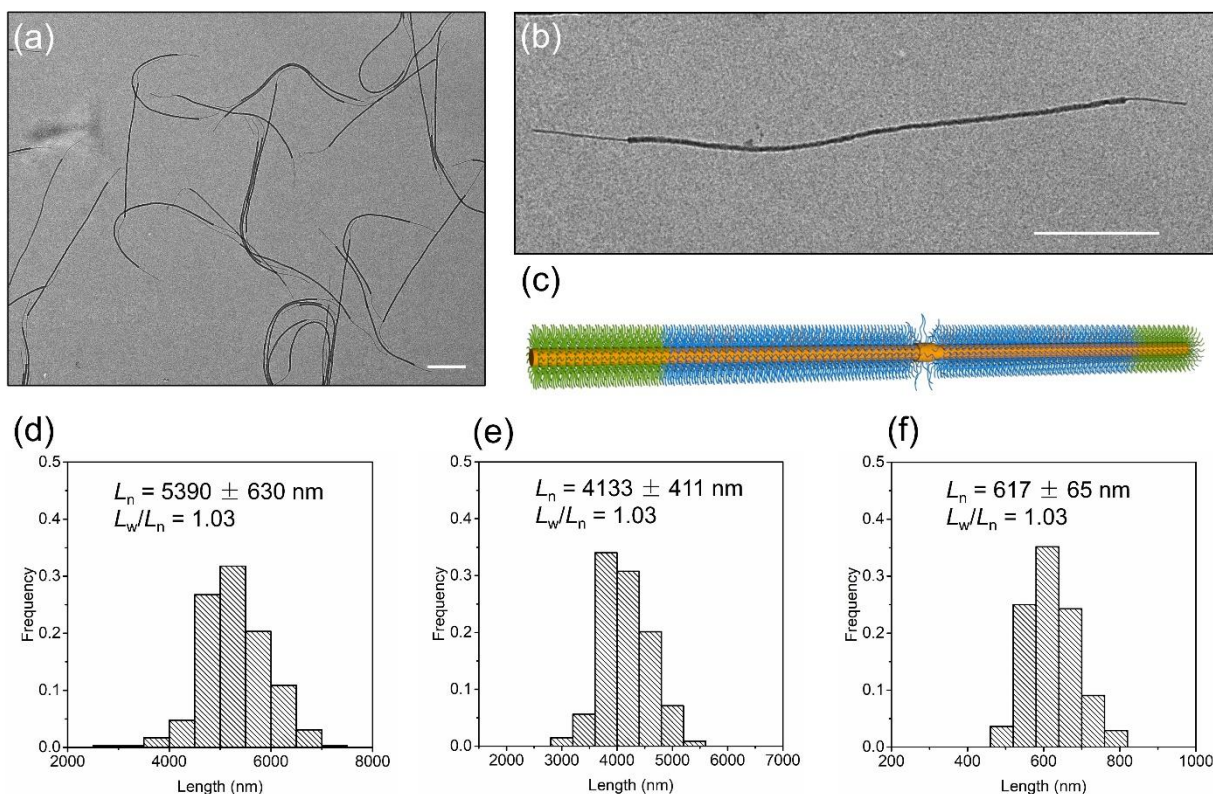


**Fig. S15** (a) (c) TEM images, (b) histogram and (d) scheme of the fiber-like patchy comicelles formed by PFS<sub>45</sub>/(PFS<sub>48</sub>-*b*-PI<sub>325</sub> + PFS<sub>48</sub>-*b*-PDMS<sub>340</sub>) (0.2 w/w%, 90 °C, 30 min) (BCP mass ratio 2:3) through slow cooling process. The PI block is stained with Pt nanoparticles derived from Karstedt's catalyst.



