# **Supporting Information**

## Solution Self-Assembly of ABC Triblock Terpolymers with a Central Crystallizable

# Poly(ferrocenyldimethylsilane) Core-Forming Segment

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## Experimental

#### Materials and Techniques

Anhydrous solvents were obtained using a modified Grubbs system of alumina columns manufactured by Anhydrous Engineering. Tetrahydrofuran (THF) was distilled from Na/benzophenone under nitrogen immediately prior to use. Cyclohexane was washed with concentrated sulphuric acid, 10 mol % sodium hydroxide solution, distilled water, and was subsequently dried over CaH<sub>2</sub> before distillation. Dichlorodimethylsilane was purchased from Aldrich and distilled under nitrogen and freeze-pump-thawed three times prior to use. Styrene, isoprene and 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V<sub>3</sub>) were purchased from Acros, Aldrich, and Alfa Aesar respectively, dried over CaH<sub>2</sub> and distilled twice under reduced pressure. Methyl methacrylate was purchased from Aldrich and was passed through a basic alumina column prior to use. 4-((Trimethylsilyl)ethynyl)benzaldehyde was sublimed onto a cold finger and stored under nitrogen, and *sec*-butyllithium (1.4M in THF) was

purchased from Aldrich and used as received. All other reagents were used without further purification. The procedure for the preparation of dimethylsila[1]ferrocenophane has been reported previously.<sup>1</sup>

Unless otherwise stated, all reactions were carried out on an all-glass vacuum line under nitrogen or in an MBraun glovebox under an inert purified nitrogen atmosphere.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Varian 400 MHz spectrometer and all resonances were referenced to residual NMR solvent peaks.

Gel permeation chromatography (GPC) was conducted on a Viscotek VE2001 GPCmax chromatograph equipped with a triple detector array, equipped with an automatic sampler, pump, injector, inline degasser, column oven (30 °C), elution columns consisting of styrene/divinylbenzene gels (with pore sizes between 500 Å and 100,000 Å), refractometer (VE 3580), four-capillary differential viscometer, UV/Vis detector (VE 3210,  $\lambda$  = 440 nm) and dual angle laser light scattering detector (VE 270, 7° and 90°). THF (Fisher) was used as the eluent, with the flow rate set at 1 mL/min. Samples were dissolved in the eluent (2 mg/mL) and filtered through a Ministart SRP 15 filter (polytetrafluorethylene membrane, pore size = 0.45 µm) before analysis. The detectors were calibrated using polystyrene standards (Viscotek).

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker UltrafleXtreme 4700 instrument. Samples of poly(methyl)methacrylate (PMMA) were prepared by combining a solution of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile matrix (20 mg/mL in THF), AgOTf (10 mg/mL in THF) and the polymer (2 mg/mL in THF) in a 10 : 0.5 : 1 (v/v/v) ratio. All other samples were prepared without the addition of AgOTf using the same concentrations and ratios. Approximately 1.5  $\mu$ L of the mixed sample was deposited onto a stainless steel plate and allowed to dry in air.

DLS experiments were performed using a nano series Malvern zetasizer instrument equipped with a 633 nm red laser and a detector oriented at 173° to the incident radiation. The results of DLS studies are reported as apparent hydrodynamic radius ( $R_{H,app}$ ), recognizing that the particles have been modelled as spheres in the experiments conducted.

Bright-field transmission electron microscopy (TEM) micrographs were acquired on a JEOL JEM 1400 microscope operating at 120 kV and equipped with a Gatan Orius SC1000 CCD camera. Each sample was analyzed by drop-casting one drop (ca. 8  $\mu$ L) of the micelle colloidal solution onto a carbon-coated copper grid placed on a piece of filter paper to remove excess solvent. Copper grids (600 mesh) were purchased from Agar Scientific and carbon films were prepared by using a Quorum TEM Turbo Carbon Coater by sputtering carbon onto mica sheets. The carbon films were deposited onto the copper grids by floatation on water and the carbon-coated grids were allowed to dry for at least two days in air. Samples that required staining were exposed to the vapour of aqueous OsO<sub>4</sub>, or RuO<sub>4</sub> solution (2 wt%) overnight.

Transmission electron microtomography (TEMT) images of cylindrical micelle networks dropcast onto carbon-coated TEM grids were generated from a series of TEM tilt images collected from -64.5° to +64.5° at an angular increment of 1.5° on a Gatan K2 Summit direct detection camera mounted on an automated FEI Tecnai F20 field-emission microscope operated at 200 kV. The resulting aligned and mass-normalised image sets were reconstructed using the filtered (*r*-weighted) back-projection algorithm, and three-dimensional volume elements were produced with the National Institutes of Health ImageJ software package by qualitative pixel thresholding.

