Supplementary Information for

Scalable and Uniform 1D Nanoparticles by Synchronous Polymerisation, Crystallisation, and Self-Assembly

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Wide angle X-ray scattering

The X-ray diffraction data was taken with a Ganesha small angle X-ray scattering apparatus (SAXSLAB, Denmark). The instrument uses copper K alpha radiation (1.5 Å) and the scattering pattern is detected by Pilatus 300K X-Ray Detector (Dectris, Switzerland). The detector was placed at approximately 100 mm from the sample for the WAXS measurements. In situ samples from a PI-CDSA experiment (concentration = ca. 75 mg/ml) were sealed into a 1.5 mm diameter quartz capillary tubes (Capillary Tube Supplies, Cornwall, UK). The instrument was evacuated during measurements to reduce air scattering.

A single rod with its long axis lying perpendicular to the incident beam and the hexagonal axis of its internal structure aligned perpendicular to the long axis will produce a hexagonal reciprocal lattice.[1] Its strongest features are the six possible Bragg reflections (at $Q \sim 1$ Å^{-1}) on the apices of a hexagon in reciprocal space. For an ensemble of rods, all aligned perpendicular to the incident beam but free to rotate around their long axes, these six reflections become three rings in reciprocal space. These intersect the surface of the Ewald sphere at six points and so appear on the detector as 6 spots as shown in Supplementary Fig. 7a. The shapes and positions of the spots can be described by the convolution of the particle form factor (a function which depends of the geometry and alignment of the particles) with the reciprocal lattice of the internal structure. In the case of well-aligned rod-like particles, the form factor is given by:

$$(1) \qquad P(\boldsymbol{Q}) = \left(\frac{2J_1(Q_\perp R)}{Q_\perp R}\right)^2 \left(\frac{\sin\left(Q_\parallel (L/2)\right)}{Q_\parallel (L/2)}\right)^2$$

where L is the length, R is the radius $Q_\perp = Q \sin(\beta)$, $Q_\parallel = Q \cos(\beta)$, β is the angle between the rod axis and the scattering vector $\boldsymbol{Q}$. Applying the Guinier approximation, valid for $\Delta Q_\perp < 2/R$ and $\Delta Q_\parallel < \sqrt{12}/L$ (where ΔQ represents the distance from the centre of the peak), equation 1 becomes:

$$(2) \qquad P(\boldsymbol{Q}) \approx exp\left(-\frac{\Delta Q_\perp^2 R^2}{4} - \frac{\Delta Q_\parallel^2 L^2}{12}\right)$$

As the length of the rods is much larger than the radius, the extent of the peaks in the direction parallel to the alignment axis will be very small. The shape of the peaks in the radial direction can therefore be approximated by a Gaussian of the form:

$$(3) \qquad I(\boldsymbol{Q}) \propto exp\left(\frac{\Delta Q^2 R^2}{4}\right)$$

For the two peaks perpendicular to the long axis of the micelles, the radius can be calculated from the standard deviation, $\sqrt{2}/R$. The radial extent of the other four peaks will be smaller by a factor of 2 as

the $Q_{\perp}$ direction is oriented at 60° to the radial direction (such that the standard deviation becomes $\sqrt{2}\cos(60°)/R$).

Synthesis of polydisperse PIP-*b*-PFDMS diblock copolymer micelles via PI-CDSA

A representative example of the synthesis of PIP_{193}-*b*-$PFDMS_{45}$ polydisperse micelles at 10% w/w solids in 10% v/v THF/n-hexanes was conducted as follows (see Supplementary Fig. 1a):

In a glove box under an nitrogen atmosphere 1.4 M *s*-butyllithium (40 µL, 0.06 mmol) was added in one portion to a vigorously stirring solution of isoprene (1 mL, 681 mg, 10.0 mmol) in dry THF (1 mL) in a 28 mL glass vial at 0 °C and the reaction mixture was stirred for 1.5 h. An aliquot (1 mL) for later analysis was removed, diluted with THF (1 mL) and quenched with a small quantity of 4-*tert*-butylphenol. To a solution of dimethylsila[1]ferrocenophane (60 mg, 0.25 mmol) in a mixture of dry THF/n-hexanes (1.8 mL, 10% v/v THF/n-hexanes) was added the living PIP solution (0.25 mL, 85 mg, 7.50 µmol). The reaction mixture was left to stir slowly at room temperature for 3 h and then quenched with a small quantity of 4-*tert*-butylphenol. GPC and ^{1}H NMR analysis was used to determine the final BCP composition for the micelles (Supplementary Table 2). A series of diblock copolymer micelles were synthesized over a range of PIP DPs at various solids concentrations by systematic variation of the isoprene/dimethylsila[1]ferrocenophane molar ratio and THF/n-hexanes content, respectively. ^{1}H NMR (400 MHz; CD_2Cl_2): d_H 5.85–5.66 (m, vinyl protons), 5.16–4.46 (br, vinyl protons), 4.23 (t, *J* = 1.7 Hz, Cp*H*), 4.02 (t, *J* = 1.7 Hz, Cp*H*), 2.23-0.74 (br, alkyl protons), 0.48 (s, $Si(CH_3)_2$) ppm.

Yields appear to be close to quantitative based on the lack of film derived from unimer by TEM although small amounts of PIP homopolymer are sometimes detected by GPC.

An analogous procedure was used at 25% w/w solids using 20% v/v THF/n-hexanes and gave cylinders of PIP_{174}-*b*-$PFDMS_{39}$ BCP (block ratio 4.5:1.0, Supplementary Table 6). Attempts to go beyond 25% w/w solids are expected to be challenging as the PIP synthesis appears problematic at concentrations above 1 mL isoprene / 1 mL THF.

Synthesis of polydisperse PIP-*b*-PFMPS diblock copolymer micelles via PI-CDSA

The experimental procedure used was analogous to that for PIP-*b*-PFDMS except that methyphenylsila[1]ferrocenophane[2] was used as the monomer.

Self-Assembly of PIP_{58}-*b*-$PFDMS_{59}$ by CDSA

The self-assembly of the platelet forming PIP_{58}-*b*-$PFDMS_{59}$ (Sample 2, Supplementary Table 2) was carried out by the injection of a unimer solution (25 μL, 75 mg/ml, THF) into n-hexanes to give a 20% v/v THF/n-hexanes solution followed by aging for 24 h. The resulting solution was imaged by TEM to reveal platelet micelles reminiscent of those prepared by PI-CDSA (Supplementary Fig. 4).

Synthesis of polydisperse cylindrical PtBS-*b*-PFDMS diblock copolymer micelles via PI-CDSA

In a glove box under an nitrogen atmosphere 1.4 M *s*-butyllithium (40 μL, 0.06 mmol) was added in one portion to a vigorously stirring solution of 4-tert-butylstyrene (1.83 mL, 1.60 g, 10.0 mmol) in dry THF (3 mL) in a 28 mL glass vial at -78 °C and the reaction mixture was stirred for 1 h. An aliquot (1 mL) for later analysis was removed, diluted with THF (1 mL) and quenched with a small quantity of 4-*tert*-butylphenol. To a solution of dimethylsila[1]ferrocenophane (30 mg, 0.12 mmol) in a mixture of dry THF/n-hexanes (1.8 ml, 20% v/v THF/n-hexanes) was added the living PtBS solution (0.30 mL, 99 mg, 3.72 μmol). The reaction mixture was left to stir slowly at room temperature for 3 h and then quenched with a small quantity of 4-*tert*-butylphenol. GPC and ^{1}H NMR analysis were used to determine the final BCP composition of $PtBS_{256}$-*b*-$PFDMS_{51}$ (block ratio: 5.1:1.0, PDI = 1.36). ^{1}H NMR (400 MHz; CD_2Cl_2): d_H 7.39-6.84 (m, aryl protons), 6.81–6.22 (m, aryl protons), 4.23 (t, *J* = 1.7 Hz, Cp*H*), 4.02 (t, *J* = 1.7 Hz, Cp*H*), 1.28 (br, alkyl protons), 0.48 (s, $Si(CH_3)_2$) ppm.

Monitoring formation of polydisperse PIP-*b*-PFDMS diblock copolymer micelles via PI-CDSA as a function of time

In a glove box under an nitrogen atmosphere 1.4 M *s*-butyllithium (40 µL, 0.06 mmol) was added in one portion to a vigorously stirring solution of isoprene (0.2 mL, 136 mg, 2.0 mmol) in dry THF (0.8 mL) in a 28 mL glass vial at 0 °C and the reaction mixture was stirred for 1.5 h. An aliquot (1 mL) for later analysis was removed, diluted with THF (1 mL) and quenched with a small quantity of 4-*tert*-butylphenol. To a solution of dimethylsila[1]ferrocenophane (121 mg, 0.50 mmol) in a mixture of dry 20% v/v THF/n-hexanes (6 mL) was added the living PIP solution (0.25 mL, 34 mg, 0.02 mmol). The reaction mixture was stirred for 40 min at room temperature and 0.3 mL aliquots were removed after 0.5 min, 1 min, 2 min, 5 min, 10 min, 20 min and 40 min diluted with THF (0.5 mL) and quenched with 4-*tert*-butylphenol. Each aliquot was then analysed by MALDI-TOF mass spectrometry and GPC. 10 µL were also removed at the time points and directly spotted onto a carbon coated copper grid for TEM analysis.