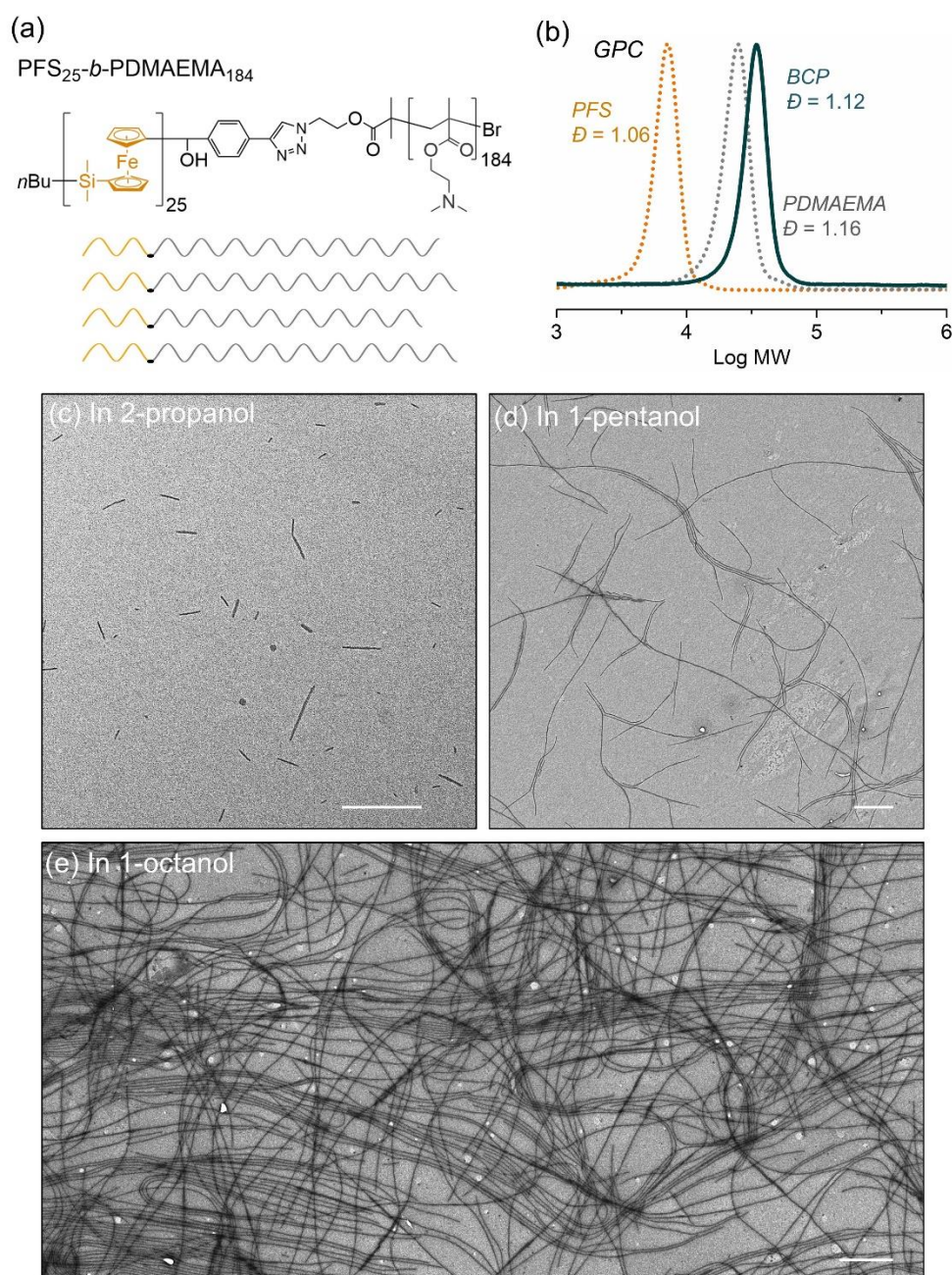


**Fig. S16** (a) (b) (c) TEM images of branched micelles formed by PFS<sub>45</sub>/(PFS<sub>134</sub>-*b*-PI<sub>965</sub> + PFS<sub>48</sub>-*b*-PDMS<sub>340</sub>) (0.2 w/w%, 90 °C, 30 min) (BCP mass ratio 5:1) through a quick cooling process. Here the PI block is stained with Pt nanoparticles derived from Karstedt's catalyst., (d) histogram of the length distributions and (e) scheme of the branched micelle structure with block details along the branches.