AFM analyses were performed using a Bruker Multimode 8 atomic force microscope equipped with a ScanAsyst-HR fast scanning accessory and a ScanAsyst-Air-HR probe (tip radius, 2 nm). Samples were prepared by placing one drop (ca. 10  $\mu$ L) of solution on a piece of freshly cleaved mica. Imaging was conducted in air at ambient temperature.

#### **Experimental Procedures**

Synthesis of alkyne-functionalized polyisoprene-block-polyferrocenylsilane (PIP-b-PFDMS) diblock copolymers

The method outlined below was used for the preparation of all PIP-*b*-PFDMS diblock copolymers. Isoprene (0.5 mL, 5.0 mmol) in THF (3 mL) was initiated with *sec*-butyllithium (1.4 M in cyclohexane, 72  $\mu$ L) at 0 °C and a colour change from colourless to yellow was observed. After 2 h, an

aliquot for analysis was taken and subsequently dimethylsilaferrocenophane (605 mg, 2.5 mmol) in THF (5 mL) was rapidly added and was allowed to react for a further 1 h, noting a colour change from orange to amber. 4-((trimethylsilyl)ethynyl)benzaldehyde (40 mg, 0.2 mmol) in THF (1 mL) was added to quench the reaction, stirring for 1 h to ensure complete end-capping. The diblock copolymer was precipitated three times into methanol and dried in a vacuum oven overnight, affording an orange gummy material. The diblock copolymer was then dissolved in THF/MeOH (10:1 v/v, 25 mL total) and to this was added sodium methoxide (50 mg). The reaction mixture was allowed to stir overnight under atmospheric conditions. The material was purified by precipitation three times into methanol and dried overnight in a vacuum oven (705 mg, 91 %).



4: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.56 (s, 6H, Si*Me*<sub>2</sub>), 0.80-2.59 (br, alkyl), 4.12 (m, 4H, *Cp*), 4.28 (m, 4H, *Cp*), 4.70-6.16 (br, 2.2H, vinyl); *M<sub>n</sub>* (GPC) = 37.6 kg/mol, *M<sub>w</sub>/M<sub>n</sub>* = 1.05; block ratio = 6.2 : 1.0, PIP<sub>313</sub>-*b*-PFDMS<sub>50</sub>.



5: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.56 (s, 6H, Si*Me*<sub>2</sub>), 0.80-2.59 (br, alkyl), 4.12 (m, 4H, *Cp*), 4.28 (m, 4H, *Cp*), 4.70-6.16 (br, 2.2H, vinyl); *M<sub>n</sub>* (GPC) = 16.9 kg/mol, *M<sub>w</sub>/M<sub>n</sub>* = 1.08; block ratio = 1.2 : 1.0, PIP<sub>46</sub>-*b*-PFDMS<sub>39</sub>.

Synthesis of azide-terminated poly(methyl)methacrylate (PMMA)

Methyl methacrylate (2.66 mL, 25.0 mmol), 2-azidoethyl-2-bromoisobutyrate (68.2  $\mu$ L, 0.42 mmol) N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) (43.4  $\mu$ L, 0.21 mmol) and dry toluene (2.5 mL) were added to a dried Young's tube fitted with a stirrer bar. The mixture was freeze-pump-thawed three times to remove oxygen. The reaction vessel was transferred to a glovebox and copper (I) bromide (29.8 mg, 0.21 mmol) was added to the mixture. The polymerization was carried out at 80 °C for 2 h. To terminate the polymerization, the reaction vessel was rapidly cooled to room temperature and immediately exposed to air. Copper salts were removed by passing the mixture through a short basic alumina column and the material was purified by precipitation three times into methanol (913 mg, 37 %).



7: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.73-1.28 (br, 3H,  $\alpha$ -CCH<sub>3</sub>), 1.34-2.10 (br, 2H,  $\alpha$ -CCH<sub>2</sub>), 3.59 (s, 3H, -OCH<sub>3</sub>);  $M_n$  (GPC) = 38.1 kg/mol,  $M_n$  (MALDI-TOF) = 38.3 kg/mol;  $M_w/M_n$  = 1.10, PMMA<sub>381</sub>.



8: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.73-1.28 (br, 3H,  $\alpha$ -CCH<sub>3</sub>), 1.34-2.10 (br, 2H,  $\alpha$ -CCH<sub>2</sub>), 3.59 (s, 3H, -OCH<sub>3</sub>);  $M_n$  (GPC) = 7.5 kg/mol,  $M_n$  (MALDI-TOF) = 7.6 kg/mol;  $M_w/M_n$  = 1.02, PMMA<sub>75</sub>.

