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Supplementary Materials for

Uniform “Patchy” Platelets by Seeded Heteroepitaxial Growth of Crystallizable Polymer Blends in Two Dimensions

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General Experimental Considerations

All air- or moisture-sensitive reactions were carried out in oven (200 °C) dried glassware under a positive nitrogen pressure using standard Schlenk techniques or in an MBraun MB150B-G glove box under nitrogen. Tetrahydrofuran (THF) for living anionic polymerizations was pre-dried with sodium and distilled off sodium/benzophenone prior to use. Anhydrous solvents were obtained using a modified Grubbs system of alumina columns manufactured by Anhydrous Engineering and degassed by bubbling nitrogen prior to use. All other commercially available compounds were used without further purification. Standard laboratory solvents were purchased from VWR or Fisher Scientific. Solvents for self-assembly were filtered (polytetrafluoroethylene membrane with 0.45 μm pore size) before use. ^1H NMR spectra were recorded using Jeol Eclipse 400 MHz or Varian VNMR 400 MHz spectrometers. PFDMS₂₇-*b*-PDMS₃₆₈, PFDMG₂₄-*b*-PDMS₂₆₄, and PFDMS₂₅-*b*-P2VP₅₀₀ block copolymers (BCPs) were synthesized as previously reported.¹⁻³

Polymer Characterization

Gel permeation chromatography was carried out on PFDMS₂₇-*b*-PDMS₃₆₈, PFDMG₂₄-*b*-PDMS₂₆₄, and their corresponding homopolymers using a Viscotek VE 2001 Triple-Detector Gel Permeation Chromatograph equipped with an automatic sampler, a pump, an injector, an inline degasser, and a column oven (30 °C). The elution columns consist of styrene/divinylbenzene gels with pore sizes between 500 Å and 100,000 Å. Detection was conducted by means of a VE 3580 refractometer, a four-capillary differential viscometer, and 90° and low angle (7°) laser light ($\lambda_0 = 670$ nm) scattering detectors, VE 3210 & VE 270. THF (Fisher) was used as the eluent, with a flow rate of 1.0 mL/min. The calibration was conducted using a PolyCAL™ polystyrene standard (PS115K) from Viscotek. For PFDMS₂₅-*b*-P2VP₅₀₀ and its corresponding PFDMS aliquot, conventional calibration gel permeation chromatography (GPC-CC) measurements were carried out at 35 °C at a flow rate of 1.0 mL/min in *n*Bu₄NBr/THF (0.1 % wt. *n*Bu₄NBr) on a Viscotek GPCmax equipped with both a UV-Vis detector operating at 450 nm and differential refractometer. The column was calibrated with polystyrene standards. Samples were dissolved in the eluent (2 mg/mL) and filtered with a Ministart SRP 15 filter (polytetrafluoroethylene membrane of 0.45 μm pore size) before analysis. Matrix-assisted laser desorption/ionization time of flight (MALDI-

TOF) mass spectrometry measurements of polyferrocenyldimethylsilane (PFDMS) and polyferrocenyldimethylgermane (PFDMG) were performed using a Bruker Ultraflex extreme running in linear mode. Samples were prepared using a *trans*-2-(3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene) malononitrile matrix (20 mg mL⁻¹ in THF) and the polymer sample (2 mg mL⁻¹ in THF), mixed in a 10:1 (v/v) ratio. Approximately 1 µL of the mixed solution was deposited onto a MALDI sample plate and allowed to dry in air. The molecular weights of the diblock copolymers were then determined by combining the molecular weight M_n of the first block from MALDI-TOF measurements with the block ratio of the diblock copolymer obtained by integrating the ¹H NMR spectroscopic signal intensities of the respective blocks.