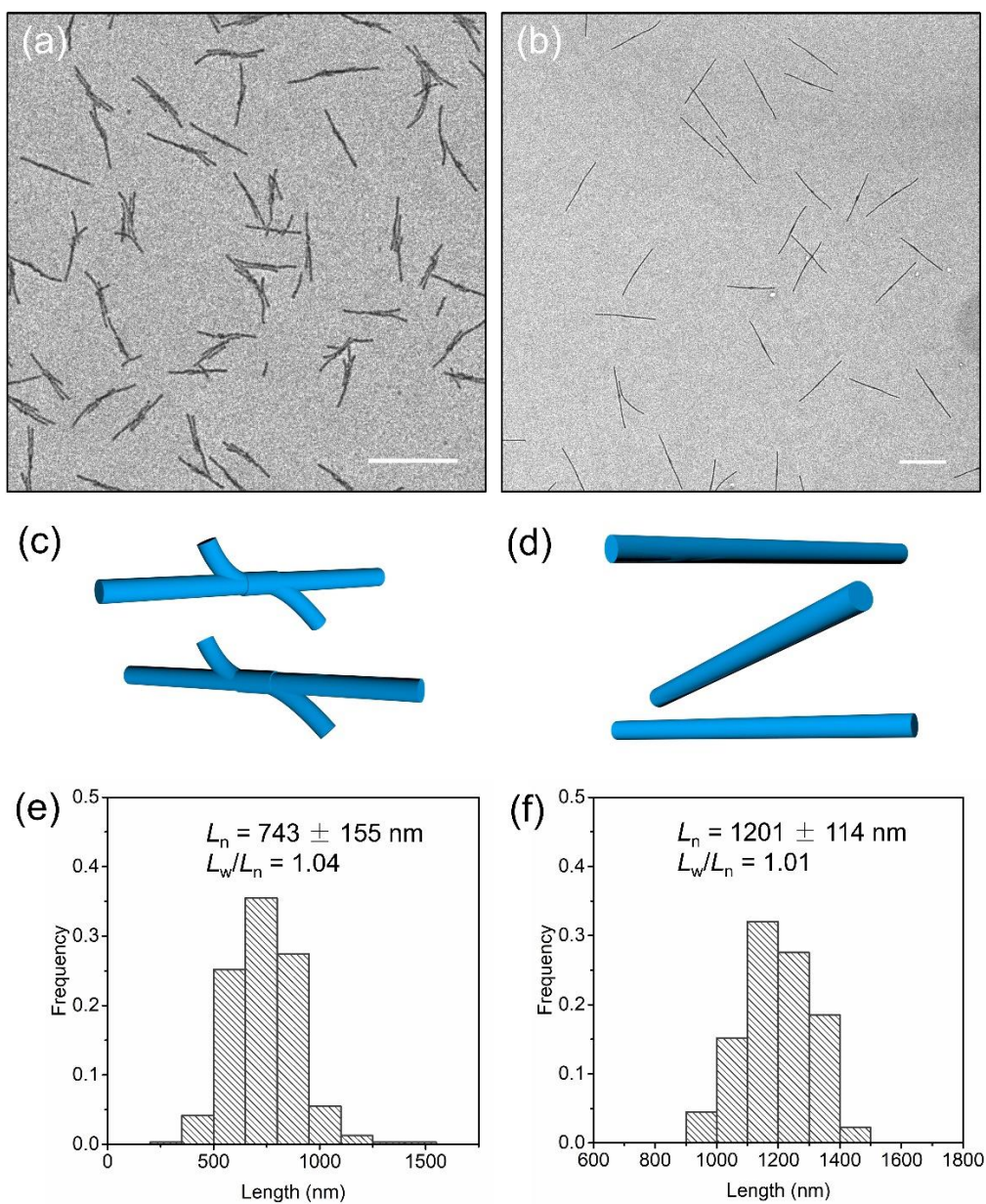


**Fig. S17** (a) (b) TEM images of the fiber-like triblock comicelles formed by co-self-assembly of PFS<sub>45</sub>/(PFS<sub>134</sub>-*b*-PI<sub>965</sub> + PFS<sub>48</sub>-*b*-PDMS<sub>340</sub>) (0.2 w/w%, 90 °C, 30 min) (BCP mass ratio 5:1) through a slow cooling process. The PI block is stained with Pt nanoparticles derived from Karstedt's catalyst. (c) drawing of the triblock comicelle structure. (d) (e) (f) Histograms of (d) the total length, (e) the length of the center block, (f) the length of the outer block. Scale bars: 1  $\mu$ m.