Preparation of PIP-b-PFDMS-b-PMMA triblock terpolymers 1 and 2 via the CuAAC Click Reaction

The method outlined below was used for the preparation of all PIP-*b*-PFDMS-*b*-PMMA triblock terpolymers. Alkyne-functionalized PIP-*b*-PFDMS (100 mg, 5.88 µmol) and azide-functionalized PMMA (53 mg, 8.82 µmol) were dissolved in dry THF (10 mL) in a dried Young's tube fitted with a

stirrer bar. The reaction vessel was transferred to a glovebox and PMDETA (12.3  $\mu$ L, 58.8  $\mu$ mol), followed by copper (I) bromide (8.4 mg, 58.8  $\mu$ mol) were added to the mixture. The reaction had a molar ratio of [PIP-*b*-PFDMS] : [PMMA] : [PMDETA] : [CuBr] of [1] : [1.5] : [10] : [10] and was allowed to proceed at 50 °C for 48 h. The reaction was stopped by cooling to room temperature and exposing to air. Copper salts were removed by passing the reaction mixture through a basic alumina column. The material was purified by precipitation into methanol three times and by size exclusion chromatography (SEC) to remove unreacted PMMA, yielding a pale orange powder (43 mg, 32 %).



1: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.56 (s, 6H, Si*Me*<sub>2</sub>), 0.73-2.59 (br, alkyl, PIP and PMMA), 3.59 (s, 3H, -OC*H*<sub>3</sub>), 4.12 (m, 4H, *Cp*), 4.28 (m, 4H, *Cp*), 4.70-6.16 (br, 2.2H, vinyl);  $M_n$  (GPC) = 60.0 kg/mol,  $M_w/M_n$  = 1.12; block ratio = 6.2 : 1.0 : 7.6, PIP<sub>313</sub>-*b*-PFDMS<sub>50</sub>-*b*-PMMA<sub>381</sub>.



2: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.56 (s, 6H, SiMe<sub>2</sub>), 0.73-2.59 (br, alkyl, PIP and PMMA), 3.59 (s, 3H, -OCH<sub>3</sub>), 4.12 (m, 4H, Cp), 4.28 (m, 4H, Cp), 4.70-6.16 (br, 2.2H, vinyl); *M<sub>n</sub>* (GPC) = 22.2 kg/mol, *M<sub>w</sub>/M<sub>n</sub>* = 1.05; block ratio = 1.2 : 1.0 : 1.9, PIP<sub>46</sub>-*b*-PFDMS<sub>39</sub>-*b*-PMMA<sub>75</sub>.

Synthesis of polystyrene-block-polyferrocenylsilane-block-polymethylvinylsiloxane (PS-b-PFDMS-b-PMVS) triblock terpolymer **3** 

Styrene (1.15 mL, 10 mmol) in cyclohexane (4 mL) was initiated with *sec*-butyllithium (11.9  $\mu$ L, 16.7  $\mu$ mol) at room temperature and a colour change from colourless to orange was observed. After 2 h, an aliquot for analysis was taken and subsequently dimethylsilaferrocenophane (0.218 mg, 0.9 mmol) in THF (1 mL) was rapidly added and this reacted for a further 1h, noting a colour change from orange to amber. After 1 h, a second aliquot was taken for analysis. 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (V<sub>3</sub>) (0.72 mL, 2.70 mmol) in THF (1.5 mL) was then added and the reaction mixture was allowed to react for a further 2 h. The reaction was quenched with chlorotrimethylsilane (100  $\mu$ L) and the resulting material was purified by precipitation three times into methanol and preparative size exclusion chromatography, affording a pale orange powder (1.42 g, 82 %).



**3**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.40 (s, 3H, Si*Me*), 0.56 (s, 6H, SiMe<sub>2</sub>), 1.44-2.48 (br, 3H, C*H*<sub>2</sub>C*H*(Ph)), 4.12 (m, 4H, *Cp*), 4.28 (m, 4H, *Cp*), 5.97-6.27 (m, 3H, SiC*H*C*H*<sub>2</sub>), 6.41-7.21 (br, 5H, CH<sub>2</sub>CH(*Ph*)) *M<sub>n</sub>* (GPC) = 92.6 kg/mol, *M<sub>w</sub>/M<sub>n</sub>* = 1.08; block ratio = 7.9 : 1.0 : 5.7, PS<sub>340</sub>-*b*-PFDMS<sub>43</sub>-*b*-PMVS<sub>247</sub>.



6: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.56 (s, 6H, SiMe<sub>2</sub>), 1.44-2.48 (br, 1H, CH<sub>2</sub>CH(Ph)), 4.12 (m, 4H, Cp), 4.28 (m, 4H, Cp), 6.41-7.21 (br, 5H, CH<sub>2</sub>CH(Ph)) M<sub>n</sub> (GPC) = 49.2 kg/mol, M<sub>w</sub>/M<sub>n</sub> = 1.10; block ratio = 7.9 : 1.0, PS<sub>340</sub>-b-PFDMS<sub>43</sub>.