Preparation of Small Seed Micelles in n-Hexanes

In order to minimise premature quenching of the polymerisation, prior to seed formation, the PIP_{168}-*b*-$PFDMS_{24}$ BCP (PDI = 1.13, M_n = 18,470 g/mol, M_w = 20,830 g/mol) was dried thoroughly by azeotroping with toluene three times to remove any remaining moisture. A sample of long PIP_{168}-*b*-$PFDMS_{24}$ cylinders (> 10 µm) was prepared by heating 300 mg of PIP_{168}-*b*-$PFDMS_{24}$ in 10 mL anhydrous n-hexanes for 1 h at 70 ˚C, then allowing the resulting solution to cool to room temperature and stand for 24 h. Small PIP_{168}-*b*-$PFDMS_{24}$ seed micelles were then prepared by sonication of this solution for 8 cycles of 30 min at 0 ˚C using a sonication bath. L_n = 64 nm; L_w = 73 nm; PDI = 1.14; σ = 24 nm; σ/L_n = 0.37; N = 204 (Supplementary Fig. 12).

The PIP_{168}-*b*-$PFDMS_{24}$ used was prepared by PI-CDSA after purification from the quenching agent.

Synthesis of low dispersity cylindrical PIP-*b*-PFDMS diblock copolymer micelles of controlled length via living PI-CDSA

A typical procedure for the synthesis of monodisperse cylindrical PIP-*b*-PFDMS micelles at 10% w/w solids was conducted as follows (see Supplementary Fig. 1b):

In a glove box under an nitrogen atmosphere 1.4 M *s*-butyllithium (40 µL, 0.06 mmol) was added in one portion to a vigorously stirring solution of isoprene (1 mL, 681 mg, 10.0 mmol) in dry THF (2 mL) in a 28 mL glass vial at 0 °C and the reaction mixture was stirred for 1.5 h. An aliquot (1 mL) for later analysis was removed, diluted with THF (1 mL) and quenched with a small quantity 4-*tert*-butylphenol. To a solution of dimethylsila[1]ferrocenophane (48 mg, 0.20 mmol) and small PIP_{168}-*b*-$PFDMS_{24}$ seed micelles (0.5 mL, 15 mg, 8.7 $\times 10^{-4}$ mmol, L_n = 64 nm, PDI = 1.14) of a 30 mg/mL seed solution in n-hexanes) in dry n-hexanes was added the living PIP solution (0.36 mL, 82 mg, 7.20 µmol). The reaction mixture was left to stir slowly at room temperature for 3 h and then quenched with a small quantity of 4-*tert*-butylphenol. GPC, MALDI-TOF mass spectrometry and ^{1}H NMR analysis was used to determine the final BCP composition. A series of samples of cylindrical micelles with different contour lengths were prepared by the systematic variation of the isoprene/seed molar ratio. Yields appear to be close to quantitative based on GPC data and the lack of films derived from unimer by TEM.

Synthesis of low dispersity cylindrical PIP-*b*-PFDMS diblock copolymer micelles of controlled length via living PI-CDSA at 22% w/w solids

In a glove box under an nitrogen atmosphere 1.4 M *s*-butyllithium (40 µL, 0.06 mmol) was added in one portion to a vigorously stirring solution of isoprene (1 mL, 681 mg, 10.0 mmol) in dry THF (1 mL) in a 28 mL glass vial at 0 °C and the reaction mixture was stirred for 1.5 h. An aliquot (1 mL) for later analysis was removed, diluted with THF (1 mL) and quenched with a small quantity of 4-*tert*-butylphenol. To a solution of dimethylsila[1]ferrocenophane (96 mg, 0.40 mmol) and PIP_{168}-*b*-$PFDMS_{24}$ crystallite seeds (1.2 mL, 36 mg, 2.1 $\times 10^{-3}$ mmol, L_n = 64 nm, PDI = 1.14) of a 30 mg/mL seed solution in n-hexanes) in dry n-hexanes (0.30 mL) was added the living PIP solution (0.72 mL, 245 mg, 0.02 mmol) to give a monomer-to-seed ratio of 5:1. The reaction mixture was left to stir slowly at room temperature for 3 h and then quenched with a small quantity of 4-*tert*-butylphenol. ^{1}H NMR analysis was used to determine a final BCP composition of PIP_{204}-*b*-$PFDMS_{29}$ (block ratio 7.0:1.0) and GPC to obtain a PDI = 1.18.

Supplementary Table 1: Characterisation data of PIP homopolymers prepared by living anionic polymerisation in THF obtained from MALDI-TOF mass spectrometry and GPC

	MALDI			GPC			DP_n[a]
Sample	M_n (g/mol)	M_w (g/mol)	PDI	M_n (g/mol)	M_w (g/mol)	PDI	
1	3925.33	4019.68	1.02	4600	4900	1.07	PIP_{58}
2	13161.3	13236.2	1.01	13800	14000	1.02	PIP_{193}
3	26523.4	26542	1.00	27800	29100	1.05	PIP_{389}
4	7870.74	7969.98	1.01	7100	7300	1.03	PIP_{116}

a DP_n based on MALDI-TOF mass spectrometry

Supplementary Table 2: Characterisation data of PIP-*b*-PFDMS BCPs prepared by PI-CDSA in THF/n-hexanes at 10% w/w solids obtained from GPC and ^{1}H NMR.

	Target Block Ratio	% THF v/v	GPC			^{1}H NMR[c]
Sample			M_n (g/mol)	M_w (g/mol)	PDI	BCP
1	1.0:1.0	10	13000	18400	1.41[b]	PIP_{58}-*b*-$PFDMS_{66}$
2		20	12700	16700	1.32[b]	PIP_{58}-*b*-$PFDMS_{59}$
3		40	14700	20900	1.25	PIP_{58}-*b*-$PFDMS_{72}$
4	5.0:1.0	10	21200	26300	1.24	PIP_{193}-*b*-$PFDMS_{45}$
5		20	22100	27500	1.25	PIP_{193}-*b*-$PFDMS_{54}$
6		40	20200	23400	1.16	PIP_{193}-*b*-$PFDMS_{42}$
7[a]		10	16700	19100	1.15	PIP_{116}-*b*-$PFMPS_{28}$
8	10.0:1.0	10	39300	44600	1.13	PIP_{389}-*b*-$PFDMS_{47}$
9		20	43200	52600	1.22	PIP_{389}-*b*-$PFDMS_{73}$
10		40	41600	47200	1.14	PIP_{389}-*b*-$PFDMS_{55}$

a Using methylphenylsila[1]ferrocenophane as monomer.

b The higher PDI values are likely a result of the high degree of polymerisation targeted for the PFDMS block which would lead to reduced solubility of the block copolymer at lower THF concentrations and some micelle formation before the [1]ferrocenophane monomer is completely consumed.

c ^{1}H NMR data was obtained by dissolution of the micelles in CD_2Cl_2 (a good solvent for both PIP and PFDMS/PFMPS).

Supplementary Table 3: Summary of PIP-*b*-PFDMS nanoparticles obtained for samples prepared at 10% w/w solids with varying targeted block ratios and with different THF/n-hexanes solvent compositions.

THF %	1:1	5:1	10:1
10	Platelets	Cylinders	Cylinders
20	Platelets	Cylinders	Cylinders
40	Unimer	Unimer	Unimer

Supplementary Table 4: WAXS data for cylindrical PIP-*b*-PFDMS micelles (ca. 75 mg/mL and 7.5 mg/ml) of 10% w/w solids in 20% v/v THF/n-hexanes.

Sample	Peak	FWHM[a] ($Å^{-1}$)	Error ($Å^{-1}$)	σ[b] ($Å^{-1}$)	σ error ($Å^{-1}$)	Guinier Radius (nm)[c]
7.5 mg/mL	1	3.95×10^{-2}	1.77×10^{-3}	1.68×10^{-2}	7.52×10^{-4}	4.2 (0.2)
	2	7.07×10^{-2}	5.44×10^{-3}	3.00×10^{-2}	2.31×10^{-3}	4.7 (0.4)
75 mg/mL	1	4.19×10^{-2}	9.57×10^{-4}	1.78×10^{-2}	4.06×10^{-4}	4.0 (0.1)
	2	6.80×10^{-2}	2.02×10^{-3}	2.80×10^{-2}	8.58×10^{-4}	4.9 (0.1)

a FWHM = full width at half maximum

b σ = standard deviation

c Associated error in brackets

Supplementary Table 5: Characterisation data of PIP-*b*-PFDMS BCP aliquots removed at specific time points from the PI-CDSA in 20% v/v THF/n-hexanes at 3% w/w solids obtained from ^{1}H NMR and GPC.