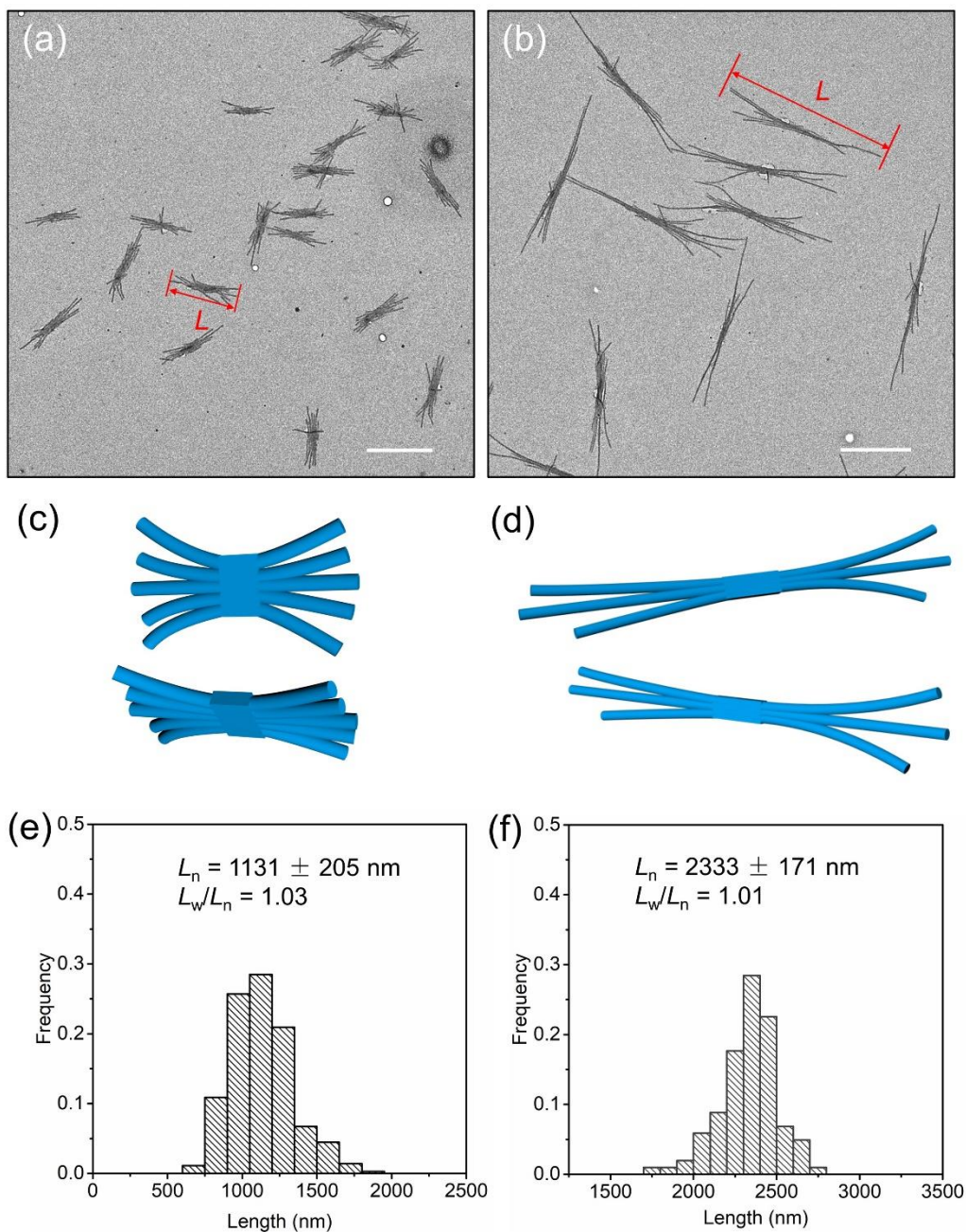


**Fig. S18** (a) Drawings of the structure of PFS<sub>25</sub>-*b*-PDMAEMA<sub>184</sub> and the molecular chain scheme showing uniform PFS block and PDMAEMA blocks and the narrow distribution of the BCP molecules. (b) GPC traces of PFS, PDMAEMA and the BCP PFS<sub>25</sub>-*b*-PDMAEMA<sub>184</sub>. (c) (d) (e) TEM images of structure formed by PFS<sub>25</sub>-*b*-PDMAEMA<sub>182</sub> in different solvents after heating to 90 °C for 30 min and then slow cooling to 23 °C. Scale bars: 1 μm. As in the case of Figure 2 (main text), polydisperse micelles were formed. Note that faster nucleation associated with polar alcohol solvents leads to short micelles in 2-propanol (c) and very long micelles in 1-octanol (e).