**9**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.44-2.48 (br, 3H, CH<sub>2</sub>CH(Ph)), 6.41-7.21 (br, 5H, CH<sub>2</sub>CH(Ph))  $M_n$  (GPC) = 35.4 kg/mol,  $M_n$  (MALDI-TOF) = 35.2 kg/mol;  $M_w/M_n$  = 1.08; PS<sub>340</sub>.

Self-Assembly of ABC PFDMS-Containing Triblock Terpolymers 1 - 3

Direct dissolution studies were performed by making up a 0.1 mg/mL suspension of the triblock terpolymer in the desired solvent which was selective for the corona-forming block(s). The solvents investigated are outlined in Table S2 The mixture was heated up to just below the boiling point of the solvent for 1 h, and subsequently cooled slowly to room temperature (23°C). The samples were allowed to age for a minimum of 24 h and were subsequently analyzed by TEM after solvent evaporation.

Seeded Growth of PIP-b-PFDMS-b-PMMA (1 or 2) from  $PIP_{404}$ -b-PFDMS<sub>48</sub> seeds in acetone/alkane mixtures

PIP<sub>404</sub>-*b*-PFDMS<sub>48</sub> short stub-like seed micelles ( $L_n = 61 \text{ nm}$ ,  $L_w/L_n = 1.11$ ) were prepared by sonicating a solution of polydisperse PIP<sub>404</sub>-*b*-PFDMS<sub>48</sub> micelles (1 mg/mL in hexanes or decane) at 0 °C for 2 h in a sonic bath. Longer seed micelles were prepared by the addition of a PIP<sub>404</sub>-*b*-PFDMS<sub>48</sub> unimer solution (10 mg/mL in THF) to a colloidal solution of the stub-like micelles. The samples were allowed to age for 24 h, after which the micelles were analyzed by TEM. Staining was not necessary to observe the coronal structure for these samples.

Seeded growth studies were undertaken by adding a known amount of PIP-*b*-PFDMS-*b*-PMMA triblock terpolymer unimer in THF (5 mg/mL, between 1 and 40  $\mu$ L) to a colloidal solution of PIP-*b*-PFDMS seed micelles (50  $\mu$ L, 0.05 mg/mL,  $L_n = 252$  nm,  $L_w/L_n = 1.07$ ) in various acetone/ alkane mixtures (the alkanes investigated were hexanes and decane). The sample was gently stirred for 2 s and then left to age for 72 h. The samples were analyzed by TEM after solvent evaporation. Multiple TEM

images were obtained and the micelle contour lengths were measured for a minimum of 200 nanoparticles.

# Seeded Growth of PIP-b-PFDMS-b-PMMA (1 or 2) off PFDMS<sub>52</sub>-b-PDMS<sub>414</sub> seeds in ethyl acetate

PFDMS<sub>52</sub>-*b*-PDMS<sub>414</sub> seed micelles ( $L_n = 49 \text{ nm}$ ,  $L_w/L_n = 1.10$ ) were prepared by sonicating a solution of polydisperse PFDMS-*b*-PDMS micelles (1 mg/mL in EtOAc) at 0 °C for 2 h in a sonic bath.

Seeded growth studies were undertaken by adding a known amount of PIP-*b*-PFDMS-*b*-PMMA triblock terpolymer unimer in THF (5 mg/mL, between 1 and 40  $\mu$ L) to a colloidal solution of seed micelles (50  $\mu$ L, 0.05 mg/mL in ethyl acetate,  $L_n = 49$  nm,  $L_w/L_n = 1.10$ ). The sample was gently stirred for 2 s and then left to age for 72 h. The samples were analyzed by TEM. Multiple TEM images were obtained and the contour lengths were measured for a minimum of 200 micelles.

## Seeded Growth of PS-b-PFDMS-b-PMVS (3) from PFDMS<sub>52</sub>-b-PDMS<sub>414</sub> seeds

Seeded growth studies were undertaken by adding a known amount of PS-*b*-PFDMS-*b*-PMVS triblock terpolymer unimer in THF (5 mg/mL, between 1 and 40  $\mu$ L) to a colloidal solution of seed micelles (50  $\mu$ L, 0.05 mg/mL in ethyl acetate,  $L_n = 49$  nm,  $L_w/L_n = 1.10$ ). The sample was gently stirred for 2 s and then left to age for 72 h. The samples were analyzed by TEM. Multiple TEM images were obtained and the contour lengths were measured for a minimum of 200 micelles.