Sample	GPC			^{1}H NMR[b]	
	M_n (g/mol)	M_w (g/mol)	PDI	DP_n	Block ratio
PIP[a]	2800	3000	1.06	PIP_{44} (MALDI)	
30 secs	4500	6400	1.41	PIP_{44}-*b*-$PFDMS_4$	11.0:1.0
1 min	6300	8200	1.30	PIP_{44}-*b*-$PFDMS_9$	4.9:1.0
2 min	6100	10500	1.30	PIP_{44}-*b*-$PFDMS_{17}$	2.6:1.0
5 min	13900	18500	1.33	PIP_{44}-*b*-$PFDMS_{35}$	1.3:1.0
10 min	16200	21500	1.33	PIP_{44}-*b*-$PFDMS_{44}$	1.0:1.0
20 min	18000	23900	1.33	PIP_{44}-*b*-$PFDMS_{50}$	0.9:1.0
40 min	19600	26100	1.33	PIP_{44}-*b*-$PFDMS_{57}$	0.8:1.0

a MALDI-TOF mass spectrometry data for PIP: M_n = 3014.38 g/mol, M_w = 3099.78 g/mol, PDI = 1.03

b ^{1}H NMR data was obtained by dissolution of the micelles in CD_2Cl_2 (a good solvent for both PIP and PFDMS).

Supplementary Table 6: Characterisation data of PIP-*b*-PFDMS BCPs prepared by PI-CDSA in THF/n-hexanes at 25% w/w solids obtained from MALDI-TOF mass spectrometry, GPC and ^{1}H NMR.

Sample	MALDI			GPC			^{1}H NMR
	M_n (g/mol)	M_w (g/mol)	PDI	M_n (g/mol)	M_w (g/mol)	PDI	BCP
PIP	11855	11927.6	1.01	12000	12300	1.02	PIP_{174}
25% w/w				26900	30700	1.14	PIP_{174}-*b*-$PFDMS_{39}$

Supplementary Table 7: Characterisation data of PIP-*b*-PFDMS BCPs prepared by seeded/living PI-CDSA in 10% v/v THF/n-hexanes at 10% w/w solids obtained from MALDI-TOF mass spectrometry, GPC and ^{1}H NMR.

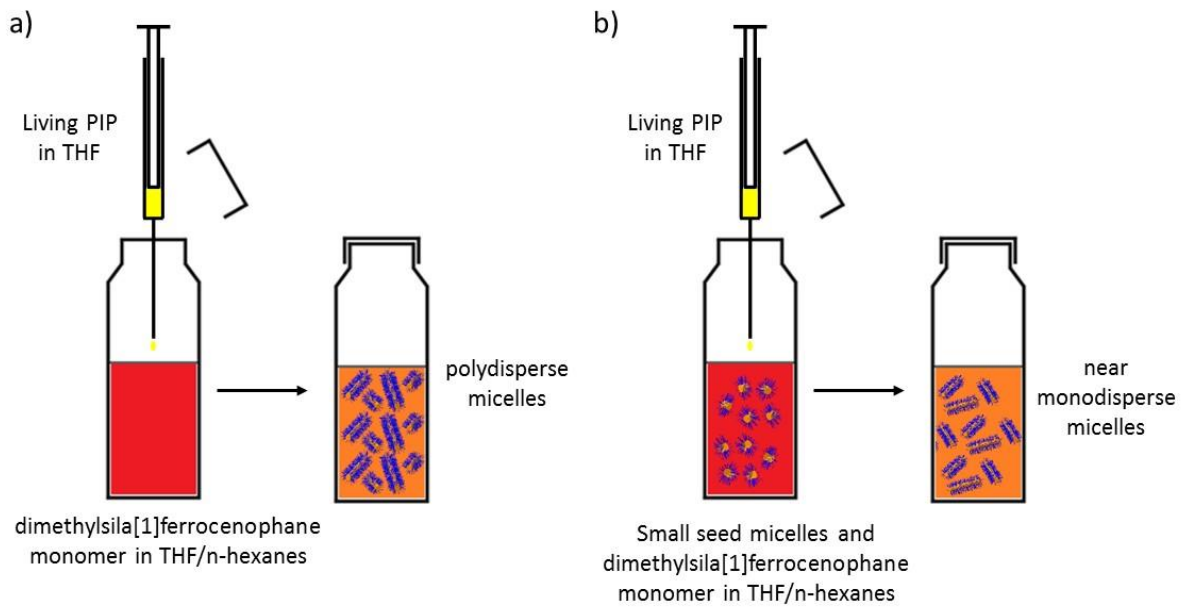
	GPC[c]			^{1}H NMR[d]
Sample	M_n (g/mol)	M_w (g/mol)	PDI	BCP
PIP[a]	12100	12500	1.03	PIP_{154} (MALDI)
3:1[b]	19000	20600	1.08	PIP_{154}-*b*-$PFDMS_{29}$
6:1[b]	17200	18900	1.09	PIP_{154}-*b*-$PFDMS_{28}$
9:1[b]	16700	18000	1.08	PIP_{154}-*b*-$PFDMS_{29}$
12:1[b]	17300	18800	1.07	PIP_{154}-*b*-$PFDMS_{29}$
15:1[b]	14700	15800	1.08	PIP_{154}-*b*-$PFDMS_{29}$
18:1[b]	16100	17700	1.10	PIP_{154}-*b*-$PFDMS_{29}$
21:1[b]	17200	18600	1.08	PIP_{154}-*b*-$PFDMS_{29}$

a MALDI-TOF mass spectrometry data for PIP: M_n = 10456.7 g/mol, M_w = 10559.5 g/mol, PDI = 1.01

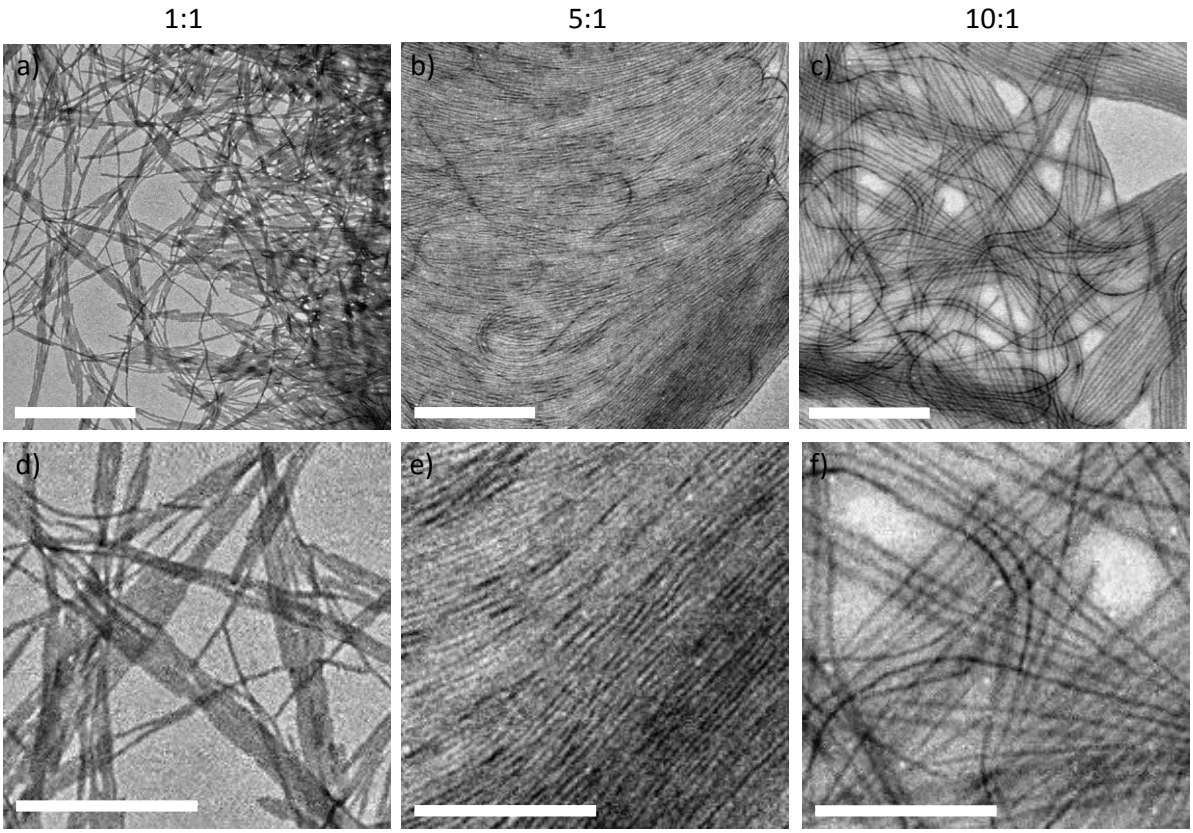
b For characterization data on the seeds used in these experiments see page S5. The block copolymer used had a PDI of 1.13.

c The GPC data for the block copolymers also includes a contribution from the seed as the samples were formed by dissolution of the resulting cylindrical micelles.