Transmission Electron Microscopy

Copper grids from Agar Scientific, mesh 400, were coated with a carbon film. Carbon coating was done using an Agar TEM Turbo Carbon Quorum where carbon was sputtered onto mica sheets before deposition on the grids via flotation on water. The samples for electron microscopy were prepared by drop casting one drop (*ca.* 10 µL) of the micelle colloidal solution onto a carbon coated copper grid placed on a piece of filter paper. Bright field TEM micrographs were obtained on a JEOL1200EX II microscope operating at 120 kV and equipped with an SIS MegaViewIII digital camera. Images were analyzed using the ImageJ software package developed at the US National Institute of Health. For the statistical length or area analyses, approximately 200 objects were measured to determine the contour length or area. Area measurements for rectangular platelet micelles were performed by measuring the length and width of each platelet micelle followed by multiplying these values to obtain each platelet's area. Histograms of the length distribution were constructed. From these data, values of the standard deviation of the length or area distribution 'sigma' were determined. In addition, values of L_n and L_w (for cylindrical micelles) or A_n and A_w (for rectangular platelets) were calculated as shown below (L , length of object; N , number; A , area of object).

$$L_n = \frac{\sum_{i=1}^n N_i L_i}{\sum_{i=1}^n N_i} \quad L_w = \frac{\sum_{i=1}^n N_i L_i^2}{\sum_{i=1}^n N_i L_i} \quad A_n = \frac{\sum_{i=1}^n N_i A_i}{\sum_{i=1}^n N_i} \quad A_w = \frac{\sum_{i=1}^n N_i A_i^2}{\sum_{i=1}^n N_i A_i}$$

Energy dispersive X-ray Spectroscopy

A Jeol 2100F TEM instrument and Oxford Instruments Aztec X-Max 80 mm² SDD were used to collect Energy Dispersive X-ray (EDX) analysis data. Elemental maps were typically collected with dwell times of 3 ms using STEM in high angle annular dark field imaging (HAADF) mode. Line scans were typically collected from 500 points with 1 ms dwell times using STEM in high angle annular dark field imaging (HAADF) mode.

Atomic force microscopy

Atomic force microscopy (AFM) images were obtained in ambient conditions utilizing a Multimode VIII with a Nanoscope V controller with PeakForce feedback control. Platelets drop-cast on carbon-coated copper grids were used for AFM measurements. All AFM images from which dimensions were determined were obtained with a fresh SCANASYST-HR (Bruker) cantilever of nominal tip radius 2 nm. The dimensions quoted in the text have not been corrected for tip effects, which are expected to be negligible. Images were analyzed using Gwyddion, an open source software program for SPM images (www.gwyddion.net).

Selected area electron diffraction (SAED) analysis

Electron diffraction (ED) patterns for platelet block comicelles were collected by Philips CM200 LaB6 TEM equipped with 4 pi imaging system with spot size of 10 at 200 kV. The d-spacing values for the SAED patterns were calibrated using gold nanoparticle standards.

Table S1. Composition and characteristics of the polymers used in this study.

Sample	M_n (g/mol)	PDI	Block ratio
PFDMS ₂₇	4400	1.19	-
PFDMG ₂₄	7200	1.24	-
PFDMS ₂₇ - <i>b</i> -PDMS ₃₆₈	36000	1.09	1:14
PFDMG ₂₄ - <i>b</i> -PDMS ₂₆₄	35000	1.08	1:11
PFDMS ₂₅ - <i>b</i> -P2VP ₅₀₀	41000	1.14	1:20

Figure S1. Overlaid refractive index GPC traces for (a) PFDMS₂₇-*b*-PDMS₃₆₈ ($M_w/M_n = 1.09$), (b) PFDMG₂₄-*b*-PDMS₂₆₄ ($M_w/M_n = 1.08$), and (c) PFDMS₂₅-*b*-P2VP₅₀₀ ($M_w/M_n = 1.14$).