# **Supporting Information**

**Table S1**: Characterisation data of relevant homopolymers and diblock copolymers prepared in the synthesis of PFDMS-containing ABC triBCP materials, including number-average molecular weight  $(M_n)$ , degree of polymerization  $(DP_n)$ , block ratio and polydispersities (PDI).

Composition	Material	Block Ratio a	Mn / kg mol <sup>-1</sup>	PDI b
PIP <sub>313</sub> - <i>b</i> -PFDMS <sub>50</sub> <sup>d</sup>	4	6.2 : 1.0	37.6 <sup>a,b</sup>	1.05
PIP <sub>46</sub> - <i>b</i> -PFDMS <sub>39</sub> <sup>d</sup>	5	1.2 : 1.0	16.9 <sup> a,b</sup>	1.08
PS <sub>340</sub> - <i>b</i> -PFDMS <sub>43</sub> <sup>f</sup>	6	7.9 : 1.0	49.2 <sup>b,c</sup>	1.12
PMMA <sub>381</sub> <sup>e</sup>	7	-	38.1 <sup>b,c</sup>	1.10
PMMA <sub>75</sub> <sup>e</sup>	8	-	7.5 <sup>b,c</sup>	1.02
$PS_{340}$ f	9	-	35.4 <sup>b,c</sup>	1.13

<sup>a</sup> Determined by <sup>1</sup>H NMR through comparative integration of aromatic protons (5H) of PS and methyl protons (6H) of PFDMS, <sup>b</sup> Determined by GPC with a triple-detector array, <sup>c</sup> Determined by MALDI-TOF <sup>d</sup> alkyne capped, <sup>e</sup> azide capped, <sup>f</sup> proton capped

Polymer	δ (MPa) <sup>1/2</sup>
Polymethylvinylsiloxane (PMVS)	15.0
Polyisoprene (PIP)	16.6
Polystyrene (PS)	18.5
Poly(ferrocenyldimethylsilane) (PFDMS)	18.7
Polymethylmethacrylate (PMMA)	19.0

Table S2: Hansen solubility parameters of homopolymers.<sup>1-4</sup>

Table S3: Hansen solubility parameters of solvents (with relevant boiling points). <sup>1-4</sup>

Solvent	δ (Mpa) <sup>1/2</sup>	Boiling Point (°C)
Hexane	14.9	68
Diglyme	15.8	188
Decane	15.8	174
DMAA	16.8	165
BuOAc	17.6	126
EtOAc	18.1	68
THF	18.5	66
Acetone	19.9	56



**Scheme S1**: Generalised synthesis for the formation of PIP-*b*-PFDMS-*b*-PMMA triBCPs (1, 2); (A) reaction procedure for the sequential living anionic polymerization and (B) subsequent deprotection of the protected alkyne for the preparation of alkyne-capped PIP-*b*-PFDMS; (C) reaction procedure for the ATRP of methyl methacrylate with an azide-functionalized initiator for the preparation of PMMA-azide; (D) reaction procedure for the azide/alkyne cycloaddition (CuAAC) click reaction of PIP-*b*-PFDMS-alkyne and PMMA-azide for the synthesis of PIP-*b*-PFDMS-*b*-PMMA triBCPs. Note the structural tautomers and their relative representation of PIP are detailed at the bottom.



**Scheme S2**: Generalised synthesis for the formation of PS-*b*-PFDMS-*b*-PMVS triBCPs (3) by sequential living anionic polymerization.



Figure S1: GPC chromatographs (refractive index response) in THF of purified 1 (blue,  $PIP_{313}$ -*b*-PFDMS<sub>50</sub>-*b*-PMMA<sub>381</sub>) and its precursors 4 (red,  $PIP_{313}$ -*b*-PFDMS<sub>50</sub>) and 7 (black, PMMA<sub>381</sub>)



**Figure S2**: GPC chromatographs (refractive index response) in THF of purified 2 (blue, PIP<sub>46</sub>-*b*-PFDMS<sub>39</sub>-*b*-PMMA<sub>75</sub>) and its precursors **5** (red, PIP<sub>46</sub>-*b*-PFDMS<sub>39</sub>) and **8** (black, PMMA<sub>75</sub>)



Figure S3: GPC chromatographs (refractive index response) in THF of purified 3 (blue,  $PS_{340}$ -*b*-PFDMS<sub>43</sub>-*b*-PMVS<sub>247</sub>) and its precursory BCP 6 (red,  $PS_{340}$ -*b* PFDMS<sub>43</sub>) and homopolymer 9 (black,  $PS_{340}$ )



Figure S4: TEM micrograph of 1 prepared in, and drop-cast from, EtOAc. TEM image taken after solvent evaporation of at 0.1 mg/mL solution. Scale bar is 1000 nm.