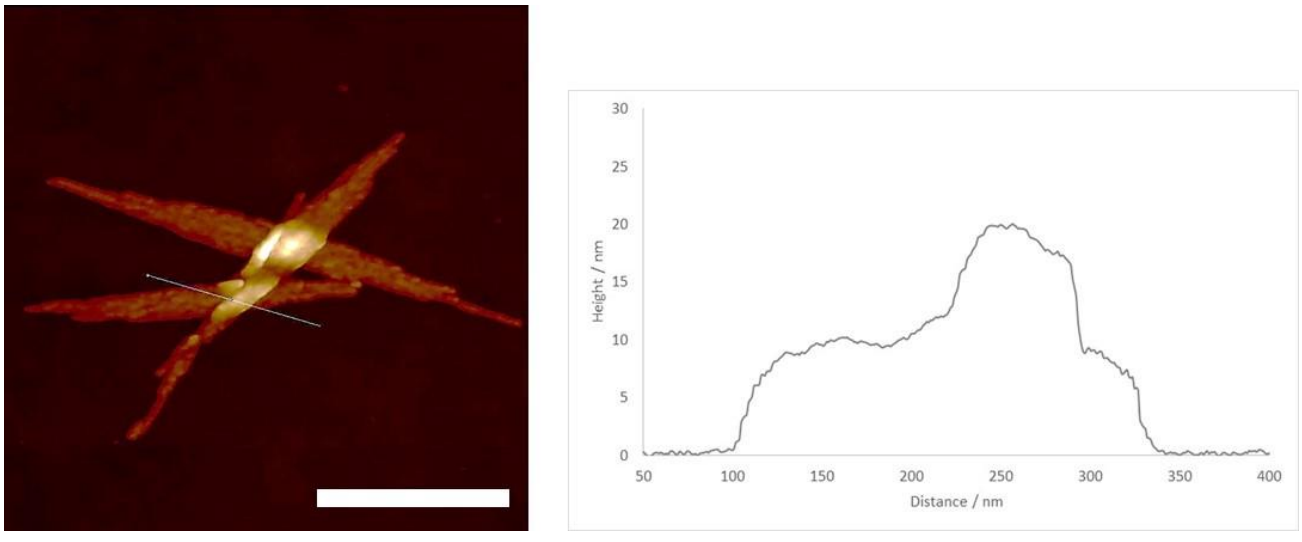
d ^{1}H NMR data was obtained by dissolution of the micelles in CD_2Cl_2 (a good solvent for both PIP and PFDMS).



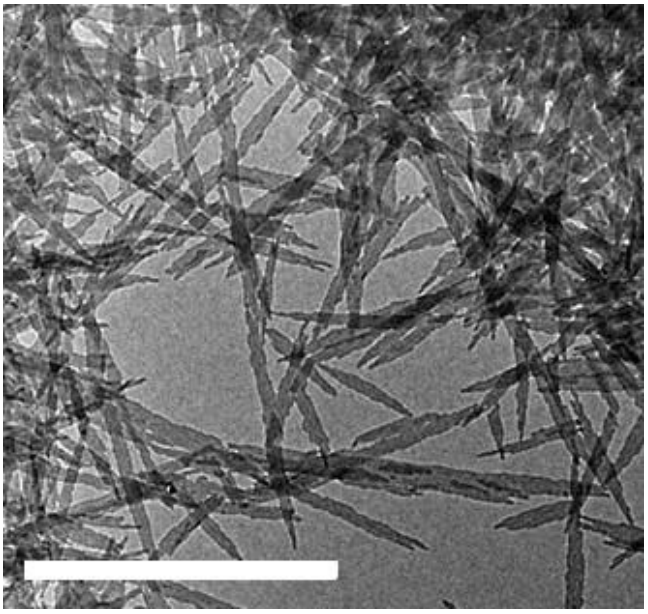
Supplementary Figure 1: Schematic representation of the "one pot" synthetic process to prepare PIP-*b*-PFDMS micelles: a) polydisperse cylindrical micelles by PI-CDSA, b) near monodisperse cylindrical micelles by "living" PI-CDSA.



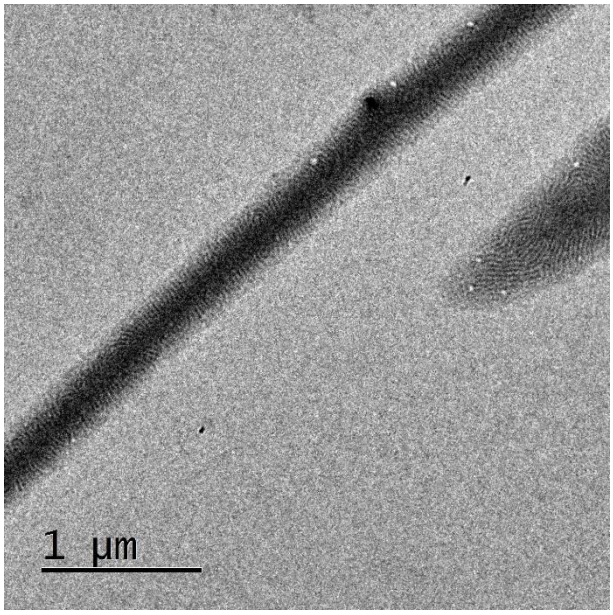
Supplementary Figure 2: PI-CDSA at 10% w/w solids of PIP-*b*-PFDMS in 20% v/v THF/n-hexanes with varying block ratios. a-c) Low resolution and d-f) high resolution bright field TEM micrographs of polydisperse micelles of PIP-*b*-PFDMS with varying block ratios prepared by PI-CDSA at 10% w/w solids diluted to 1 mg/mL for TEM imaging. Scale bars: a-c) = 1 μm d-f) = 500 nm.



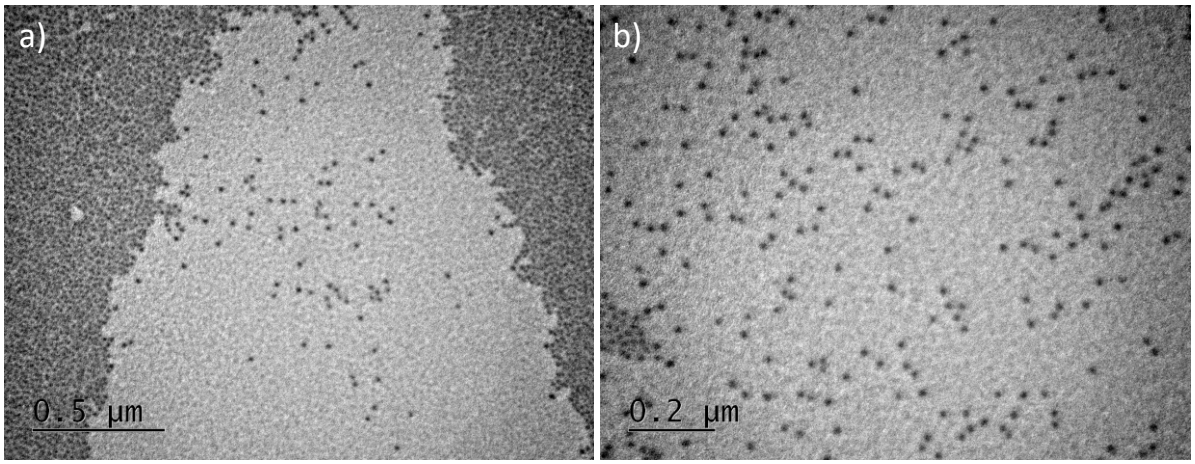
Supplementary Figure 3: AFM height image and profile of PIP_{58}-*b*-$PFDMS_{66}$ platelet micelles prepared by PI-CDSA at 10% w/w solids and 10% v/v THF/n-hexanes. Scale bar = 500 nm.