Preparation of PFDMS₂₅-*b*-P2VP₅₀₀ cylindrical seed micelles for 2D platelet formation

PFDMS₂₅-*b*-P2VP₅₀₀ BCP was dissolved in *iso*-propanol (*i*-PrOH) (0.5 mg/mL, 10 mL). This sample was heated at 80 °C on a heating block for 1 h. After this time, the sample was slowly cooled down to room temperature and aged for 2 days. The resulting long cylinders (Figure S2a) were subjected to sonication at -78 °C in a dry ice-acetone bath for 2 h using a probe ultrasonic processor (Hielscher UP50H operating at 30 kHz and 50 W equipped with a Hielscher MS1 titanium sonotrode) followed by annealing at 80 °C for 30 min (Figure S2b) ($L_n = 98$ nm, $L_w = 114$ nm, $L_w/L_n = 1.16$, $\sigma/L_n = 0.4$). To 0.1 mL of this sample was added *i*-PrOH (0.4 mL) followed by PFDMS₂₅-*b*-P2VP₅₀₀ unimer dissolved in THF (10 mg/mL, 30 μ L, $m_{\text{unimer}}/m_{\text{seed}} = 6$) and aged for 2 days. TEM analysis of this sample showed the formation of uniform cylinders (Figure S2c) which were used for the platelet formation in this study ($L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$).

Figure S2. TEM micrographs of a) long cylinders formed by heating PFDMG₂₄-*b*-PDMS₂₆₄ BCP in *i*-PrOH (0.5 mg/mL, 10 mL) at 80 °C for 1 h followed by cooling to room temperature and aging for 2 days; b) small seed crystallites ($L_n = 98$ nm, $L_w = 114$ nm, $L_w/L_n = 1.16$, $\sigma/L_n = 0.4$) formed by sonicating long cylinders in (a) at -78 °C for 2 h followed by annealing at 80 °C for 30 min; c) uniform cylinders ($L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) formed by the addition of PFDMG₂₄-*b*-PDMS₂₆₄ unimer in THF (10 mg/mL, 30 μ L) to the seeds shown in (b) (0.1 mg/mL, 0.5 mL). This sample was diluted to 0.25 mg/mL in *i*-PrOH for all the platelet formation experiments. Scale bars 500 nm.

Living CDSA of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend using PFDMG₂₄-*b*-PDMS₂₆₄ cylinder seeds

To six separate 1.5 mL screw cap vials was added 25 μ L of a 0.25 mg/mL solution of PFDMG₂₄-*b*-PDMS₂₆₄ seed micelles (6 μ g, $L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) and *i*-PrOH:ethyl acetate (EtOAc) (0.2 mL, 1:1, v/v). These samples were heated at 45 °C for 10 min after which varying amounts of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend (1:1, w/w) dissolved in THF (5 mg/mL) (15 μ g, 30 μ g, 45 μ g, 60 μ g, 75 μ g, and 90 μ g) were added. After shaking the vials for 5 s, the solutions were annealed at 45 °C for an additional 30 min. After this time, the samples were cooled down to room temperature (22-25 °C) and aged for 18 h. Multiple TEM images were obtained and the contour areas were measured from ca. 200 micelles (for comprehensive characterization of these platelets see Table S2 and Figure S3-8). It is noteworthy that similar results were obtained when the self-assembly experiments were carried out at 35 °C.

Table S2. Contour area data for PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend platelets using PFDMG₂₅-*b*-P2VP₅₀₀ cylinders as seed ($L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$).

Area data	$m_{\text{unimer}}/m_{\text{seed}}$					
	2.5	5	7.5	10	12.5	15
A_n (nm ²)	7.79×10^4	1.74×10^5	2.11×10^5	2.95×10^5	4.07×10^5	4.98×10^5
A_w (nm ²)	8.48×10^4	1.84×10^5	2.21×10^5	3.08×10^5	4.22×10^5	5.13×10^5
A_w/A_n	1.09	1.06	1.05	1.04	1.04	1.03
σ/A_n	0.30	0.24	0.22	0.21	0.20	0.17

Figure S3. TEM micrograph of platelets formed by the addition of 15 μ g of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend unimer (5 mg/mL) to PFDMG₂₅-*b*-P2VP₅₀₀ seed micelles (6 μ g, $L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 $^{\circ}$ C (left) and area histogram of the resulting structures (right).