Figure S5: TEM micrographs of cylindrical and spherical micelles of 1 prepared in, and drop-cast from, (A), (C) hexanes and (B), (D) decane after 3 months ((A) and (B)) and 12 months ((C) and (D)). TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.

Ageing of the samples for longer periods of time (> 3 months) showed evolution of the micellar morphology. In hexanes, the number of spherical micelles detected by TEM decreased, whilst the number of long cylindrical micelles increased when aged for 3 months (Figure S5A). A similar

morphological evolution was detected for samples prepared in decane, with an increase in the number of cylindrical micelles detected by TEM after 3 months (Figure S5B). When the micelle solutions were left to age for 12 months, further maturation of both samples from spherical to cylindrical micelles was observed (Figure S5C, S5D).



Figure S6: TEM micrographs of unimer film derived 1 prepared in, and drop-cast from, EtOAc after ageing for 6 months. TEM image taken after drying from solution at 0.1 mg/mL. Scale bar is 1000 nm.



**Figure S7**: TEM micrographs of cylindrical and spherical micelles of **1** prepared in, and drop-cast from, (A) hexanes and (B) decane after sonication and annealing for 1 w at 45 °C. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.

In an attempt to promote the morphological evolution of the samples in hexanes and decane, the aged micelle solutions were initially sonicated, followed by annealing the samples at 45 °C for 1 week. The samples were sonicated to increase the number of potential nucleation sites, or "seeds", available for epitaxial growth of unimer and to aid the formation of cylindrical micelles. However, this was

unsuccessful; spherical micelles were still present after annealing and the long polydisperse cylinders had been fragmented into much shorter micelles which were ineffective as seeds.



Figure S8: TEM micrograph of seed micelles of 1 prepared in, and drop-cast from, acetone after sonicating a 0.1 mg/mL solution of polydisperse micelles for 1 h at 0 °C. TEM image taken after drying from solution at 0.1 mg/mL. Scale bar is 100 nm.



**Figure S9**: TEM micrographs of micelles of 1 from initial seeded growth experiments to determine the ideal acetone/decane solvent mixture for micelle growth; (A) 1 : 0, (B) 2 : 1, (C) 1 : 2 and (D) 0 : 1 (all (v/v). TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.



**Figure S10**: TEM micrographs of aggregated cylindrical micelles of 1 drop-cast from acetone/decane 2:1 (v/v) after the addition of (A) 1, (B) 2, (C) 5 and (D) 10 equivalent of unimer 3.1. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.



**Figure S11**: TEM micrographs of block co-micelles prepared by seeded growth of 1 from PIP<sub>404</sub>-*b*-PFDMS<sub>49</sub> seed micelles in decane ( $L_n = 493$  nm,  $L_w/L_n = 1.03$ ) and drop-cast from decane/acetone 1 : 1 (v/v) showing a mixture of coiled micelles, straight micelles and micelles that appeared to have grown from one end of the seed which are more likely to arise from cleavage at a comicelle junction due to the bending forces applied to the crystalline core associated with solvent evaporation on the carbon film. The arrows denote where unidirectional growth may have occurred due to seed micelle breakage. TEM image taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.



**Figure S12**: TEM micrographs of block co-micelles prepared by seeded growth of 1 off PIP<sub>404</sub>-*b*-PFDMS<sub>49</sub> seed micelles ( $L_n = 493 \text{ nm}$ ,  $L_w/L_n = 1.03$ ) prepared in, and drop-cast from, decane/acetone 1 : 1 (v/v) and diluted in (A) DMF and (B) DMSO. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.

The cylindrical block co-micelles formed tightly coiled structures upon drying from decane/acetone. Dilution using higher boiling point co-solvents that were good for the PMMA block was investigated in an attempt to reduce this. Addition of either DMF or DMSO caused a reduction of the coiling of the block co-micelles (Figure S12). However, significant aggregation upon drying was still observed by TEM.



**Figure S13**: TEM micrographs of block co-micelles prepared by seeded growth of 1 off PIP<sub>404</sub>-*b*-PFDMS<sub>49</sub> seed micelles in hexanes ( $L_n = 252 \text{ nm}$ ,  $L_w/L_n = 1.07$ ) drop-cast from various solvent systems; (A) a mixture of spherical and short cylindrical micelles in hexanes; (B) a mixture of spherical and slightly longer cylindrical micelles in hexanes/acetone (3 : 1 (v/v)); (C) a mixture of film presumably derived from unimer, spheres and long cylinders in hexanes/acetone (1 : 1 (v/v)). TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.