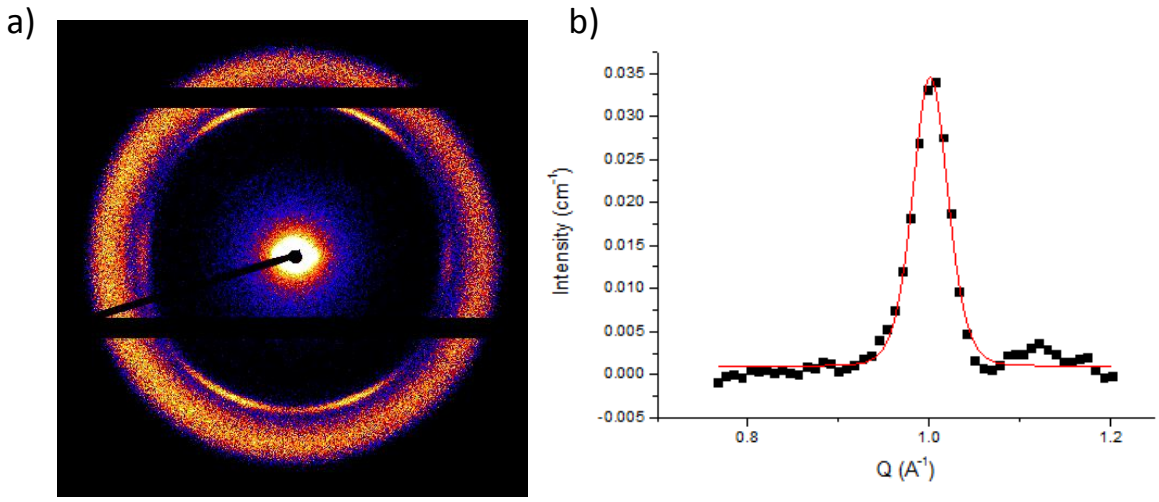
Supplementary Figure 4: Self-Assembly of PIP_{58}-*b*-$PFDMS_{59}$ by CDSA by the injection of a unimer solution (25 μL, 75 mg/ml, THF) into n-hexanes to give a solution of 20 % v/v THF/n-hexanes followed by aging for 24 h. The platelet micelles observed by TEM are reminiscent of those obtained by PI-CDSA (Supplementary Fig. 2 a and d). Scale bar = 2 μm.



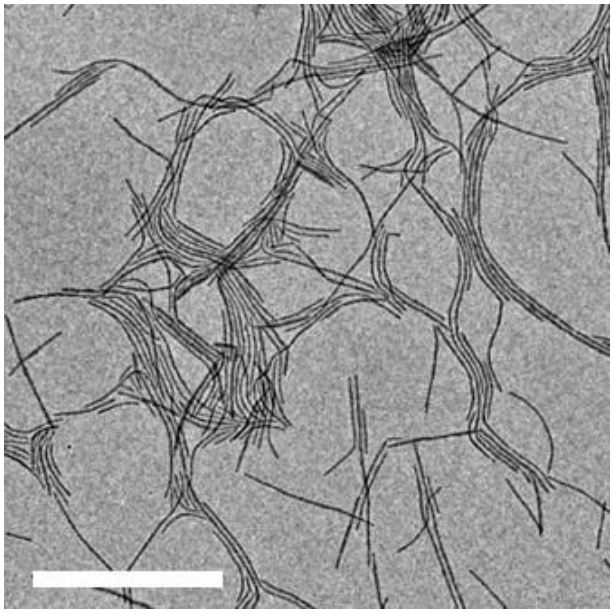
Supplementary Figure 5: Representative TEM image of PIP_{193}-*b*-$PFDMS_{42}$ BCP prepared at 10% w/w solids and 40% v/v THF/n-hexanes showing the phase-separated film obtained at this high volume fraction of THF.



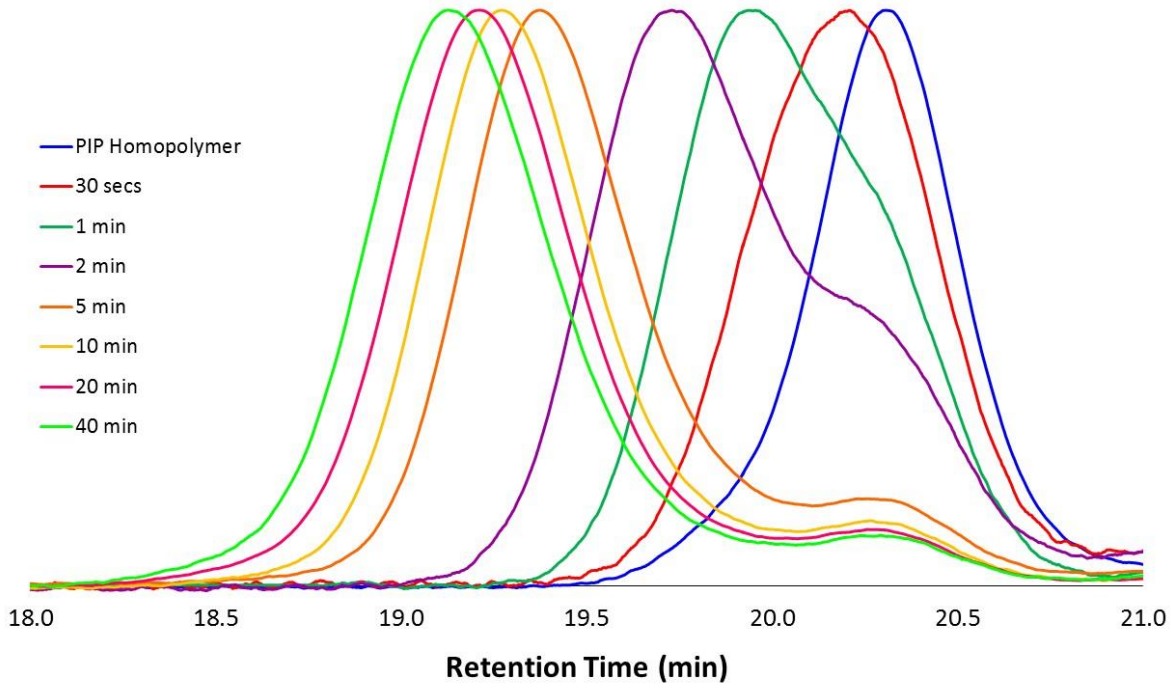
Supplementary Figure 6: Representative TEM images of PIP_{116}-*b*-$PFMPS_{28}$ BCP prepared at 10% w/w solids and 10% v/v THF/n-hexanes showing spherical micelles obtained using this amorphous-core BCP imaged at 1 mg/mL a) lower magnification TEM image, b) higher magnification TEM image. Sample was prepared by drop casting a solution onto a pre-cooled (ca. -78 °C) carbon coated copper grid and subsequent solvent removal under vacuum.



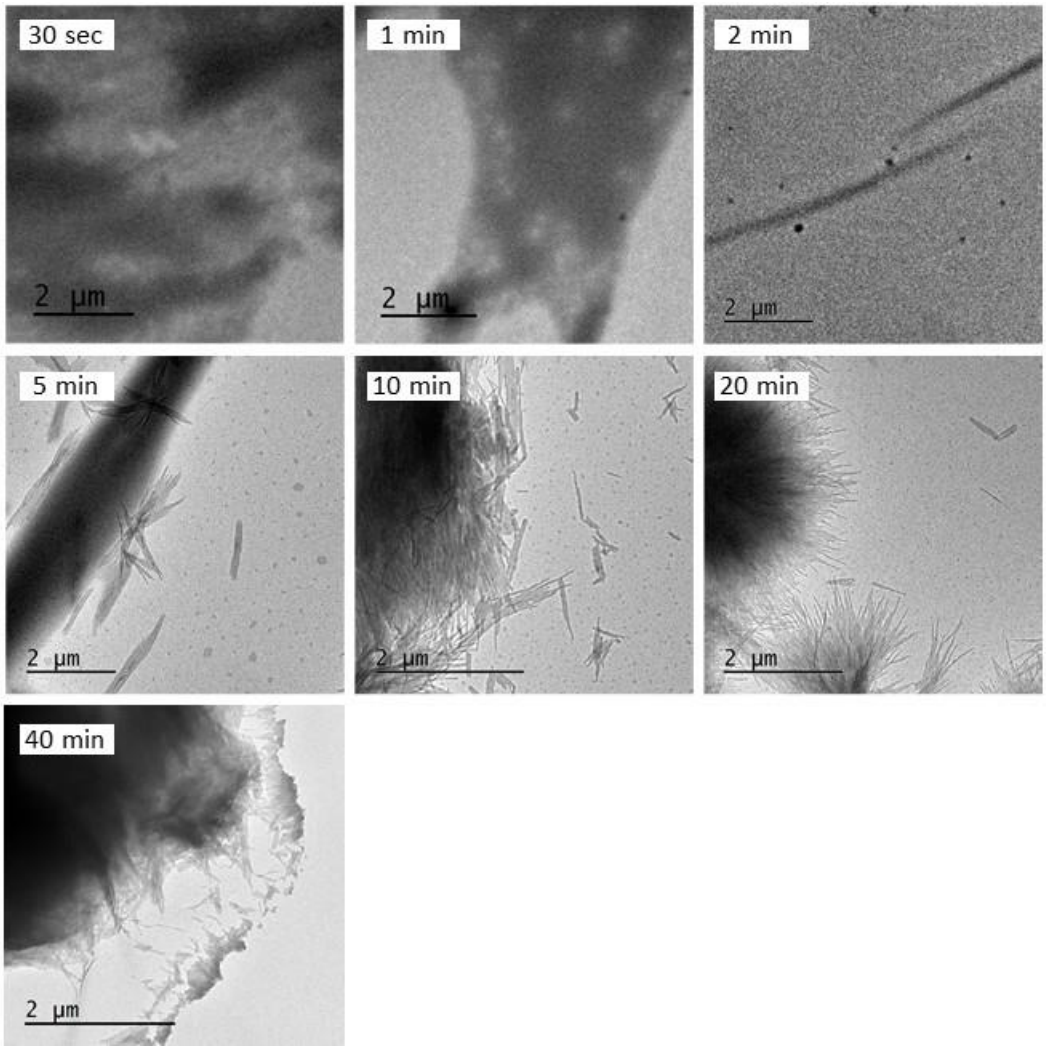
Supplementary Figure 7 a) Wide angle X-ray scattering (WAXS) plot b) Azimuthally averaged intensity wide angle X-ray scattering form PIP-*b*-PFDMS cylindrical micelles formed in situ at 10% w/w solids in 20% v/v THF/n-hexanes by PI-CDSA (diluted to ca. 7.5 mg/mL).