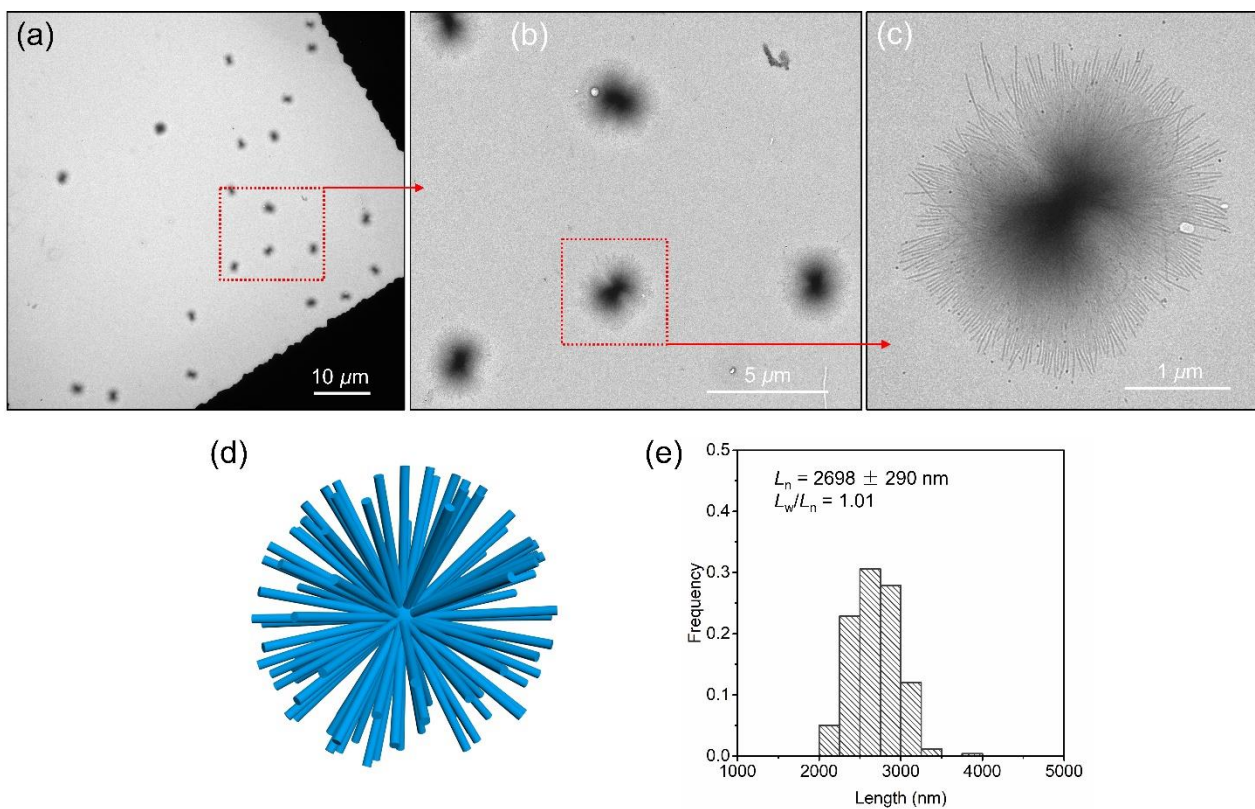


**Fig. S19** (a) (b) TEM images, (c) (d) schemes and (e) (f) length histograms of micelles formed by PFS<sub>25</sub>-*b*-PDMAEMA<sub>182</sub> (broad corona chain length distribution)<sup>S6</sup> in 2-propanol (1 mg/mL) through (a) (c) (e) quick cooling and (b) (d) (f) slow cooling, respectively, after heating at 80 °C for 30 min and cooling to RT. Scale bars: 1  $\mu$ m.