**Figure S14**: TEM micrographs of block co-micelles in the dry state prepared by seeded growth of 1 from PIP<sub>404</sub>-*b*-PFDMS<sub>49</sub> seed micelles ( $L_n = 493$  nm,  $L_w/L_n = 1.03$ ) prepared in, and drop-cast from, decane/acetone 1 : 1 (v/v) after the addition of (A) 1, (B) 2.5, (C) 5, (D) 7.5, (E) 10, and (F) 15 equivalents of unimer. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.



**Figure S15**: Graph showing the linear dependence of micelle length upon the unimer-toseed ratio for block co-micelles prepared by seeded growth of **1** from PIP<sub>404</sub>-*b*-PFDMS<sub>49</sub> seed micelles ( $L_n = 493$  nm,  $L_w/L_n = 1.03$ ) prepared in and drop-cast from decane/acetone 1 : 1 (v/v).



**Figure S16**: TEM micrographs of cylindrical block co-micelles prepared by seeded growth of 1 off PFDMS<sub>52</sub>-*b*-PDMS<sub>414</sub> seed micelles ( $L_n = 49 \text{ nm}$ ,  $L_w/L_n = 1.10$ ) in EtOAc after the addition of (A) 2, (B) 5 and (C) 15 equivalents of unimer. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are (A)-(E) 1000 nm.



**Figure S17**: Histogram showing the contour length distribution of cylindrical block comicelles prepared by seeded growth of 1 off PFDMS<sub>52</sub>-*b*-PDMS<sub>414</sub> seed micelles ( $L_n = 49$  nm,  $L_w/L_n = 1.10$ ) in EtOAc.



**Figure S18**: TEM micrographs of cylindrical block co-micelles prepared by seeded growth of 1 from PFDMS<sub>52</sub>-*b*-PDMS<sub>414</sub> seed micelles ( $L_n = 49 \text{ nm}$ ,  $L_w/L_n = 1.10$ ) in EtOAc after exposure to OsO<sub>4</sub> vapour. This shows a "patchy" structure in the dry state upon solvent evaporation with phase-segregated PIP and PMMA coronal chains. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 500 nm.



**Figure S19**: TEM micrographs of cylindrical block co-micelles in the dry state after the addition of decane, to make the final solvent system (A), (B) 3 : 1 EtOAc/decane and (C), (D) 1 : 1 EtOAc/decane. The images show the solvent-induced aggregation of block co-micelles after the addition of decane, a very poor solvent for the PMMA patches. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are (A), (C) 2000 nm, (B), (D) 1000 nm.



**Figure S20**: TEM micrographs of triBCP micelles of **2** prepared in, and drop-cast from, EtOAc after (A) 1 day and (B) 9 months. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.



**Figure S21**: AFM micrographs of amorphous network triBCP micelles of **2** prepared in, and drop-cast from, (A) hexanes and (B) decane. AFM images taken after drying from solution at 0.1 mg/mL. Scale bars are 500 nm.



**Figure S22**: DLS data (number, intensity and correlation function) for micellar solutions of **2** in hexanes after sonication for 2 min, with a  $R_{H,app}$  of 1622 nm. Samples that were not sonicated possessed a  $R_{h,app}$  of greater than 10,000 nm and hence could not be detected by DLS.



**Figure S23**: Series of (A) TEM and (B) TEMT images of triBCP micelles of **2** prepared in, and drop-cast from, decane after drying from solution at 0.1 mg/mL. The TEM images have been acquired and aligned at different tilt angles (labelled) and are displayed at two different magnifications (low, top row; high, bottom row). The TEMT images are x-yslices of the reconstructed volume element presented at sequential planes along the zaxis (labelled, in nm) at two different magnifications (low, top row; high, bottom row). The enlargements correspond to the identified region. Scale bars are 200 nm (low magnification) and 50 nm (high magnification).



Figure S24: TEM micrographs of triBCP micelles of 2 prepared in, and drop-cast from, (A)-(C) hexanes, (D)-(F) decane after (A), (D) 24 h, (B), (E) 3 weeks and (C), (F) 9 months. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are (A)-(C) 500 nm, (D)-(F) 1000 nm.



**Figure S25**: TEM micrographs of triBCP cylindrical block co-micelles prepared by seeded growth of 2 off PFDMS<sub>52</sub>-*b*-PDMS<sub>414</sub> seed micelles ( $L_n = 49 \text{ nm}$ ,  $L_w/L_n = 1.10$ ) in EtOAc after the addition of (A) 2, (B) 4, (C) 8, (D) 12 and (E) 20 equivalents of unimer; (F) Graph showing the linear dependence of micelle length upon the unimer-to-seed ratio. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are (A)-(E) 1000 nm.



**Figure S26**: Histogram showing the contour length distribution of cylindrical block comicelles prepared by seeded growth of **2** off PFDMS<sub>52</sub>-*b*-PDMS<sub>414</sub> seed micelles ( $L_n = 49$  nm,  $L_w/L_n = 1.10$ ) in EtOAc.