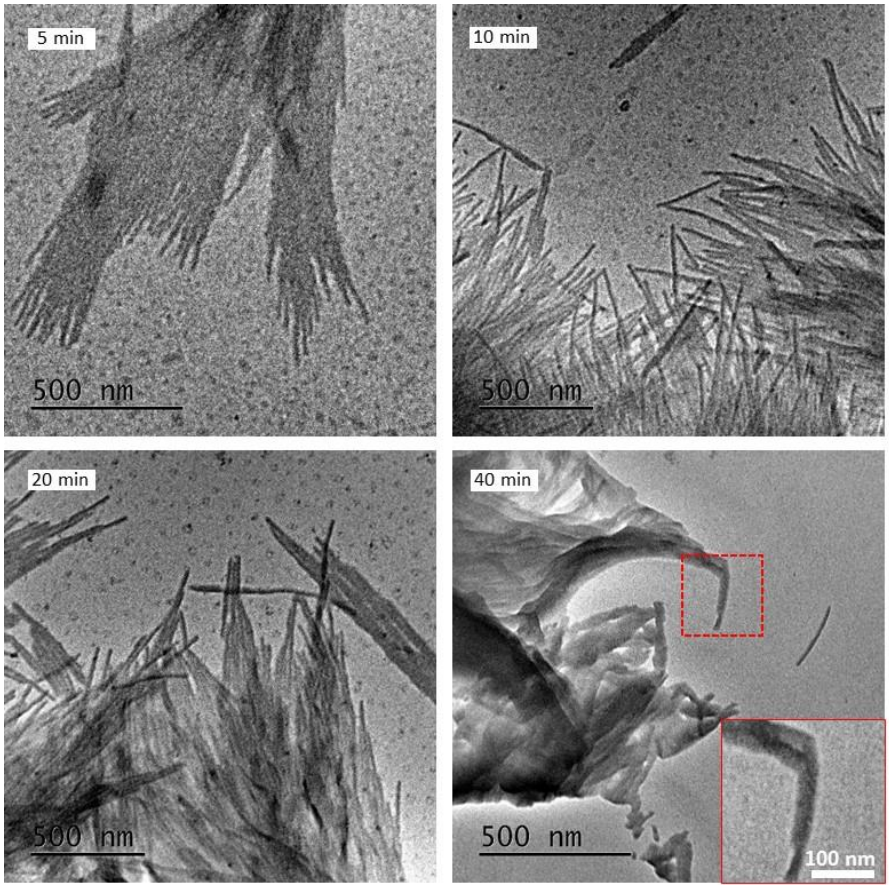
Supplementary Figure 8: TEM analysis of an aliquot of a PI-CDSA process at 10% w/w solids of $PtBS_{256}$-*b*-$PFDMS_{51}$ at 20% v/v THF/n-hexanes diluted to 1 mg/mL for TEM imaging. Scale bar = 2 μm.



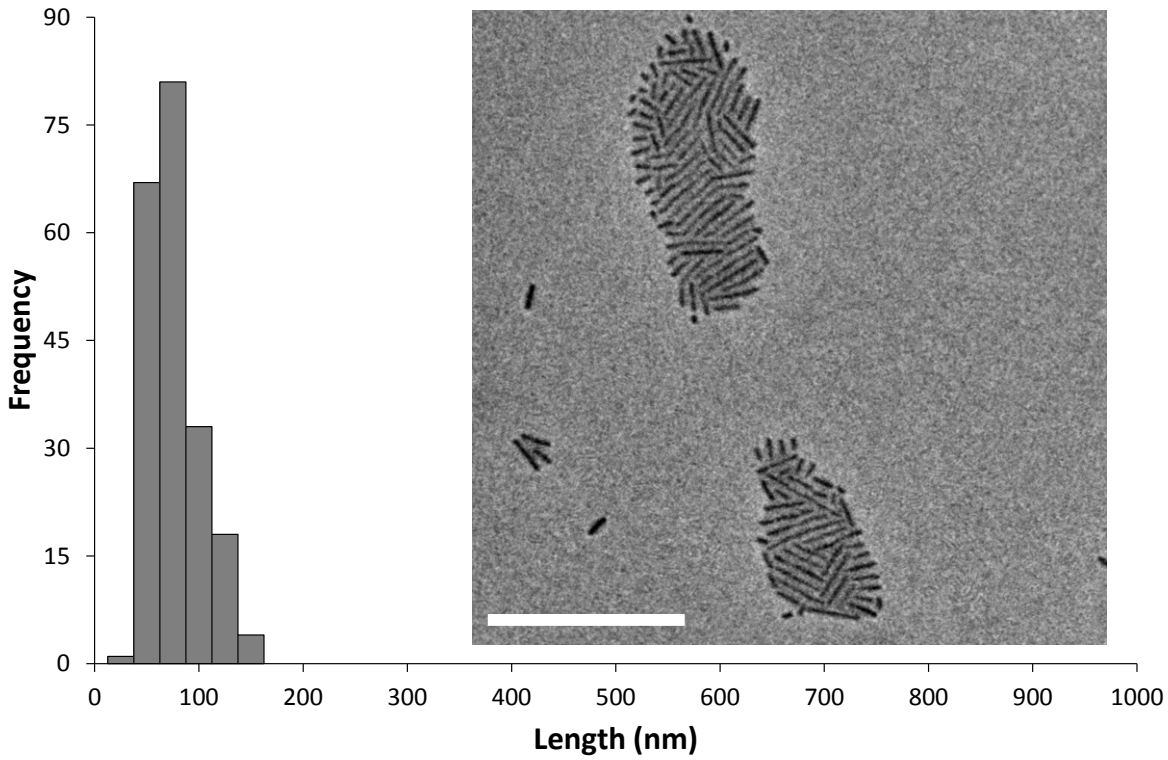
Supplementary Figure 9: Overlaid GPC traces (refractive index response) of PIP-*b*-PFDMS aliquots in THF removed at specific time points during PI-CDSA in 20% v/v THF/n-hexanes at 3% w/w solids showing the starting PIP homopolymer (blue trace) and the subsequent extension of the PFDMS block to form BCPs with an earlier retention time, corresponding to a higher M_w. A Bimodal distribution is observed due to some PIP homopolymer being present (retention time = 20.3 min) due to premature quenching of the active chain end induced by the removal of the aliquots. PDI values given in Supplementary Table 5.