Figure S4. TEM micrograph of platelets formed by the addition of 30 μg of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend unimer (5 mg/mL) to PFDMG₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , $L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 °C (left) and area histogram of the resulting structures (right).

Figure S5. TEM micrograph of platelets formed by the addition of 45 μg of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend unimer (5 mg/mL) to PFDMG₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , $L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 °C (left) and area histogram of the resulting structures (right).

Figure S6. TEM micrograph of platelets formed by the addition of 60 μg of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend unimer (5 mg/mL) to PFDMS₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , L_n = 680 nm, L_w = 699 nm, L_w/L_n = 1.03, σ/L_n = 0.15) in *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 °C (left) and area histogram of the resulting structures (right).

Figure S7. TEM micrograph of platelets formed by the addition of 75 μg of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend unimer (5 mg/mL) to PFDMS₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , L_n = 680 nm, L_w = 699 nm, L_w/L_n = 1.03, σ/L_n = 0.15) in *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 °C (left) and area histogram of the resulting structures (right).

Figure S8. TEM micrograph of platelets formed by the addition of 90 μg of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend unimer (5 mg/mL) to PFDMG₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , $L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 °C (left) and area histogram of the resulting structures (right).

Figure S9. TEM micrographs of aggregates of polydisperse 2D platelets with poorly defined edges formed by the addition of 30 μg of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend unimer (5 mg/mL) to *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 °C in the absence of PFDMG₂₅-*b*-P2VP₅₀₀ seed micelles.

Figure S10. Additional dark field TEM image (a), STEM-EDX Si-mapping (b), STEM-EDX Ge-mapping (c), and overlaid STEM-EDX Si and Ge maps (d) of the PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend platelets formed by the addition of 30 μg of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend unimer (5 mg/mL) to PFDMG₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , $L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 $^{\circ}\text{C}$. Scale bars 250 nm.

Preparation of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₇ platelets

PFDMG₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , $L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in 1:1 (v/v) *i*-PrOH: EtOAc (0.2 mL, 30 $\mu\text{g/mL}$) were heated at 45 $^{\circ}\text{C}$ for 10 min in a screw cap vial. PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₇ blend (1:1, w/w) dissolved in THF (5 mg/mL, 6 μL) was then added and, after shaking the vial for 5 s, the solution was annealed at 45 $^{\circ}\text{C}$ for an additional 30 min. After this time, the sample was cooled down to room temperature (22-25 $^{\circ}\text{C}$) and aged for 18 h. Multiple TEM images were obtained and the contour areas were measured from ca. 200 micelles (Figure S11).

Figure S11. a) TEM micrograph and b) area histogram of platelets formed by the addition of 30 μg of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMS₂₇ blend unimer (5 mg/mL) to PFDMS₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , $L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 °C. AFM height image (c) and height profile (d) of PFDMG₂₄-*b*-PDMS₂₆₄/PFDMS₂₇ blend platelets showing cylinder seed height of ~16 nm and platelet height of ~10 nm. Additional dark field TEM image (e), STEM-EDX Si-mapping (f), STEM-EDX Ge-mapping (g), and overlaid STEM-EDX Si and Ge maps (h) of the resulting structures.

Attempted preparation of PFDMS₂₇-*b*-PDMS₃₆₈/PFDMG₂₄ platelets

PFDMS₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , $L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in 1:1 (v/v) *i*-PrOH: EtOAc (0.2 mL, 30 $\mu\text{g/mL}$) were heated at 45 °C for 10 min in a screw cap vial. PFDMS₂₇-*b*-PDMS₃₆₈/PFDMG₂₄ blend (1:1, w/w) dissolved in THF (5 mg/mL, 6 μL) was then added and, after shaking the vial for 5 s, the solution was annealed at 45 °C for an additional 30 min. After this time, the sample was cooled down to room

temperature (22-25 °C) and aged for 18 h. At this point, deposition of a precipitate was observed at the bottom of the vial. TEM analysis of the supernatant showed the formation of polydisperse, irregular elongated platelet-type structures (Figure S12).