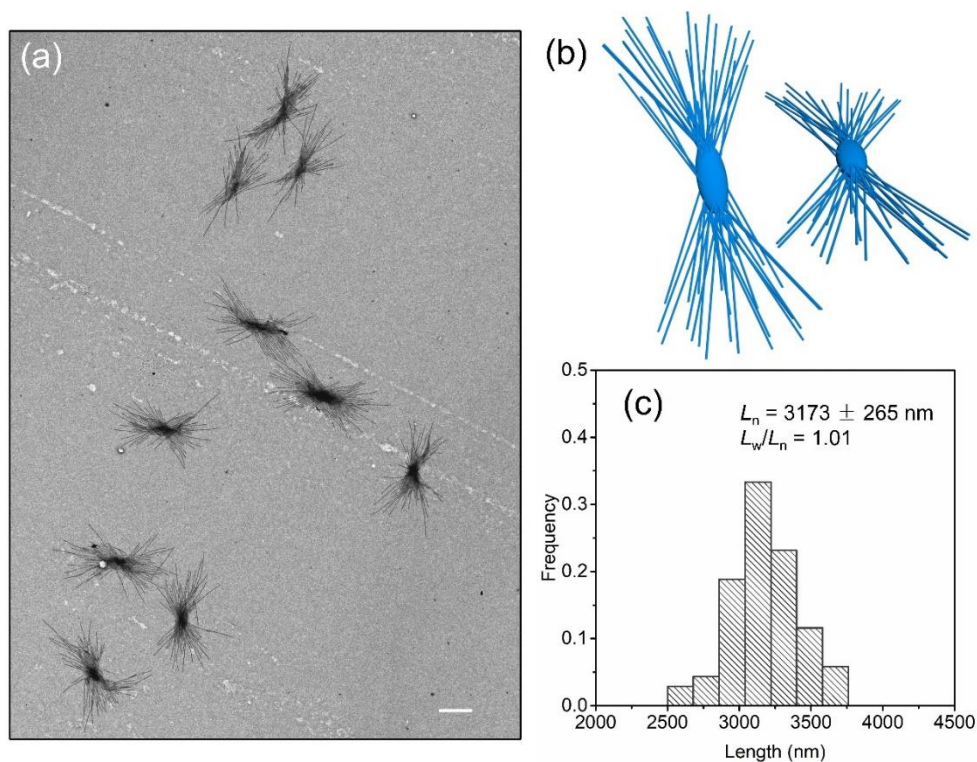




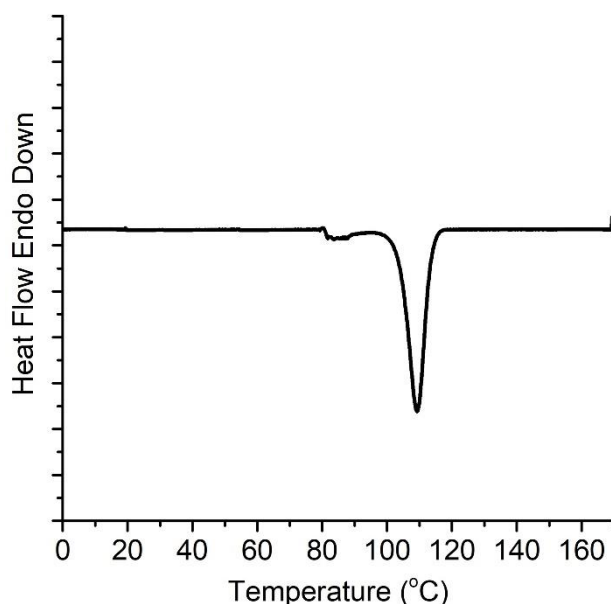
**Fig. S20** (a) (b) TEM images, (c) (d) schemes and (e) (f) length histograms of micelles formed by PFS<sub>25</sub>-*b*-PDMAEMA<sub>182</sub> (broad corona chain length distribution)<sup>S6</sup> in 1-pentanol (1 mg/mL) through (a) (c) (e) quick cooling and (b) (d) (f) slow cooling, <sup>S6</sup> respectively, after heating at 80 °C for 30 min and cooling to RT. Scale bars: 1  $\mu$ m.



**Fig. S21** (a) (b) (c) TEM images, (d) scheme and (e) length histogram of micelles formed by PFS<sub>25</sub>-*b*-PDMAEMA<sub>182</sub> (broad corona chain length distribution)<sup>S6</sup> in 1-octanol (1 mg/mL) through quick cooling after heating at 80 °C for 30 min and cooling to RT.



**Fig. S22** (a) TEM image, (b) scheme and (c) length histogram of micelles formed by PFS<sub>25</sub>-*b*-PDMAEMA<sub>182</sub> (broad corona chain length distribution)<sup>S6</sup> in 1-octanol (1 mg/mL) after heating at 80 °C for 30 min and slow cooling to RT.<sup>S6</sup> Scale bar: 1  $\mu$ m.



**Fig. S23** DSC trace (heating run) of homopolymer PFS<sub>45</sub> (3.5 mg/mL in decane). The sample was first heated to 180 °C, then cooled to 0 °C, and then heated to 170 °C. The second heating at 1 °C/min run is presented here.

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