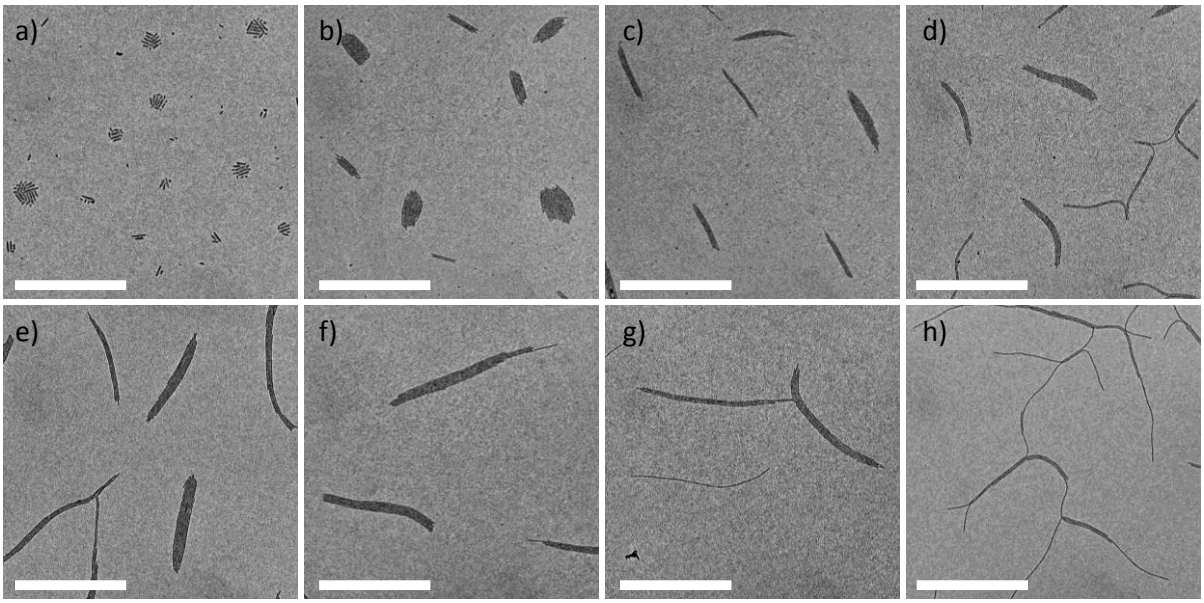
Supplementary Figure 10: Representative TEM images of dried PIP-*b*-PFDMS aliquots removed at specific time points during PI-CDSA in 20% v/v THF/n-hexanes at 3% w/w solids illustrating the morphological transition from unimer film to bundled cylinders and then finally to platelets. Higher magnification images of the samples at 5 min, 10 min, 20 min, and 40 min are shown in Supplementary Fig. 11.



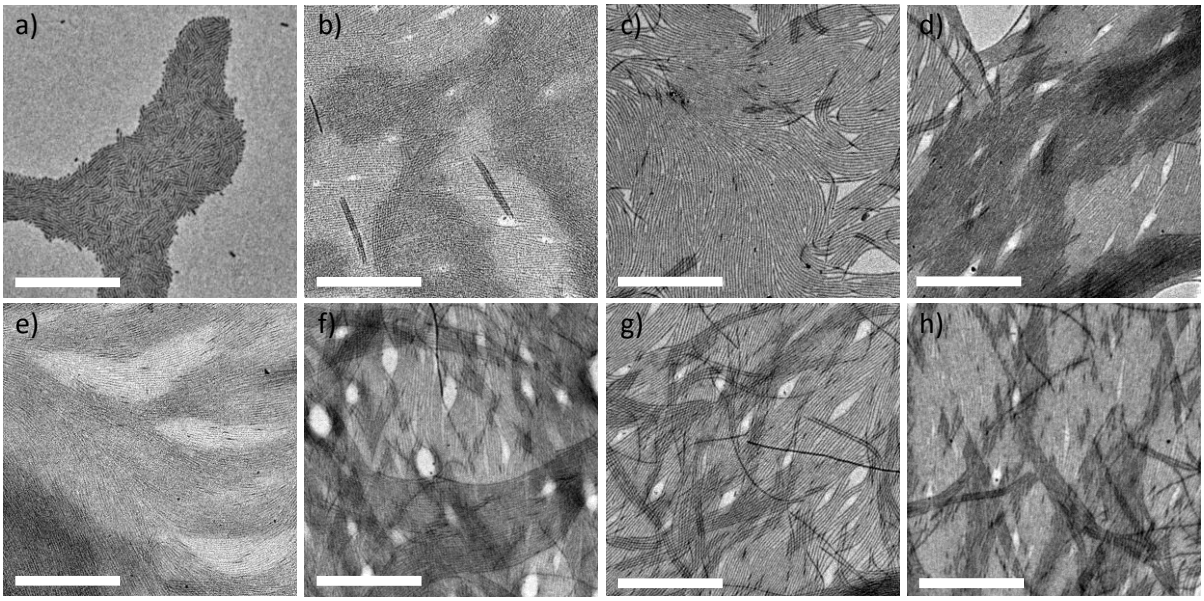
Supplementary Figure 11: Representative TEM images at high magnification of dried PIP-*b*-PFDMS aliquots removed at specific time points during PI-CDSA in 20% v/v THF/n-hexanes at 3% w/w solids illustrating the morphological transition from unimer film to bundled cylinders and then finally to platelets.



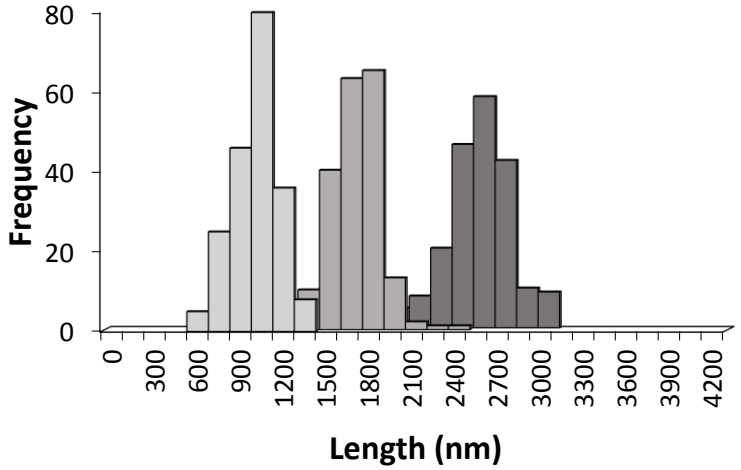
Supplementary Figure 12: Histogram of contour lengths of small seed micelles of PIP_{168}-*b*-$PFDMS_{24}$ prepared by the ultrasonication of multi-micron long polydisperse cylindrical micelles at 30 mg/mL in n-hexanes and TEM image at 0.25 mg/mL illustrating the distribution of contour lengths. L_n = 64 nm; PDI = 1.14. Scale bar = 500 nm.



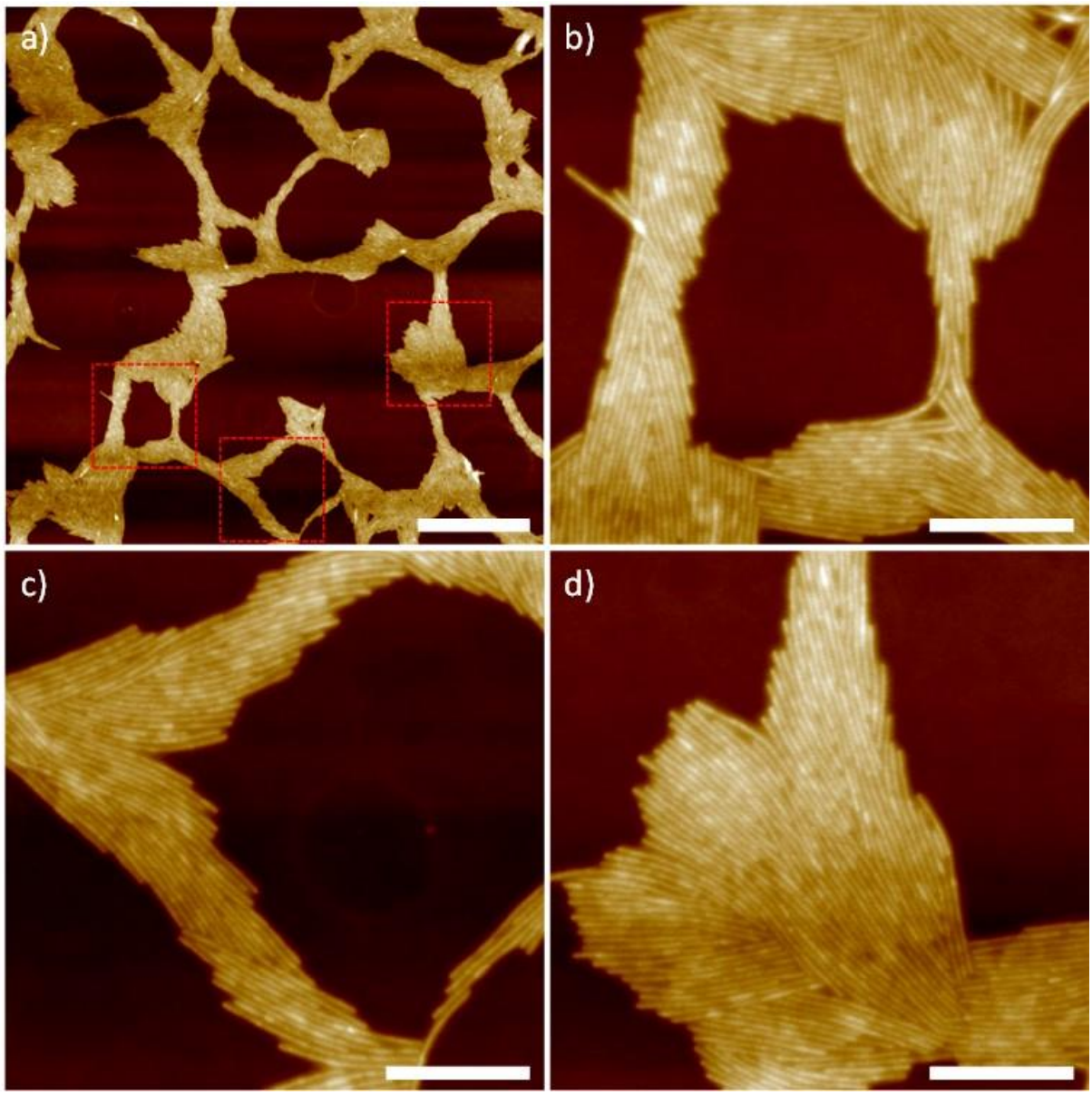
Supplementary Figure 13: Living PI-CDSA of PIP-*b*-PFDMS at 10% w/w solids. a-h) Moderately low magnification bright field TEM micrographs of dried samples of monodisperse cylindrical micelles of PIP-*b*-PFDMS prepared by PI-CDSA at monomer-to-seed ratios imaged after dilution to 1 mg/mL by addition of THF/n-hexanes (10% v/v THF). a) small seed micelles, b) 3:1, c) 6:1, d) 9:1, e) 12:1, f) 15:1, g) 18:1, h) 21:1 illustrating the linear relationship between micelle contour length and monomer-to-seed ratio. Scale bars a) = 1000 nm b-h) = 2000 nm.