Figure S12. TEM micrographs of polydisperse, irregular platelet-type structures formed by the addition of 30 μg of PFDMG₂₄-*b*-PDMS₃₆₈/PFDMG₂₄ blend unimer (5 mg/mL) to PFDMG₂₄-*b*-P2VP₅₀₀ seed micelles (6 μg , $L_n = 680$ nm, $L_w = 699$ nm, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 °C.

Preparation of concentric rectangular [PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄]-*b*-[PFDMG₂₄-*b*-PDMS₃₆₈/PFDMG₂₄] platelet block comicelles

PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend platelets ($A_n = 1.74 \times 10^5$ nm², $A_w = 1.84 \times 10^5$ nm², $A_w/A_n = 1.06$, $\sigma/A_n = 0.24$) in 1:1 v/v EtOAc:*i*-PrOH (0.14 mg/mL, 0.1 mL) were first heated at 45 °C for 10 min. At this point, PFDMG₂₄-*b*-PDMS₃₆₈/PFDMG₂₄ blend unimer in THF (1 mg/mL, 2.5 μL) was added and, after shaking for 5 s, the resulting sample was annealed at 45 °C for 30 min. At this point, the sample was cooled down to room temperature and aged for 18 h. TEM analysis revealed the formation of well-defined concentric rectangular platelet block comicelles ($A_n = 3.00 \times 10^5$ nm², $A_w = 3.14 \times 10^5$ nm², $A_w/A_n = 1.05$, $\sigma/A_n = 0.22$) (Figure S13).

Figure S13. a) TEM micrograph and b) area histogram of concentric rectangular platelet block comicelles ($A_n = 3.00 \times 10^5 \text{ nm}^2$, $A_w = 3.14 \times 10^5 \text{ nm}^2$, $A_w/A_n = 1.05$, $\sigma/A_n = 0.22$) prepared through the sequential addition of the PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ and PFDMS₂₇-*b*-PDMS₃₆₈/PFDMS₂₇ blends to PFDMS₂₅-*b*-P2VP₅₀₀ cylindrical seed micelles ($L_n = 680 \text{ nm}$, $L_w = 699 \text{ nm}$, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in *i*-PrOH: EtOAc (0.1 mL, 1:1, v/v) at 45 °C. Additional dark field TEM image (c), STEM-EDX Si-mapping (d), STEM-EDX Ge-mapping (e), and overlaid STEM-EDX Si and Ge maps (f) of the resulting structures. Scale bars 500 nm.

Preparation of PFDMS₂₇-*b*-PDMS₃₆₈/PFDMS₂₇ platelets

PFDMS₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , $L_n = 680 \text{ nm}$, $L_w = 699 \text{ nm}$, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in 1:1 (v/v) *i*-PrOH: EtOAc (0.2 mL, 30 $\mu\text{g/mL}$) were heated at 45 °C for 10 min in a screw cap vial. PFDMS₂₇-*b*-PDMS₃₆₈/PFDMS₂₇ blend (1:1, w/w) dissolved in THF (5 mg/mL, 6 μL) was then added and, after shaking the vial for 5 s, the solution was annealed at 45 °C for an additional 30 min. After this time, the sample was cooled down to room temperature (22-25 °C) and aged for 18 h. Multiple TEM images were obtained and the contour areas were measured from ca. 200 micelles (Figure S14).

Figure S14. TEM micrograph of platelets ($A_n = 1.46 \times 10^5 \text{ nm}^2$, $A_w = 1.59 \times 10^5 \text{ nm}^2$, $A_w/A_n = 1.09$, $\sigma/A_n = 0.31$) formed by the addition of 30 μg of PFDMS₂₇-*b*-PDMS₃₆₈/PFDMS₂₇ blend unimer (5 mg/mL) to PFDMS₂₅-*b*-P2VP₅₀₀ seed micelles (6 μg , $L_n = 680 \text{ nm}$, $L_w = 699 \text{ nm}$, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in *i*-PrOH: EtOAc (0.2 mL, 1:1, v/v) at 45 °C (left) and area histogram of the resulting structures (right).