**Figure S27**: TEM micrographs of triBCP cylindrical block co-micelles prepared by seeded growth of 2 off PFDMS<sub>52</sub>-*b*-PDMS<sub>414</sub> seed micelles ( $L_n = 49 \text{ nm}$ ,  $L_w/L_n = 1.10$ ) in EtOAc after the addition of (A) 16 and (B) 20 equivalents of unimer, highlighting the formation of some branched micelles (red ovals). TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are s1000 nm.



**Figure S28**: AFM micrograph of triBCP cylindrical block co-micelles prepared by seeded growth of 2 off PFDMS<sub>52</sub>-*b*-PDMS<sub>414</sub> seed micelles ( $L_n = 49 \text{ nm}$ ,  $L_w/L_n = 1.10$ ) in EtOAc after the addition of 20 equivalents of unimer. AFM image taken after drying from solution at 0.1 mg/mL. Scale bar is 1000 nm.



Figure S29: TEM micrographs of (A) 2 seed micelles prepared by the sonication of polydisperse micelles in acetone for 2 h at 0 °C, and the proceeding 2D micelles of triBCP 2 prepared by seeded growth after the addition of (B) 2, (C) 4, (D) 6, (E) 8 and (F) 10 equivalents of unimer to 2 seed micelles. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are (A) 500 nm, (B)-(F) 1000 nm.



**Figure S30**: TEM micrographs of self-assembled samples of triBCP **3** prepared in, and drop-cast from, (A) EtOAc, (B) BuOAc, (C) hexanes, (D) decane and (E) DMAA. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.



**Figure S31**: Higher magnification TEM micrographs to interrogate the coronal structure of cylindrical triBCP micelles of **3** prepared in, and drop-cast from, (A) acetone, (B) acetone/EtOAc 1 : 1 (v/v) and (C) diglyme. Dry state TEM images taken after solvent evaporation from solution at 0.1 mg/mL. Scale bars are 500 nm.



**Figure S32**: TEM micrographs of cylindrical triBCP micelles of **3** prepared in, and dropcast from, various acetone/EtOAc (v/v) mixtures; (A) 4 : 1, (B) 3 : 2, (C) 2 : 3 and (D) 1 : 4 (note this sample oddly produced film derived from unimer). TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.

For the samples that afforded only cylindrical micelles, the coronal microstructure was probed to determine whether patchy structures had been formed in the dry state. The samples did not need to be stained due to the presence of the long PS coronal chains which exhibited greater electron contrast by TEM compared to PMVS. The samples which contained acetone in the solvent system clearly showed the microphase separation between the PS and PMVS coronal chains, affording patchy materials (Figure S31A, S31B). The definition of the patches was much more prevalent when neat acetone was used compared to PMVS. As the solvent quality increased for the PMVS block upon the addition of EtOAc, the definition of the patches decreased. Further acetone/EtOAc mixtures were investigated, showing that the definition of the patches was diminished as the EtOAc content increased (Figure S32). In contrast to this, samples prepared in diglyme showed no demarcation between the two corona-forming blocks, affording structures with seemingly homogeneous mixing of PS and PMVS (Figure S31C).



**Figure S33**: TEM micrographs of triBCP cylindrical micelles prepared by seeded growth of **3** in acetone/EtOAc 1 : 1 (v/v) after the addition of (A) 2, (B) 4, (C) 10 and (D) 20 equivalents of unimer. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.



Figure S34: TEM micrographs of triBCP cylindrical micelles prepared by seeded growth of 3 in diglyme after the addition of (A) 2, (B) 4, (C) 10 and (D) 20 equivalents of unimer. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.



**Figure S35**: TEM micrographs of triBCP cylindrical block co-micelles prepared by seeded growth of **3** from PFDMS<sub>52</sub>-*b*-PDMS<sub>414</sub> seed micelles ( $L_n = 49 \text{ nm}, L_w/L_n = 1.10$ ) in EtOAc after the addition of (A) 2, (B) 4, (C) 8 and (D) 12 equivalents of unimer, showing the clear microphase separation between the PS (dark) and PMVS (light) coronal chains in the dry state. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 500 nm.



**Figure S36**: Histogram showing the contour length distribution of cylindrical block comicelles prepared by seeded growth of **3** off PFDMS<sub>52</sub>-*b*-PDMS<sub>414</sub> seed micelles ( $L_n = 49$  nm,  $L_w/L_n = 1.10$ ) in EtOAc.



**Figure S37**: AFM height micrograph of cylindrical block co-micelles after the addition of 20 equivalents of unimer. TEM images taken after drying from solution at 0.1 mg/mL. Scale bars are 1000 nm.

# References

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