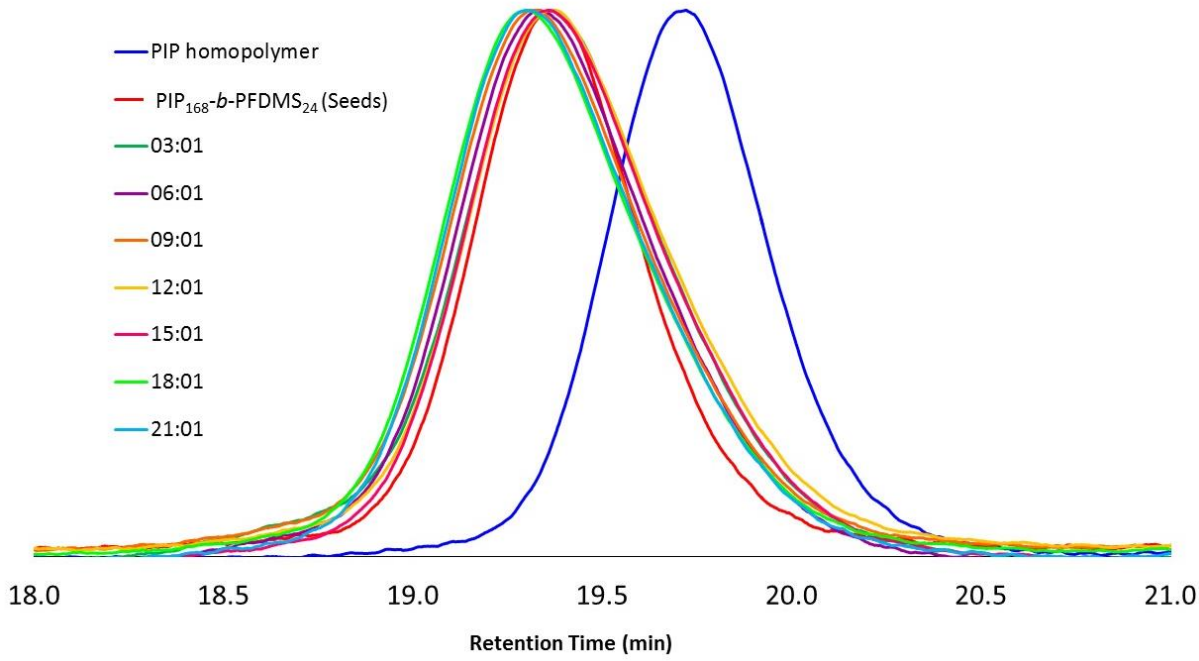
Supplementary Figure 14: Living PI-CDSA of PIP-*b*-PFDMS at 10% w/w solids. a-h) Low magnification bright field TEM micrographs of monodisperse cylindrical micelles of PIP-*b*-PFDMS prepared by PI-CDSA at monomer-to-seed ratios imaged at 10 mg/mL after dilution by addition of THF/n-hexanes (10% v/v THF). a) crystallite seeds, b) 3:1, c) 6:1, d) 9:1, e) 12:1, f) 15:1, g) 18:1, h) 21:1 illustrating the high density of the samples prepared by this method. Scale bars = 1000 nm.



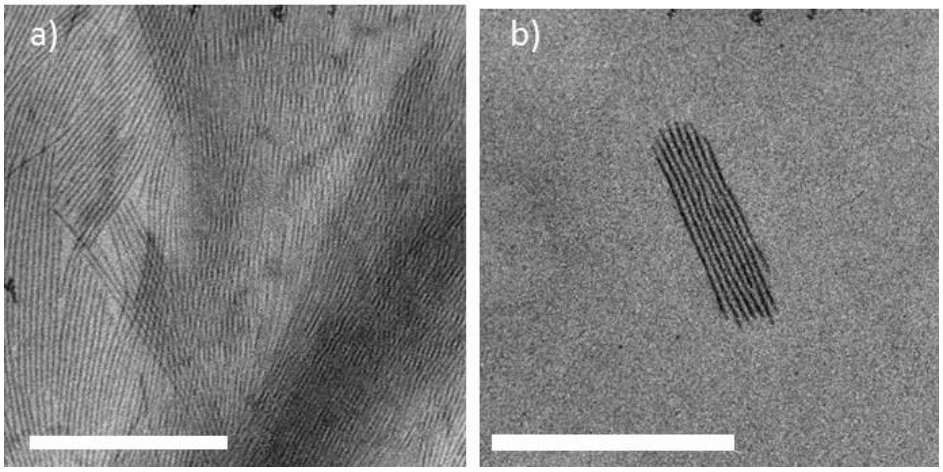
Supplementary Figure 15: Living PI-CDSA of PIP-*b*-PFDMS at 10% w/w solids in THF/n-hexanes 10% v/v. Histogram of the contour length distribution of monomer-to-seed ratios of 6:1, 12:1 and 18:1 illustrating the low polydispersities of the cylindrical nanostructures (which are 1.03, 1.01 and 1.01, respectively).



Supplementary Figure 16: AFM images of near monodisperse PIP-*b*-PFDMS cylindrical micelles (L_n = 560 nm, PDI = 1.04) prepared at 10% w/w solids by living PI-CDSA. a) Low magnification AFM height profile images of monodisperse cylindrical micelles of PIP-*b*-PFDMS b-d) high magnification AFM height profile images illustrating the high density of the monodisperse micelles prepared by this method. Scale bars a) 2000 nm, b-d) = 500 nm.



Supplementary Figure 17: Overlaid GPC traces (refractive index response) of PIP-*b*-PFDMS BCPs prepared by living PI-CDSA at 10% w/w solids. All BCPs have very similar retention times regardless monomer-to-seed ratio (see key at top left) illustrating the controlled nature of this process. PDI values are given in Supplementary Table 7.



Supplementary Figure 18: Living PI-CDSA of PIP_{204}-*b*-$PFDMS_{29}$ at 22% w/w solids. Bright field TEM micrographs of monodisperse cylindrical micelles of PIP-*b*-PFDMS prepared by PI-CDSA at a monomer-to-seed ratios of 5:1 imaged after dilution to 10 mg/mL (a) and 1 mg/ml (b) by addition of THF/n-hexanes (20% v/v THF). L_n = 995 nm; PDI = 1.05. Scale bars a) = 1000 nm.

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2. Temple, K. *et al.* Living Anionic Ring-Opening Polymerization of Unsymmetrically Substituted Silicon-Bridged [1]Ferrocenophanes; A Route to Organometallic Block Copolymers with Amorphous Poly(ferrocenylsilane) Blocks. *J. Inorg. Organomet. Polym.* **9,** 189–198 (1999).