Preparation of concentric rectangular [PFDMS₂₇-*b*-PDMS₃₆₈/PFDMS₂₇]-*b*-[PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄] platelet block comicelles

PFDMS₂₇-*b*-PDMS₃₆₈/PFDMS₂₇ blend platelets ($A_n = 1.46 \times 10^5 \text{ nm}^2$, $A_w = 1.59 \times 10^5 \text{ nm}^2$, $A_w/A_n = 1.09$, $\sigma/A_n = 0.31$) in 1:1 v/v EtOAc:*i*-PrOH (0.14 mg/mL, 0.1 mL) were first heated at 45 °C for 10 min. At this point, PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blend unimer in THF (1 mg/mL, 10 μL) was added and, after shaking for 5 s, the resulting sample was annealed at 45 °C for 30 min. At this point, the sample was cooled down to room temperature and aged for 18 h. TEM analysis revealed the formation of well-defined concentric rectangular platelet block comicelles ($A_n = 1.08 \times 10^6 \text{ nm}^2$, $A_w = 1.09 \times 10^6 \text{ nm}^2$, $A_w/A_n = 1.01$, $\sigma/A_n = 0.10$).

Figure S15. a) TEM micrograph and b) area histogram of concentric rectangular platelet block comicelles ($A_n = 1.08 \times 10^6 \text{ nm}^2$, $A_w = 1.09 \times 10^6 \text{ nm}^2$, $A_w/A_n = 1.01$, $\sigma/A_n = 0.10$) prepared through the sequential addition of the PFDMS₂₇-*b*-PDMS₃₆₈/PFDMS₂₇ and PFDMG₂₄-*b*-PDMS₂₆₄/PFDMG₂₄ blends to PFDMS₂₅-*b*-P2VP₅₀₀ cylindrical seed micelles ($L_n = 680 \text{ nm}$, $L_w = 699 \text{ nm}$, $L_w/L_n = 1.03$, $\sigma/L_n = 0.15$) in *i*-PrOH: EtOAc (0.1 mL, 1:1, v/v) at 45 °C.

NMR experiments to evaluate relative solubilities of PFDMS₂₇ and PFDMG₂₄ homopolymers

Solid PFDMS₂₇ and PFDMG₂₄ homopolymers (3 mg) were transferred to J Young capped NMR tubes. To these was added hexane/cyclohexane (0.5 mL, 1:1 v/v) with 0.25 μL of benzene as an internal reference per mL of solvent. The sealed tubes were heated to 65 °C for 30 minutes to dissolve the solid homopolymers to erase potential thermal history effects that might result in different degrees of crystallinity. Upon cooling the samples, the homopolymers precipitated to leave saturated solutions. ¹H NMR spectra were obtained without locking and shimming due to a lack of an adequate ²H signal. The downfield singlet peak was determined to originate from the added benzene and was assigned a resonance of 7.16 ppm. Peaks at 3.91 and 4.10 ppm in the PFDMS₂₇ spectrum and 3.90 and 4.07 ppm in the PFDMG₂₄ spectrum were assigned to cyclopentadienyl ring protons of ferrocene units in the polymer main chains. Presaturation of the cyclohexane peak at 1.40 ppm allowed for a more linear baseline close to the region of interest. Integration of signals relative to the benzene spike has shown that PFDMS₂₇ homopolymer is 45% more soluble than PFDMG₂₄. Note: Hexane/cyclohexane was selected as a representative marginal medium that allowed

solubility at elevated temperature and also permitted ^1H NMR analysis due to the lack of overlapping peaks with those of the polymers. Based on the solubility parameters for PFDMS and the solvents concerned the solvency conditions are quite similar to those used in the manuscript.

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